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Determination of aniline and quinoline compounds in textiles

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ABSTRACT

A simple method for simultaneous determination of twenty-one analytes, belonging to two classes of compounds, aromatic amines and quinolines, is presented. Several of the analytes considered in this study frequently occur in textiles goods on the open market and have been related to allergic contact dermatitis and/or are proven or suspected carcinogens. The method includes an efficient clean-up step using graphitized carbon black (GCB) that simplifies and improves the robustness of the subsequent GC–MS analysis. Briefly, after solvent extraction of the textile sample, the extract is passed through a GCB SPE cartridge that selectively retain dyes and other interfering compounds present in the matrix, producing a clean extract, suitable for GC–MS analysis, is obtained.

The method was evaluated by spiking blank textiles with the selected analytes. Method quantification limits (MQL) ranged from 5 to 720 ng/g depending on the analyte. The linear range of the calibration curves ranged over two order magnitude with coefficients of determination (R^2) higher than 0.99. Recoveries ranged from 70 to 92% with RSDs 1.7–14%. The effectiveness of the method was tested on a variety of textile materials samples from different origin.

In a pilot explorative survey, 2,6-dichloro-4-nitroaniline was detected in all the analysed clothing samples in concentrations ranging from 1.0 to 576 μg/g. 2,4-dinitroaniline was detected in four of the seven samples with a highest concentration of 305 μg/g. Quinoline was detected in all samples in concentrations ranging from 0.06 to 6.2 μg/g.

1. Introduction

The growing interest in chemicals present in clothes and their effects on environment and human health is proved by several papers recently published on the topic [1–4]. Aromatic amines in textile products are used for many purposes, such as synthetic polymers, biocides but mainly in the production of azo-dyes [5,6]. Among the over eight hundred commercially available dyes, fifty of them, mostly disperse dyes, have proved to be contact allergens [7]. The lipophilic property of disperse azo-dyes might increase their migration from the fabric to the epidermal skin [8]. When absorbed, they are metabolized with cleavage of the azo bond and consequent release of amines [9,10]. Bacteria of the human skin have also been demonstrated to metabolize azo-dyes in to aromatic amines [11]. Several compounds belonging to this class of compounds have been shown an increased risk of bladder cancer [12–14]. Quinolines, which are considered to be possible carcinogenic to humans [15–17] and toxic for the aquatic environment [18], are also extensively used in textile industry for the manufacture of dyes [19–21]. The presence of this class of compounds has been reported in textile materials [22,23], as well as in wastewater and sludge from dye processing plants [24–26].

Major problems of the analytical procedures used in those studies were the poor clean up and the large amount of solvents and time required. In recent times the use of graphitic sorbents in so called QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) has increased in order to improve the cleanup of samples with complex matrices rich in natural pigments. A number of authors have reviewed the applications of graphitic sorbent QuEChERS in different fields [27–29].

Briefly, in QuEChERS methods a small amount of graphitic sorbent is used for dispersive solid phase extraction (dSPE) in order to retain abundant interfering compounds [30]. Large, planar molecules, such as carotenoids, chlorophylls, flavonoids and other polyphenolic compounds, are stronger retained by interaction with the flat surface of the graphitic sorbent compared to the

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smaller, non-planar analytes, leading to an efficient removal from the supernatant organic solvent [27].

In the past decades GCBs as sorbents for SPE have been investigated in depth by Di Corcia and other authors for the effectiveness in extracting very polar and ionic compound from aqueous matrices [31–35], and for their ability of performing fractionated elution of the analytes [36,37]. Analytical procedures based on GCBs have also shown an improved cleanup efficiency of environmental and foodstuff samples compared to methods based on conventional reversed phases, especially C18 sorbents [37]. Effective removal of potentially interfering species such as aromatic hydrocarbons [38], humic and fulvic acids [39] as well as plant pigments [40] has been reported. In a previous study on the analysis of pesticides and related degradation products in water the interaction of few anilines with GCBs was investigated [41,42].

In this study the potential of using a GCBs to improve the cleanup of the textile sample extracts was evaluated. A method to determine ten quinolines and eleven aromatic amines by GC–MS was developed. The twenty-one analytes were all quantitatively eluted from the GCB while the interfering compounds, mainly dyes, were strongly retained. Two different GCB sorbents were tested as well as several factors influencing the recovery and separation.

2. Experimental

2.1. Materials and chemicals

The solvents used in this study were all of pesticide residue grade, with a purity ≥99.5%, methanol (MeOH), toluene, acetonitrile (ACN), acetone were acquired from VWR International S.A.S (France), dichloromethane (DCM) and trifluoracetic acid (TFA) were purchased from Merck (Germany). Quinoline-d7; 1-Indanone; 6-methylquinoline; and 8-methylquinoline were purchased from Fluka (Sweden); Quinoline was from Merk; 4-methylquinoline from SAFC, USA; 2,6-dimethylquinoline and 2,4-dimethylquinoline were from ICN.K&K, USA; all other standards were from Sigma Aldrich. Names, abbreviations, CAS number, molecular weight (g/mol) of the investigated compounds are listed in Table 1. SPE cartridges containing 250 and 500 mg of Carbograph 1 and Carbograph 4 (mesh size 120/400) were obtained from LARA Srl (Formello, Italy). The textile samples were clothes of international brands bought in retail shops in Stockholm.

2.2. Preparation of spiked samples and recovery experiments

Individual stock standard solutions of the analytes were prepared in DCM to obtain a concentration of around 600 ng/μl, 2,4-DNA was dissolved in acetone at a concentration of 1000 ng/μl, and 2,6-DiCl-4-NA dissolved in DCM:toluene (1:1 v/v) to a concentration of 300 ng/μl. These solutions were stored at −18 °C in the dark to minimize analyte degradation. A working standard solution was prepared by mixing the stock solutions in DCM to obtain a concentration of 5 ng/μl of quinolines, 40 ng/μl chloro- and nitroanilines, and 80 ng/μl dinitroanilines.

Preparation of spiked textile samples for method development was made by adding 100 μl of the working standard solution to the samples (organic cotton) placed in the 20 ml test tubes and then adding 1 ml of DCM to allow the analytes to distribute evenly in the sample. After an equilibration time of 1 h, to allow absorption of the compounds into the fibers, the solvent was removed using a gentle stream of nitrogen. Spiked samples were then extracted as reported in section 2.3 in recovery experiments.

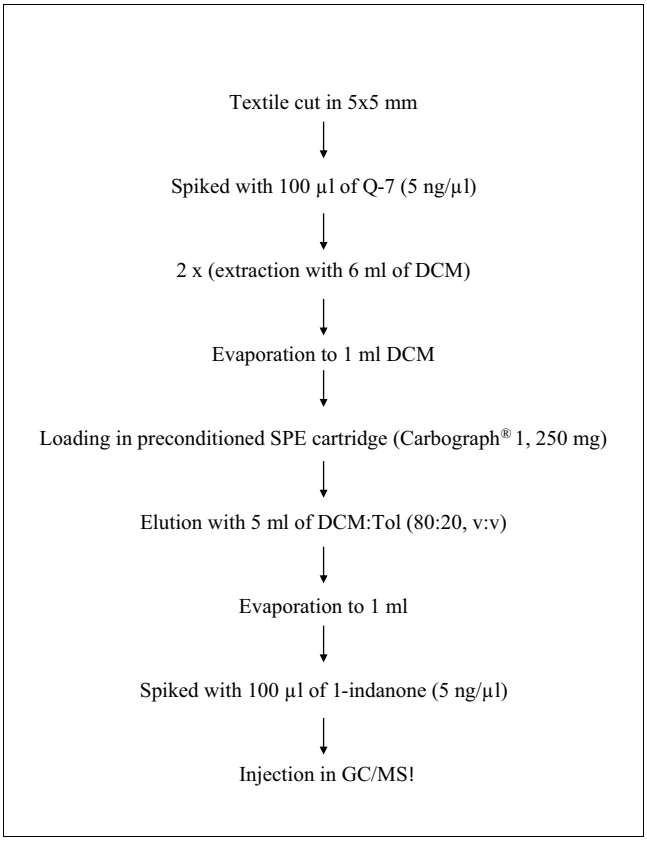

Fig. 1. Method workflow.

2.3. Extraction procedure and cleanup

A total amount of around 1 g of textile sample (cut in 5 × 5 mm) was placed in a 15 ml glass test tube and spiked with 100 μl of deuterated quinoline (Q-d7) used as surrogate internal standard at a concentration of 5 ng/μl. The sample was then subjected to ultrasonic assisted solvent extraction using 6 ml DCM and an ultrasonic bath Sonorex Digital 10P (Bandelin Electronic, Berlin, Germany) at room temperature for 10 min. The extraction was repeated once with fresh solvent. The two extracts were pooled together and the volume was reduced to 1 ml under a gentle stream of nitrogen at a temperature of 30 °C using a heater block.

An SPE cartridge containing GCB was used for the clean-up step. Prior the use each cartridge was pre-conditioned with 10 ml methanol and 5 ml elution solvent. The sample extract (1 ml) was then passed through the SPE cartridge followed by 5 ml of DCM:toluene (80:20 v/v) selected as elution solvent mixture. The eluate was collected in a 16 × 100 mm test tube and subsequently reduced to about 1.0 ml under nitrogen stream at set temperature of 30 °C, spiked with 100 μl of L-indanone (5 ng/μl) as volumetric standard, and 1 μl of the sample extract was then injected into the GC/MS system. If required, the sample was diluted ten times before the injection. The schematic method workflow is summarized in Fig. 1.

2.4. GC/MS analysis

The analyses were performed on a GC/MS system consisting of a 6890N gas chromatograph equipped with a 7683 autosampler, a programmable temperature vaporizer injector and, connected to a 5975C mass spectrometer, (Agilent Technologies, Palo Alto, CA, USA). The temperature program for the vaporizer was 70 °C for 0.5 min followed by a ramp of 700 °C/min–300 °C, which was