Supplementary Information

Determination of short-chain chlorinated paraffins in carpets by gas chromatography–electron capture negative ionization mass spectrometry

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Section 1. Sample detailed information

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Section 1. Sample detailed information

Table S1 Sample detailed information

Sample NO.	Sample types	Fibre types	Material composition of carpet backing
1	Tufted carpets	polyamide	Polyester nonwoven fabric、latex、plastic
2	Tufted carpets	polyamide	Polypropylene woven fabric、latex、plastic
3	Hand-tufted rubber-backed carpets	Acrylic	Latex、cotton linen backing cloth
4	Woven carpet	polyamide	Latex、plastic
5	Tufted carpets	Polypropylene	Polypropylene woven fabric、latex
6	Tufted carpets	Wool/polyamide blend	Polypropylene woven fabric、latex、plastic
7	Carpet tile	polyamide	Polypropylene woven fabric、latex、Polyvinyl Chloride
8	Needle-punched carpet	Polyester	Latex
9	Carpet tile	Polypropylene	Polyester nonwoven fabric、Ethylene-Vinyl Acetate Foam、latex
10	Bathroom carpet	Polyester	Ethylene-Vinyl Acetate Foam、latex
11	Woven carpet	Wool / polyamide blend	Latex、plastic
12	Hand-tufted rubber-backed carpets	Wool / polyamide blend	Latex、cotton linen backing cloth
13	Carpet tile	Polypropylene	Polyester nonwoven fabric、bitumen、latex

Section 2. Progress and Advantages of the Proposed Method for SCCPs Detection Compared with Reported Methods for Similar Matrices

1. Comparison and Advantages of Purification Technologies

For the determination of short-chain chlorinated paraffins (SCCPs) in textiles[1], silica gel column chromatography is the most commonly reported purification method. Although this approach can remove partial lipids and polar impurities, it is cumbersome and time-consuming, requiring more than 1.5 hours per sample. Additionally, silica gel columns have limited adsorption capacity, leading to poor purification efficiency for samples with high matrix interference, which easily causes peak tailing and low response values in detection.

For leather matrices[2], most existing methods employ solid-phase extraction (SPE) combined with alumina column purification. While this method improves purification efficiency, SPE cartridges are relatively expensive and tend to adsorb SCCPs, resulting in partial loss of target analytes and compromised recovery stability.

For plastic matrices[3], some studies only adopt membrane filtration (mostly 0.22 μm or 0.45 μm membranes) coupled with solvent extraction, without targeted acid purification. As a result, interfering substances such as residual additives and low-molecular-weight polymers in plastic matrices cannot be effectively removed, which are prone to overlapping with the characteristic peaks of SCCPs and interfering with quantitative analysis.

In this study, a combined pretreatment technique of 0.45 μm organic membrane filtration followed by concentrated sulfuric acid purification was developed, which exhibits significant advantages over conventional methods. First, the 0.45 μm organic membrane can efficiently retain macromolecular impurities (e.g., suspended solid particles and fiber debris) in carpet matrices, preventing these contaminants from entering the subsequent detection system and thereby reducing chromatographic column contamination and instrument wear. Compared with 0.22 μm membranes, it also minimizes the adsorption loss of SCCPs on the membrane, improving detection recovery. Second, concentrated sulfuric acid purification can specifically remove interfering substances (e.g., lipids, pigments, and unsaturated hydrocarbons) in carpet matrices, which are difficult to be completely eliminated by conventional column chromatography in similar matrix detection. Concentrated sulfuric acid converts these interferents into polar substances through sulfonation reactions, which can be effectively separated from SCCPs by centrifugation, achieving more thorough purification. Third, this combined purification technique is simple to operate and time-efficient, with the purification time per sample controlled within 40 minutes. Compared with silica gel column chromatography and SPE, it greatly improves pretreatment efficiency. Furthermore, it uses low-cost reagents, making it suitable for batch sample detection and feasible for practical application.

2. Comparison and Advantages of Limit of Detection

For the determination of short-chain chlorinated paraffins (SCCPs) in textiles by gas chromatography coupled with electron capture detector (GC-ECD), the ECD detector exhibits weak anti-interference capability against matrix effects, resulting in a limit of detection (LOD) generally ranging from 10 to 50 mg/kg. Even when gas chromatography-tandem mass spectrometry (GC-MS/MS) is applied to detect SCCPs in leather, the reported LODs are mostly between 8 and 25 mg/kg, which cannot meet the detection requirements for low-level SCCPs. For plastic matrices, GC coupled with electron capture negative ionization mass spectrometry (GC-ECNI-MS) has been adopted in some studies; however, incomplete purification during sample pretreatment leads to severe matrix interference, with LODs mostly in the range of 12–30 mg/kg.

The LOD of the proposed method in this study is 5.76 mg/kg, which is significantly lower than that of existing detection methods for similar matrices. The core reasons are as follows: on the one hand, the ECNI-MS ionization source possesses extremely high selectivity, which can generate characteristic negative ions targeting the chlorine atoms of SCCPs, effectively suppressing the interference from other matrix components and improving detection sensitivity. On the other hand, the sample pretreatment procedure combining 0.45 μm organic membrane filtration and concentrated sulfuric acid purification removes interfering substances to the maximum extent, reduces background noise, and further optimizes the LOD. This LOD can satisfy the detection requirement of low-level SCCPs in carpets. Compared with existing methods, the developed approach can more accurately capture trace SCCPs residues in carpets, providing a more reliable technical support for quality control and environmental risk assessment of carpet products.

3. Comparison and Advantages of Recovery Rate

The stability and accuracy of recovery directly reflect the reliability of a detection method. Existing methods for SCCPs determination in similar matrices suffer from large fluctuations and generally low recovery. For instance, the recoveries of SCCPs in textile detection are mostly 85%–95%, with the relative standard deviation exceeding 5% in some methods, mainly attributed to the adsorption loss and incomplete elution of analytes during column chromatography purification. Due to the complex composition of leather matrices, the recovery fluctuations of conventional methods are more pronounced, ranging widely from 80% to 100%, and the recoveries of some high-concentration spiked groups are below 85%, failing to meet the accuracy requirements for quantitative analysis. Although the recoveries of SCCPs detection in plastic matrices can reach 90%–103% in some cases, such methods are only applicable to a single type of plastic and involve high pretreatment costs, making them difficult for popularization and application.

The recoveries of the method established in this study are stably maintained at 97.2%–102.8%, featuring a narrow recovery range and minor fluctuation, with the average recovery close to 100%. It is remarkably superior to the existing detection methods for similar matrices.

Reference

1 Z. Zeng, Y. Shao, X. Li and J. Du, *Am. J. Appl. Chem.*, 2019, **3**, 104−109.

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