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Analysis of Volatile Organic Compounds in Textiles: Insights from GC–MS with Metal Content Assessment Using ICP-MS

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Abstract: This study primarily focuses on the analysis of volatile organic compounds using GC–MS, with ICP-MS employed as a complementary method to quantify trace metal content. Headspace GC–MS was conducted to detect alkylphenol ethoxylates (APEOs), formaldehyde, aromatic amines derived from azo dyes, perfluorinated carboxylic acids, chlorophenols (PCPs), tetrachlorophenols (TPCs), and phthalates in textile samples of different origin and composition. Principal component analysis was used to detect patterns in the volatilome according to the origin and the textile composition. In addition, seven metals (Cr, Ni, Cu, Mo, Cd, Hg, and Pb) were quantified in a subset of samples. The study revealed distinct chemical profiles in textiles based on their origin, with GC–MS identifying key volatile organic compounds and ICP-MS quantifying heavy metals in a subset of samples. Principal component analysis highlighted cotton content as a critical factor in differentiating textile profiles. While most samples adhered to regulatory standards, some exceeded thresholds for metals like copper and nickel, underscoring the need for enhanced quality control in manufacturing processes. By integrating advanced analytical methods, this study provides insights into sustainable and safe textile production, offering valuable benchmarks for regulatory compliance and industry best practices. The outcomes contribute to improving product safety, promoting responsible manufacturing, and supporting regulatory bodies in the enforcement of environmental and safety standards, aligning with the growing demand for sustainability in the textile sector.

Keywords: GC–MS; ICP-MS; PCA; volatilome; textile; origin; composition

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1. Introduction

The textile industry is a multifaceted global sector that produces a wide array of products, ranging from fabrics and yarns to garments and technical textiles. It utilizes both natural fibers, such as cotton, wool, silk, and linen, as well as synthetic materials like polyester, nylon, and acrylic. In recent years, the development of high-performance fibers, including carbon-based and specialized materials, has expanded applications into fields like sports and automotive manufacturing. However, despite technological advancements and increased production efficiency, the industry has come under scrutiny for its significant environmental and social impacts [1]. Key environmental concerns include the high water consumption and chemical pollution associated with dyeing and finishing processes, which release hazardous substances, such as synthetic dyes and microplastics, into waterways. The rise in "fast fashion", characterized by low-cost, rapidly produced garments, exacerbates resource depletion and textile waste generation. Social issues, including poor working

conditions, add to the industry's challenges. Initiatives such as Greenpeace's 2011 Detox Campaign and the Zero Discharge of Hazardous Chemicals (ZDHC) program have highlighted these concerns, encouraging greater transparency and sustainability efforts within the supply chain. Alongside the environmental and social challenges already highlighted, another point of concern is the quality of textiles, which can directly influence their durability, safety, and suitability for various applications [2–5]. Analytical techniques are crucial for evaluating textile quality, detecting hazardous substances, and ensuring compliance with environmental and safety regulations. Among the factors that need to be assessed are the volatile organic compounds released by textiles, which can impact air quality and human health, followed by the presence of heavy metals, which may pose additional environmental and safety concerns. Recent studies have employed advanced methodologies to assess the presence of such contaminants. For instance, Zhu et al. developed a method combining solid-phase microextraction (SPME) with gas chromatography–mass spectrometry (GC–MS) to analyze volatile organic compounds (VOCs) in textiles [6]. By employing a larger headspace volume (2000 mL) and conditioning the CAR/PDMS fiber at 280 °C, their approach addressed VOC variability and ensured reliable identification and quantification of emissions. The results were compared with international safety standards, including REACH and OEKO-TEX® STANDARD 100 [7].

Menezes et al. employed flame furnace thermospray atomic absorption spectrometry (TS-FF-AAS) to profile the mineral content of textiles from both countries. Exploratory data analysis revealed distinct patterns based on geographical origin and color differences, demonstrating the potential of advanced statistical tools for textile characterization [8].

Standardized analytical techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), and Fourier transform infrared spectroscopy (FT-IR), are commonly applied to assess textile composition and contaminants. Microwave digestion methods, as highlighted by Tuzen et al. [9], have proven effective for the rapid and reproducible preparation of complex samples for metal analysis. For VOC analysis, GC–MS is the preferred method, as demonstrated by Zhu et al. [6], due to its ability to identify and quantify trace-level emissions that may affect air quality and human health. These and other studies [10–15] underscore the importance of integrating advanced analytical methods to address the industry's environmental and health challenges effectively.

This work aims to use GC–MS for detecting the presence of some specific compounds: alkylphenol ethoxylates (APEOs), formaldehyde, aromatic amines derived from azo dyes, perfluorinated carboxylic acids, chlorophenols (PCPs), tetrachlorophenols (TPCs) and phthalates, in textiles with varying origins and compositions, focusing on their potential health and environmental risks. In addition, ICP-MS is used for quantifying some heavy metals, which vary based on fiber composition, production processes, and chemical treatments. By integrating these analytical approaches, the study seeks to contribute to the ongoing discourse on sustainable and responsible practices in the textile industry.

2. Materials and Methods

2.1. Samples

The analyzed samples consist of cotton, synthetic fibers, or a blend of both. They were purchased from various retailers and differ in origin and color. The details are provided in Table 1. All the samples listed in the table were analyzed using GC–MS, while only a subset (indicated by the superscript "a") was analyzed using ICP-MS.

Table 1. Samples analyzed using (HS)-SPME GC–MS. [a] indicates that an aliquot of the same sample has been analyzed also with ICP-MS. SPME fiber composition: DVB/CAR/PDMS; Divinylbenzene/Carboxen/Polydimethylsiloxane 50/30 μm; CAR/PDMS: Carboxen/Polydimethylsiloxane 76 μm.

Sample	Origin	Composition	SPME Fiber
TESS_96A	China	100% cotton	DVB/CAR/PDMS
TESS_96B	China	100% cotton	CAR/PDMS
TESS_96C	China	100% cotton	DVB/CAR/PDMS
TESS_96D	China	100% cotton	DVB/CAR/PDMS
TESS_97A	China	100% cotton	DVB/CAR/PDMS
TESS_97B	China	100% cotton	DVB/CAR/PDMS
TESS_97C	China	100% cotton	DVB/CAR/PDMS
TESS_97D	China	100% cotton	DVB/CAR/PDMS
TESS_98A [a]	China	100% cotton	DVB/CAR/PDMS
TESS_98B [a]	China	100% cotton	DVB/CAR/PDMS
2TESS_99A [a]	China	100% cotton	DVB/CAR/PDMS
2TESS_99B [a]	China	100% cotton	DVB/CAR/PDMS
TESS_100A [a]	China	100% cotton	DVB/CAR/PDMS
TESS_100B [a]	China	100% cotton	DVB/CAR/PDMS
2CANOV_BLUA [a]	Egypt	100% cotton	DVB/CAR/PDMS
2CANOV_BLUB [a]	Egypt	100% cotton	DVB/CAR/PDMS
CANOV_ROSSA [a]	Egypt	100% cotton	DVB/CAR/PDMS
CANOV_ROSSB [a]	Egypt	100% cotton	DVB/CAR/PDMS
CALZ_BIANCO_A [a]	Italy	100% cotton	DVB/CAR/PDMS
CALZ_BIANCO_B [a]	Italy	100% cotton	DVB/CAR/PDMS
CALZ_NRA [a]	Italy	95% cotone, 5% elastane	DVB/CAR/PDMS
CALZ_NRB [a]	Italy	95% cotone, 5% elastane	DVB/CAR/PDMS
CAMICIA_A [a]	Italy	80% cotone, 20% elastane	DVB/CAR/PDMS
CAMICIA_B [a]	Italy	80% cotone, 20% elastane	DVB/CAR/PDMS

2.2. Headspace Solid-Phase Micro-Extraction Gas Chromatography-Mass Spectrometry ((HS)-SPME GC–MS) Analysis

The SPME fiber used in this work was coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), with a 50/30 μm thickness (Supelco, Bellefonte, PA, USA).

A 1 cm side square of tissue was cut into pieces to approximately half-fill a 4 mL vial equipped with a Mininert cap for SPME. The vial was kept at 150 °C in an oil bath for 15 min. The fiber was then introduced into the vial and exposed for 15 min to the headspace of the sample. The desorption of the extracted volatiles was performed by placing the fiber into the injection port of the gas chromatograph at 270 °C for 5 min. After each analysis, the fiber was conditioned in the GC injection port at 270 °C for 5 min, after which a blank run was recorded to verify the fiber cleaning.

The analyses were carried out on a Trace 1300 ISQ LT GC–MS from Thermo Fisher Scientific (Waltham, MA, USA). The GC apparatus was equipped with a split/splitless injector with a SPME liner inside. All injections were performed in splitless mode.

A J&W capillary column HP5MS (5% phenyl- polymethylsiloxane, 30 m, 0.25 mm i.d., and 0.25 μm film thickness) was used and the carrier gas was helium 5.5 IP, supplied at a flow rate of 1.1 mL/min. GC separation was achieved using the following column oven temperature program: an initial temperature of 40 °C for 5 min, and then increasing to 250 °C at 7 °C/min, and at the end, raised to 270 °C at a rate of 75 °C/min and held for 2 min. The EI-ion trap mass spectrometer operated at the following conditions: 70 eV ionization energy; 25–700 m/z range; 0.2 s scan cycle time; 260 °C transfer line temperature; 270 °C ion source temperature.

The compounds were identified by comparison of their mass spectra with those reported in the NIST 14 library [16].

2.3. ICP-MS

2.3.1. Samples Preparation for ICP-MS Analysis

As mentioned above, a subset of the available textiles was analyzed; individuals are indicated by a superscript "a" in Table 1. In order to prepare samples for the analysis, textiles were finely shredded, and approximately 150 mg were weighed for each prepared sample (weighted masses are reported in Table A1 in Appendix A). The weighed grams were placed in appropriate, closed polytetrafluoroethylene (PTFE) vials, to which 4 mL of aqua regia, consisting of 75 mL of Suprapur hydrochloric acid and 25 mL of Suprapur nitric acid, were added, and the samples were left to react overnight. The following day, after adding 4 mL of Suprapur hydrogen peroxide, 4 mL of deionized water obtained through a Milli-Q system (Millipore, Bedford, MA, USA), and 500 µL of indium at 1 ppm as a procedural standard, the samples were digested using a high-performance microwave digestion system (Milestone Ethos One, Milestone, Italy). The digestion program involved reaching 180 °C within 10 min and maintaining this temperature for 2 h.

Once the samples were digested, they were quantitatively transferred to 50 mL plastic flasks, and 500 µL of rhodium at a concentration of 1 ppm was added as an instrumental standard. The volume was then brought to 50 mL using Milli-Q water. The samples were subsequently filtered using 0.45 µm NY filters and transferred into plastic vials for analysis with ICP-MS.

All plastic laboratory ware was conditioned with a 1% nitric acid solution and rinsed thoroughly with Milli-Q water before use.

2.3.2. Instrumental ICP-MS Analysis

The multielemental composition of the textile samples was determined through duplicate sample analysis using inductively coupled plasma mass spectrometry (ICP-MS) with an iCAP TQe ICP-MS (Thermo Scientific, Waltham, MA, USA) system. Prior to the sample analysis session, to optimize the instrument performance and operational parameters for achieving good sensitivity and resolution while minimizing interferences, an iCAP TQ TUNE Solution (Thermo Scientific, Waltham, MA, USA) was used. Instrument calibration was performed using the iCAP Q/Qnova Calibration Solution (Thermo Scientific, Waltham, MA, USA) to ensure that the instrument provided accurate results and that the sensitivities of the elements were properly calibrated.

Six multielement standard solutions containing Pb, As, Hg, Ni, Cd, Cr, Cu, Co, and Mo were analyzed, along with two additional standard solutions for Cu and three further standard solutions containing Co and Mo to cover the expected concentration range of the samples (Table A2 in Appendix A). In total, 10 ppb of In and Rh were added to the analyzed standard solutions and samples, along with 2 mL of aqua regia for every 100 mL of the prepared standard solution.

In addition, a blank solution was prepared, mineralized, and analyzed following the same steps as the samples. The solution consisted of 4 mL of aqua regia, left to react overnight. Subsequently, 4 mL of Suprapur hydrogen peroxide was added, followed by 4 mL of Milli-Q water and 500 µL of an indium standard solution. After mineralization in the microwave oven, the solution was transferred to a 50 mL volumetric flask, where 500 µL of a rhodium standard solution was added. The solution was then brought to volume with Milli-Q water, filtered, and analyzed with ICP-MS. The blank subtraction was performed to correct for interferences caused by the solvent and argon.

Trace analysis grade mono- and multielement standard solutions for ICP-MS analysis were provided by Sigma-Aldrich (St. Louis, MI, USA) and Inorganic Ventures (Christiansburg, VA, USA). For the preparation of the samples and standard and blank solutions, Suprapur nitric acid (≥69%, for trace element analysis; Honeywell Fluka, Charlotte, NC, USA), Suprapur hydrochloric acid (30%, Merck, Darmstadt, Germany), and Suprapur hydrogen peroxide (30%, Merck, Darmstadt, Germany) were used.

3. Results and Discussion

As mentioned, all described samples were analyzed using HS-SPME-GC–MS. The volatilome was then analyzed by principal component analysis, in order to identify clusters in the samples in accordance with the origin and material and to evaluate whether it is possible to estimate markers for the different groups. Subsequently, a selected subset of the samples was analyzed using ICP-MS, and the results were compared with the Öeko Tex Standard. For clarity, this work's workflow is represented in Figure 1.

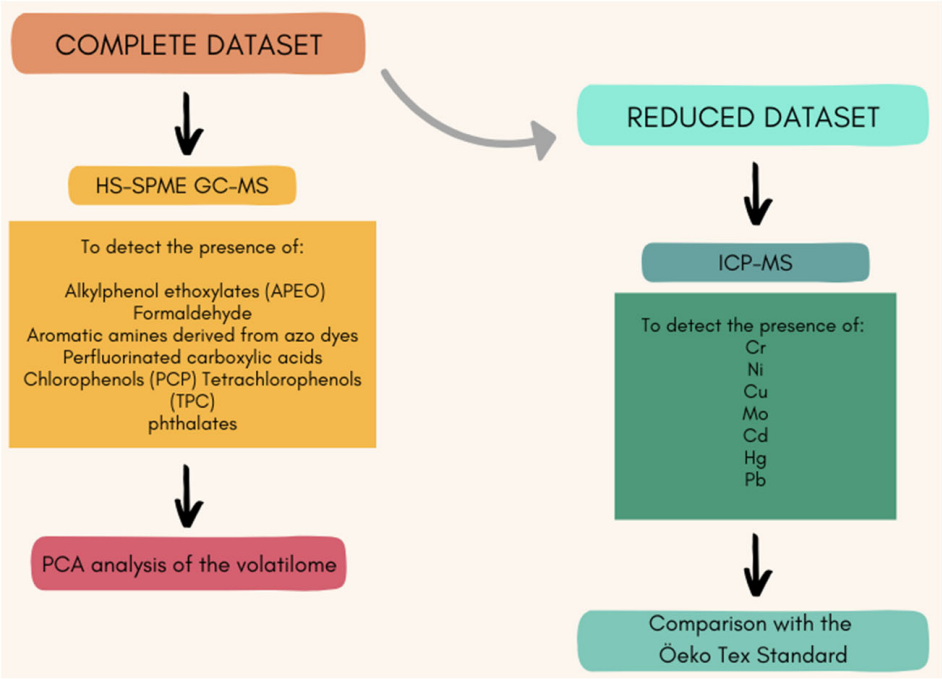


Figure 1. Schematic workflow.

3.1. GC–MS

The fabric samples were analyzed for the presence of alkylphenol ethoxylates (APEOs), formaldehyde, aromatic amines derived from azo dyes, perfluorinated carboxylic acids, chlorophenols (PCPs), tetrachlorophenols (TPCs), and phthalates. Since volatile compounds were sampled using solid-phase microextraction (SPME), only their presence or absence could be determined. The identification of the volatile compounds is based on their electron ionization mass spectrum. A more detailed table, reporting retention times and indices for all the analyzed samples has been provided in the Supplementary Materials. Results are reported in Table 2.

Special attention has been paid to these specific VOCs used in the textile industry because they can represent a hazard linked to exposure.

Alkylphenols are synthetic compounds used in textile processing processes such as washing and dyeing. Given the widespread use of these substances, the REACH regulation permits a concentration in the final product intended for sale of <100 mg/kg. The most

commonly used alkylphenols in the textile industry are synthetic ones, such as nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs) [17–19].

Table 2. Results on the detection of alkylphenol ethoxylates (APEOs), formaldehyde, aromatic amines derived from azo dyes, perfluorinated carboxylic acids, chlorophenols (PCPs), tetrachlorophenols (TPCs), and phthalates in samples. "Neg" indicates no compound has been found. When found ("Pos") the identified compounds are reported.

Sample	APEO	Aromatic Amines	Formaldeyde	Perfluorinated Carboxylic Acids	PCP and TPC	Phthalate
TESS_96	Neg	Pos (aniline, Benzenamine 3,5-dichloro)	Neg	Neg	Neg	Pos (isobutylphtalate)
TESS_97	Neg	Pos (Benzenamine 3,5-dichloro, 4-chloroanilina)	Neg	Neg	Neg	Pos (isobutylphtalate)
TESS_98	Neg	Pos (Benzenamine 3,5-dichloro)	Neg	Pos (perfluoropentane sulphonic acid)	Neg	Pos (isobutylphtalate)
TESS_99	Neg	Pos (Benzenamine 3,5-dichloro)	Neg	Neg	Neg	Neg
TESS_100	Neg	Pos (Benzenamine 3,5-dichloro)	Neg	Neg	Neg	Pos (isobutylphtalate)
CANOV_BLU	Neg	Pos (Benzenamine 3,5-dichloro)	Neg	Neg	Neg	Pos (isobutylphtalate)
CANOV_ROSS	Neg	Pos (Benzenamine 3,5-dichloro)	Neg	Neg	Neg	Pos (isobutylphtalate)
CALZ_BIANCO	Neg	Pos (Benzenamine 3,5-dichloro)	Neg	Neg	Neg	Pos (Diethyl phtalate, isobutylphtalate)
CALZ_NR	Neg	Pos (Benzenamine 3,5-dichloro)	Neg	Neg	Pos (2-chlorophenol)	Pos (isobutylphtalate)
CAMICIA	Neg	Pos (Anyline, 2,4 xylidine)	Neg	Neg	Neg	Pos (isobutylphtalate)

Formaldehyde is a volatile organic substance considered highly irritating by inhalation, sensitizing by contact, and a suspected carcinogen. Currently, it is used in the textile cycle as a fixer for dyes and pigments, in fabric printing processes, to maintain the crease in garments, and as a preservative in the final stages of packaging. There are variable limit values depending on the regulatory source; the reference values for the REACH regulation are <75 mg/kg. Stricter regulations, such as OEKO-TEX®, set limits from 20 mg/kg for articles intended for children (toys, clothing) to 30 mg/kg for clothing in direct contact with the skin, and 300 mg/kg for other textile products.

Perfluoroalkyl substances (PFAS) are a heterogeneous group of synthetic chemicals that are persistent, bioaccumulative, and toxic; they can easily migrate in the air, dust, food, soil, and water. This means they resist degradation when used, as well as in the environment. Most PFAS are also easily transported through the environment, covering long distances from the release source. They are used in the textile industry for their water-repellent, stain-resistant, and oil-repellent properties. In the examined samples, perfluorododecanoic acid (PFDoA) and perfluoropentanesulfonic acid (PFPS) were detected due to their high stability and low surface tension properties. The PFDS molecule is present in the sample "tess_98".

Azo dyes continue to be widely used for dyeing yarns, despite releasing aromatic amines that have been proven to be carcinogenic.

Aromatic amines are lipophilic, bind weakly to synthetic fibers, and are easily absorbed by the skin. In fact, if a fabric loses a lot of color after washing, it is most likely dyed with these dyes. European directives do not prohibit their use, but they do require that the residual concentration in the final product must be <30 mg/kg. The main molecules detected in fabric samples that are part of aromatic amines include 4,4′-Oxydianiline, 4-

ethyl-Aniline, and 2,4-Xylidine. These are present in 100% cotton samples made in China, such as “tess_96” and “tess_97”, “canov_blu”, and “camicia”.

Phthalates are esters of phthalic acid. These molecules are primarily used in the plastics industry as plasticizers; however, they are also found in printing inks, adhesives, and rubber. They are added to the polymer to increase flexibility and elasticity. Phthalates DEHP and DBP (bis(2-ethylhexyl) phthalate and dibutyl phthalate) have been classified in Europe as toxic to reproduction, and their use has been largely restricted. The REACH regulation sets the limit for phthalates at <1 mg/kg. The presence of phthalates was detected in almost all samples. The molecule isobutylphthalate from the phthalate class is the most present.

Chlorophenols (PCPs), tetrachlorophenols (TPCs), and their salts primarily come from use as antimicrobial and antifungal agents in treatments for natural fibers or for the protection of textile products during storage and transport. Some chlorophenols are used in the textile industry to prevent bad odors caused by bacteria from sweating in socks, shoes, and sportswear. According to European regulations and REACH, they may only be present in trace amounts in the finished product (<0.05 mg/kg). Although PCP is typically more commonly detected in fabrics made from natural fibers, it was not found in the 100% cotton samples analyzed. However, 2-chlorophenol from the PCP class was detected in “calz_nr” (made in Italy, 95% cotton, 5% elastane).

Chlorobenzenes and chlorotoluenes (generally called carriers) may be present in polyester materials (as fiber-swelling agents), and as impurities in dyes, biocides, fumigants, and pesticides. They are extremely toxic to aquatic systems and cause skin and respiratory tract irritation. A great alternative to using chlorobenzenes and chlorotoluenes is the use of benzyl benzoate. They are not classified as potentially toxic substances in the REACH regulation, so no maximum legal concentration limit has been established. In the samples analyzed, this compound has not been detected.

3.2. Explorative Analysis of the Volatilome

The relative concentrations of the VOCs identified across the different samples were used for the explorative analysis. The data were preprocessed using Pareto scaling and mean-centering to ensure that all variables contributed equally to the PCA model. Subsequently, a principal component analysis (PCA) [20,21] model was constructed using three principal components (PCs), capturing the underlying structure of the volatilome data set. The PCA model allows the generation of graphical representations of scores and loadings, providing insights into both sample clustering and the relationships between variables. The scores plot is displayed in Figure 2; it represents the projections of the samples on the principal components, highlighting their distribution and grouping. In this case, it includes red diamonds (textiles from Italy), green squares (textiles from China), and blue triangles (textiles from Egypt), allowing for a visual assessment of clustering based on sample origin.

The PCA scores plot demonstrates distinct clustering based on geographic origin. The Italian samples form a tightly grouped cluster, suggesting consistency in their properties. The Chinese samples display a moderate spread, but they are still distinguishable as a cohesive group. The Egyptian samples exhibit slightly more dispersion but maintain a clear separation from the other origins.

In the figure, the percentages of cotton in the different fabrics are displayed close to the projected individuals. Looking at the figure, it is possible to recognize that the percentages of cotton associated with each sample also correlate with their positions on the plot. It appears that Italian samples may have a higher or more uniform cotton content compared to the others. Samples with similar cotton percentages tend to cluster more closely within their respective groups, indicating a relationship between cotton content and PCs.

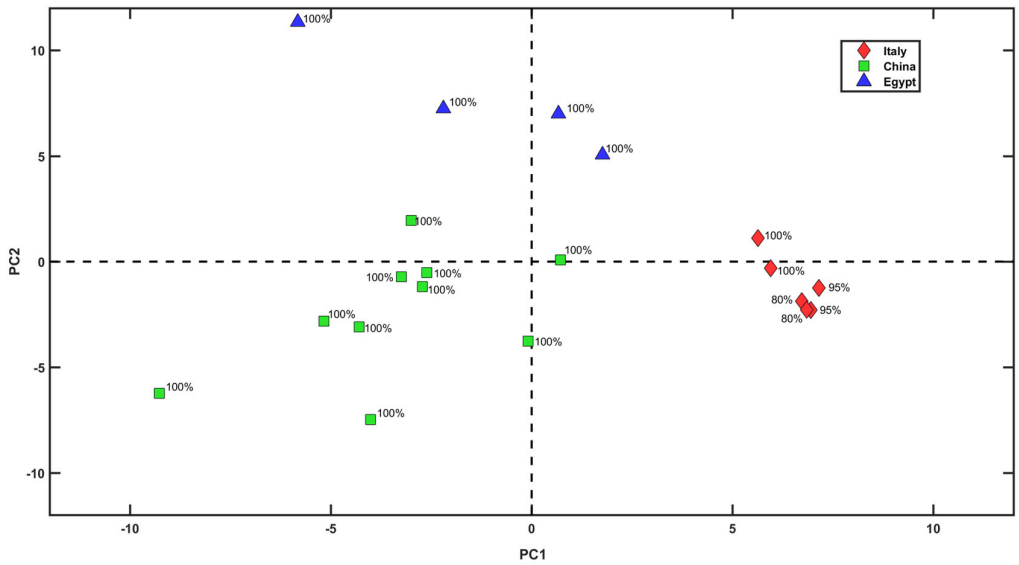


Figure 2. PCA model: projection of samples in the space spanned by the first two PCs.

The separation along the PCA axes suggests significant variation in chemical or physical characteristics among the textiles from different origins. Any outliers observed might reflect unique processing techniques or compositional differences specific to certain regions. Overall, the PCA plot validates its utility in distinguishing textiles based on their origin and highlights the importance of cotton percentage as a contributing factor to the observed variation.

A further interpretation of the data can be obtained by investigating the loading plot (Figure 3). The loading vectors indicate how the original variables contribute to the principal components and can help explain the observed sample patterns.

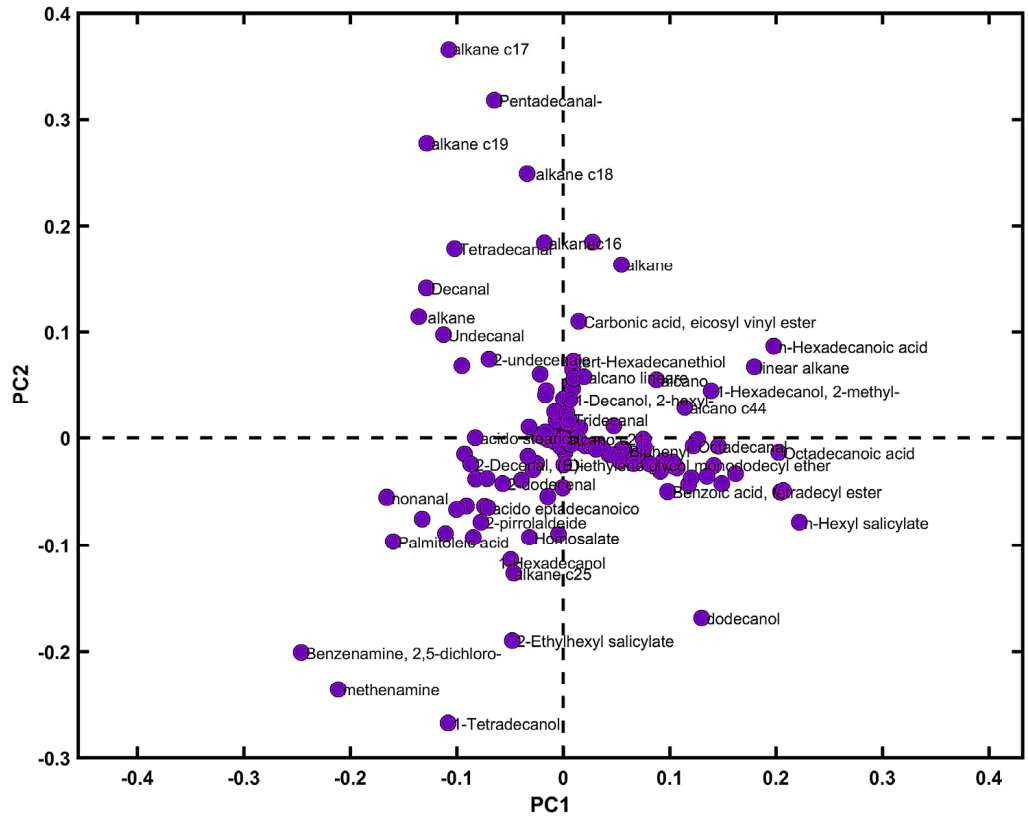


Figure 3. PCA model: loading plot.

The PCA loading plot reveals a detailed chemical profile that explains the clustering of textiles from Italy, China, and Egypt in the scores plot. Italian textiles, which cluster prominently at positive PC1, are strongly correlated with compounds such as pentadecanal, alkane C17, alkane C19, and decanal. These compounds are commonly associated with surface finishing treatments, hydrophobic coatings, and preservatives, reflecting manufacturing processes that prioritize durability, water resistance, and esthetic qualities. The consistent presence of these chemicals indicates a uniform approach to textile finishing in Italian production. Chinese textiles, on the other hand, are dispersed across the negative PC1 side, with some variability in PC2, indicating a broader chemical diversity. This group correlates with compounds such as hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), nonanal, and benzenamine, 2,5-dichloro. These chemicals suggest the use of fatty acids for softening or lubricating treatments and aldehydes from oxidized oils or fragrances, as well as variability in dyeing techniques or chemical treatments. This diversity implies that Chinese textiles employ a wider range of processes and materials, likely reflecting different manufacturing techniques or raw material sources. Egyptian textiles, which are tightly clustered on the positive PC2 side, show a unique correlation with compounds such as hexyl salicylate, carbonic acid eicosyl vinyl ester, and linear alkanes like C16 and C18. These compounds are indicative of hydrophobic and aromatic treatments, possibly derived from traditional preservation techniques or the use of natural oils and waxes. The distinctive chemical profile of Egyptian textiles highlights their unique finishing processes, which could be tailored to environmental factors or cultural practices. Overall, the clustering in the scores plot is directly influenced by the specific compounds that dominate in each region, reflecting clear differences in manufacturing and treatment approaches. The percentage of cotton appears to correlate with the types of chemical treatments used. Concerning the percentage of cotton in textiles, it is possible to observe that samples with a lower cotton percentage, particularly in Italian and Chinese textiles, seem to rely more heavily on finishing agents such as alkanes or aldehydes, which improve fabric properties like hydrophobicity and softness. Conversely, Egyptian textiles with 100% cotton content likely exhibit a more traditional approach with minimal synthetic chemical treatments, focusing on preserving the natural properties of cotton. This relationship suggests that cotton percentage can influence not only the texture and feel of the fabric but also its chemical footprint, potentially affecting its appeal in specific markets.

3.3. Metal Content Assessment

The metal content was assessed merely to gain an initial understanding of the presence of heavy metals in the textiles. While this aspect is not the central focus of the work, it provides additional insights that could be of interest. The concentration (in ppm) of heavy metals in the samples, together with the Öeko Tex Standard limits, is reported in Table 3. The limits of detection (LOD) and quantification (LOQ) and the coefficients of determination of the calibration curves are reported in Table A3 in Appendix A.

Table 3. Concentration (in ppm) of Cr, Ni, Cu, Mo, Cd, Hg, and Pb (±standard deviation) in samples and Öeko Tex Standard limits.

	^{53}Cr	^{58}Ni	^{63}Cu	^{95}Mo	^{110}Cd	^{200}Hg	^{208}Pb
canov_blu	0.120 ± 0.019	0.464 ± 0.009	0.308 ± 0.038	<LOD	0.0088 ± 0.002	<LOD	0.160 ± 0.009
canov_ross	0.118 ± 0.005	0.358 ± 0.015	2.48 ± 0.296	<LOD	0.0049 ± 0.0001	<LOD	0.0785 ± 0.010
tess_98	0.537 ± 0.068	4.65 ± 0.206	130 ± 4.47	0.244 ± 0.022	0.0171 ± 0.010	0.0106 ± 0.007	0.234 ± 0.125
tess_99	0.408 ± 0.144	3.28 ± 1.57	44.0 ± 1.21	0.014 ± 0.022	0.0232 ± 0.018	0.0158 ± 0.005	0.186 ± 0.003
tess_100	0.180 ± 0.011	1.78 ± 1.03	0.581 ± 0.057	<LOD	0.0072 ± 0.0002	0.0181 ± 0.007	0.234 ± 0.084
calznr	0.185 ± 0.061	0.838 ± 0.214	0.836 ± 0.080	<LOD	0.0067 ± 0.002	<LOD	0.360 ± 0.186
camicia	0.198 ± 0.014	0.233 ± 0.063	0.201 ± 0.026	<LOD	0.0043 ± 0.001	<LOD	0.136 ± 0.008
calzbianco	0.153 ± 0.014	1.11 ± 0.895	0.564 ± 0.275	<LOD	0.010 ± 0.003	<LOD	0.253 ± 0.139
Öeko Tex Standard limits	1–2	1–4	1–40	0.2–1	<0.1	<0.02	0.2–1

As shown in the table, all the analyzed samples comply with legal limits, except for the samples labeled "tess_98" and "tess_99", both of which are 100% cotton. In particular, sample "tess_98" has a significantly higher concentration of copper compared to the other metals present in the sample. The copper concentration in the sample is 130 ppm, more than three times the legal limit set by the Öeko-Tex Standard 100, which specifies a copper concentration range of 1–40 ppm for fabrics in direct contact with the skin. The sample "tess_99" also shows a copper concentration higher than that of the other metals, though not as high as "tess_98", but still exceeding the legal limit (Cu concentration of 44 ppm compared to the 40 ppm safety limit). The reason for this can be associated with the fact that copper can be used as a component in some dyes used in textiles; moreover, it is often involved in the dyeing process as a catalyst or stabilizer to promote the color fixation reaction on the fabric. Additionally, copper can be used in dyeing processes as a mordant or fixer for prints to improve the color stability and durability of fabrics. Therefore, we can hypothesize that the higher copper concentration in both "tess_98" and "tess_99", as printed fabrics, may be due to a print fixation treatment. Besides copper, the two samples "tess_98" and "tess_99" also present higher concentration levels of chromium, although still below the safety limit for skin contact exposure. Chromium VI (hexavalent) is used in some textile and tanning processes in the footwear industry; it is highly toxic, even at low concentrations, to many aquatic organisms. It is commonly used as a mordant in textile dyes to enhance color resistance and durability. Since 1 May 2015, the EU has banned the sale of shoes and leather goods exceeding 2 mg/kg of this metal. Additionally, cadmium, mercury, and lead have been classified as "priority hazardous substances" under EU water regulations and are subject to strict restrictions. The sample "tess_98" presents, in addition to copper, a slightly higher concentration of nickel compared to the Öeko-Tex Standard 100 safety limits. The nickel concentration is 4.65 ppm, while the safe exposure range for nickel in fabrics in contact with the skin is between 1 and 4 ppm. Nickel is found in pigments, dyes, metal alloys, and metal coatings. The most common effect of nickel exposure is an allergic reaction and sensitization due to prolonged direct skin contact with nickel. We can hypothesize that the higher nickel levels in "tess_98", exceeding the legal limit, are due to the use of nickel in dark dyes such as black, blue, brown, purple, and dark green.

4. Conclusions

This study provided a detailed analysis of volatile organic compounds (VOCs) and heavy metal content in textiles of varying origins and compositions using GC–MS and ICP-MS techniques. The results highlight significant differences in the chemical profiles of textiles based on their geographic origin, with VOC analysis via GC–MS revealing distinct patterns and clusters in the volatilome. Principal component analysis (PCA) further validated these observations, showing clear separations among textiles from Italy, China, and Egypt, with the percentage of cotton playing a key role in sample differentiation.

The detection of specific VOCs, such as alkylphenol ethoxylates (APEOs), aromatic amines, and phthalates, underscores the potential health and environmental risks posed by certain textile treatments and additives. While most samples complied with established regulatory limits, exceptions like elevated levels of copper and nickel in certain samples raise concerns about manufacturing practices and the use of specific dyes or chemical treatments.

The ICP-MS analysis conducted on a subset of samples confirmed that while most metals were within acceptable limits, deviations in copper and nickel concentrations highlight the need for stricter quality control and oversight in the textile industry. These findings suggest that certain processing methods, such as dyeing or fixation treatments, may contribute to the elevated levels observed in some textiles.

Nickel, recognized as a common allergen, can cause sensitization and allergic contact dermatitis, particularly with prolonged skin exposure. This risk is especially concerning for individuals wearing textiles in direct contact with the skin. Elevated copper levels, while beneficial in trace amounts, can lead to skin irritation and toxicity, posing risks to sensitive populations, such as children. These findings underscore the necessity for stringent quality control measures to ensure compliance with safety regulations. Non-compliance not only poses health risks but also impacts the marketability of textiles in international trade, particularly in regions with stringent regulatory frameworks, such as the European Union. By addressing these concerns, manufacturers can improve product safety, consumer trust, and market competitiveness.

In conclusion, the combined application of GC–MS and ICP-MS has proven to be a robust approach for the comprehensive evaluation of textile composition and safety. The distinct chemical profiles observed in textiles from Italy, China, and Egypt, along with their specific metal content, could serve as reliable markers for quality control and authenticity verification. For instance, the prevalence of alkanes and aldehydes in Italian textiles highlights their manufacturing emphasis on durability and water-resistant finishes, while their relatively low and uniform metal concentrations further indicate controlled processing practices. These chemical and elemental markers can be used to verify the authenticity of Italian textiles in high-value markets. Similarly, the aromatic compounds such as hexyl salicylate and linear alkanes in Egyptian textiles reflect traditional preservation methods, while the measured metal content, compliant with regulatory standards, supports their reputation for minimal chemical intervention. In contrast, the variability in both chemical composition and metal concentrations in Chinese textiles, including elevated levels of copper and nickel in some samples, suggests diverse manufacturing practices catering to different market demands. This approach, combining chemical and elemental profiling, could support industries in reducing counterfeit products, ensuring regulatory compliance, and maintaining product traceability. This study emphasizes the importance of continued monitoring and regulation of chemical and metal contaminants in textiles, as well as the promotion of sustainable and safer manufacturing practices to minimize environmental and health risks.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app15031572/s1.

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Appendix A

Table A1. Mass (g) of shredded textile used to prepare each analyzed sample.

Sample	Weighted (g)
TESS_98A	0.1506
TESS_98B	0.1505
TESS_99A	0.1553
TESS_99B	0.1504
TESS_100A	0.1535
TESS_100B	0.1544
CANOV_BLUA	0.1529
CANOV_BLUB	0.1504
CANOV_ROSSA	0.1496
CANOV_ROSSB	0.1507
CALZ_BIANCO_A	0.1543
CALZ_BIANCO_B	0.1540
CALZ_NRA	0.1646
CALZ_NRB	0.1573
CAMICIA_A	0.1516
CAMICIA_B	0.1549

Table A2. Standard solution compositions.

Standard Solution	Pb (ppb)	As (ppb)	Hg (ppb)	Ni (ppb)	Cd (ppb)	Cr (ppb)	Cu (ppb)	Co (ppb)	Mo (ppb)
1	0.4	0.38	0.1	0.1	0.04	0.04	0.04	0.05	0.05
2	1.0	0.95	0.25	0.25	0.1	0.1	0.1	0.5	0.5
3	4.0	3.8	1.0	1.0	0.4	0.4	0.4	0.08	0.08
4	10.0	9.5	2.5	2.5	1.0	1.0	1.0	0.4	0.4
5	-	-	12.5	12.5	5.0	5.0	5.0	1.0	1.0
6	-	-	25.0	25.0	10.0	10.0	10.0	-	-
7	-	-	-	-	-	-	20.0	-	-
8	-	-	-	-	-	-	40.0	-	-
9	-	-	-	-	-	-	-	0.8	0.8
10	-	-	-	-	-	-	-	4.0	4.0
11	-	-	-	-	-	-	-	10.0	10.0

Table A3. Limits of detection (LOD) and quantification (LOQ) and the coefficients of determination of calibration curves.

Element	LOD (ppm)	LOQ (ppm)	R^2
Cr	0.04	0.1	0.9996
Ni	0.008	0.003	0.9977
Cu	0.01	0.04	0.9975
Mo	0.0004	0.001	0.9976
Cd	0.002	0.007	0.9996
Hg	0.005	0.02	0.9978
Pb	0.001	0.003	0.9999

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