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METHODS OF QUALITY ASSURANCE FOR FORMALDEHYDE DETERMINATION FROM TEXTILE MATERIALS

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Abstract: *Formaldehyde (CH_2O) is a colorless, highly toxic, and flammable gas at room temperature. Exposure to formaldehyde can irritate the skin, throat, lungs, and eyes, and repeated exposure to formaldehyde can lead to cancer. Formaldehyde resin products used in the textile industry include printing inks, dyes and textile finishing products. These formaldehyde-based materials help bind dyes and pigments to fabrics, prevent colours from running, improve a fabric's resistance to wrinkles, ease clothing care and maintenance and prevent mildew. This study described two analytical methods for detecting formaldehyde in textile materials: high performance liquid chromatography and spectrophotometric. The textile materials containing formaldehyde were extracted in water at 40 degrees C, filtrated and complexed with a coloring reagent – Nash, that contains acetylacetone, acetic acid, ammonium acetate and water. The solutions were comparatively analyzed by spectrophotometry and liquid chromatography coupled with a multiwavelength detector (HPLC-MWD). The spectrophotometric method was validated for precise and reliable results, proving it fits the intented use. The method is linear from the limit of quantification of 4 mg/kg ppm up to 600 mg/kg levels of formaldehyde. This method is intended for formaldehyde analyses in textile samples with excellent recovery, good sample stability, accurate results and good sensibility.*

Keywords: *formaldehyde, method validation, liquid chromatography, spectrophotometry, textiles.*

1. INTRODUCTION

Formaldehyde (Figure 1) is a colorless, flammable, strong-smelling chemical used in building materials to produce many household products. It is used in pressed-wood products, such as particleboard, plywood, and fiberboard; glues and adhesives; permanent-press fabrics; paper product coatings; and certain insulation materials. In addition, formaldehyde is commonly used as an industrial fungicide, germicide, and disinfectant, and as a preservative in mortuaries and medical laboratories. Formaldehyde also occurs naturally in the environment. Most living organisms produce it in small amounts as part of normal metabolic processes.

Consumers are increasingly exposed to hundreds of potentially hazardous chemicals daily. These compounds can come into contact with their bodies through three different pathways: inhalation, ingestion and dermal absorption. Formaldehyde is commonly used in several textile production processes; for example, after treatment of substantive dyeing and hardening of casein fibres, as a wool protection agent, anti-mould, and cross-linking agent in resin finishing.

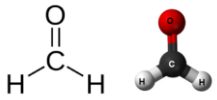

Fig. 1: Chemical structure of formaldehyde.

In 1987, the U.S. Environmental Protection Agency (EPA) classified formaldehyde as a probable human carcinogen under unusually high or prolonged exposure [1]. Since then, some studies of humans have suggested that formaldehyde exposure is associated with certain types of cancer. The International Agency for Research on Cancer (IARC) classifies formaldehyde as a human carcinogen [2]. In 2011, the National Toxicology Program, an interagency program of the Department of Health and Human Services, named formaldehyde a known human carcinogen in its 12th Report on Carcinogens [3].

Formaldehyde mediates its toxic effects by chemically modifying vital cell components, including DNA and proteins, leading to cellular dysfunction. Formaldehyde-mediated genotoxicity is caused by the formation of DNA-DNA and DNA-protein cross-links, as well as covalent DNA mono adducts [4,5,6,7].

In Europe, no legal restrictions are presently applicable to the content of formaldehyde in textiles. In contrast, limitations have been in place in other countries, such as Japan, for over thirty years. However, two voluntary labelling schemes are available: the European Ecolabel, introduced with a Commission Decision [8] and focusing more on ecological criteria, and the private Oeko-Tex Standard 100 [9], which also focuses on consumer protection. Both Ecolabel and Oeko-Tex Standard 100 foresee limits for formaldehyde that vary depending on textile categories. In particular, Ecolabel established the limits of 30 mg/kg for formaldehyde released from textiles in direct contact with the skin (75 mg/kg for Oeko-Tex Standard 100) and 150 mg/kg for textiles which have no direct contact with the skin (the same limit for Oeko-Tex Standard 100). In addition, Oeko-Tex Standard 100 established that textiles for babies up to two years old should release less than 16 mg/kg.

The standard test method for free formaldehyde determination is Japan Law 112 (Oeko-Tex Standard 100), and the accuracy of this method depends on the formaldehyde content in the sample. This method cannot determine the formaldehyde contents under 16 mg/kg. Results obtained below 16 mg/kg are reported as non-detectable. The detection of low formaldehyde contents is important, particularly in some fields, like children's clothing. Thus a more specific and sensitive analysis method was used: high-performance liquid chromatography. Textile substrates finished with different crosslinking reagents were extracted with water to detect free formaldehyde by the acetylacetone method (Nash reagent). The results obtained by the standard test method, Japan Law 112, in which UV/VIS spectrometer was used, were compared with those obtained by the HPLC method, where separation was performed on RP C18 Zorbax Eclipse XDB column with water: ACN as a mobile phase and the result were very close.

2. MATERIALS AND METHODS

2.1. Chemicals and Materials.

All chemicals and reagents were of HPLC or analytical grade. Ultrapure water used throughout the determinations was obtained from TKA GenPure system. Acetonitrile was with assay > 99%.
A standard of formaldehyde (37% methanol stabilized solution) was purchased from Sigma Aldrich. All performance parameters and statistical experiments were applied to finished textile samples.

2.2 Samples.

4 textile samples (2 knitted materials and two compression garments) collected from various textile producers in Romania were analized both by spectrometry and liquid chromatography, and the quantitative results were compared.

2.3. Spectrophotometric methods validation.

Spectrophotometric methods for formaldehyde determination in textiles were performed according to Romanian Standard SR EN ISO 14184-1:2012, and the method was validated. Method Validation (Fit for Intended Use) includes all of the parameters that demonstrate that a method used for quantitative measurement of analytes is reliable and reproducible for the intended use. Eurachem guideline [10] was followed for checking the method validation performance parameters: selectivity, limit of detection (LOD) and quantification (LOQ), sensibility, linearity, trueness, bias, the precision of repeatability and reproducibility, and robustness.

2.4. Calibration Preparation.

A calibration curve was used for both spectrophotometric and chromatographic methods to quantify the amount of formaldehyde in the textile samples. Calibration levels were: 0.15, 0.3, 0.75, 1.5, 2.25, 4.5, and 6 mg/L.

2.5. UV-VIS Analysis. For UV-VIS spectrophotometric determinations Perkin Elmer UV-VIS spectrometer was used, with a maximum absorption peak of formaldehyde at 412 nm.

2.6. HPLC Analysis. The high-performance liquid chromatography instrument used was model Agilent 1100 series from the USA equipped with a quaternary pump (G1311A), vacuum degasser (G1379B), autosampler (G1313A), MWD Agilent detector (G1365B), and analytical column: Agilent Zorbax Eclipse XDB C18 3.5 µm 4.6 × 150 mm. The sofware used was Chemstation for LC, Rev. B. 01.03. The HPLC pump flow rate was 0.8 mL/min. The formaldehyde mobile phase was acetonitrile 50: water 50 (v/v), with an analysis time of 10 minutes. The multiwavelength detector parameter was selected at 412 nm, with a 0 nm reference wavelength.

3. RESULTS AND DISCUSSION

3.1. Optimization of HPLC Analysis. The described test method was developed and optimized to provide confident results. After scanning a broad spectrum (200 -750 nm), the HPLC analysis wavelength was selected, and the maximum absorption peak was observed as 412 nm. The optimum mobile phase mixture was water: acetonitrile (50: 50 v/v), which gives high peak intensity, good resolution factor (>2), good symmetry (>0.80), and convenient run time (Figure 2).

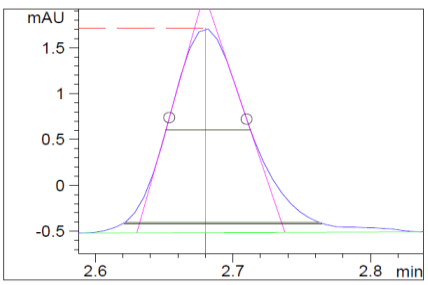

Fig. 2: Peak of formaldehyde 0.75 mg/L, with a symmetry of 0.801

3.2. Method Validation (Fit for Intended Use)

The spectrophotometric method was validated to demonstrate that this method used for quantitative measurement of formaldehyde is reliable and reproducible.

3.2.1. Selectivity

Analytical selectivity shows the method's ability to measure the analyte's response in the presence of all other impurities and compounds in the sample.

Spectrophotometric analysis was performed for the following substances: acetic anhydride 6 mL/L, formaldehyde 0.15 mg/L, formaldehyde 6 mg/L, acetaldehyde 6 mL/L, ethanol 6 mL/L, acetone 2 mL/L, ammonium acetate 150 g/L, acetic acid 3 mL/L, but also for the Nash reagent. It can be observed that the Nash reagent and its components do not spectrally interfere with formaldehyde, the spectrophotometric method being selective for the determination of formaldehyde. All readings were taken in the 350 – 500 nm range. The superimposed spectra of all substances are shown in Figure 3.

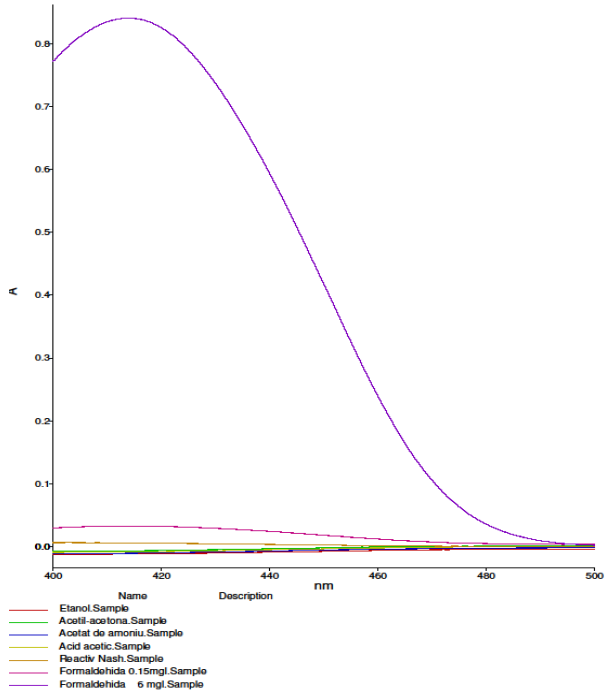

Fig. 3. Superimposed UV-VIS absorption spectra of compounds that can interfere in the determination of formaldehyde

3.2.2. Linearity

The linearity of a quantitative analytical method represents its ability to obtain results proportional to the concentration (quantity) of the analyte in the sample. The linearity was demonstrated by making an 8-point calibration curve in a concentration range of 0.1500 - 6.000 mg/L for the following concentrations: 0.15 mg/L, 0.3 mg/L, 0.75 mg/L, 1.5 mg/L, 2.25 mg/L, 3 mg/L, 4.5 mg/L, 6 mg/L.

The regression curve of corrected absorbance vs concentration was generated (Figure 4). The obtained correlation coefficient (0.999640) demonstrates excellent linearity over the 0.15 mg/L - 6 mg/L concentration range.

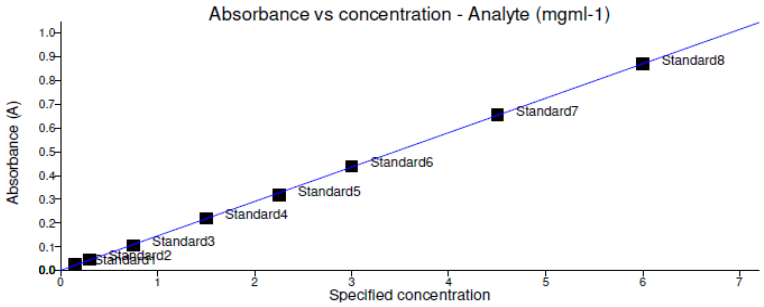

Fig. 4. 8 points - calibration curve

3.2.3. Limit of detection and limit of quantification

The limit of detection (LOD) represents the lowest analyte concentration in a sample that can be detected with reasonable statistical certainty but not necessarily quantified as an exact value under the established test conditions. The limit of quantification (LOQ) is the lowest concentration or amount of analyte that can be quantitatively determined with acceptable repeatability and accuracy. 10 independent blind samples were passed through the entire work procedure and had their absorbance measured. In the second step, 10 independent blank samples fortified at 6 concentration levels were prepared: 0.11 mg/L, 0.12 mg/L, 0.13 mg/L, 0.14 mg/L, 0.15 mg/L, 0.16 mg/L and had their absorbance measured (Table 1).

Table 1. The experimental results obtained for 6 concentration levels, standard deviation and RSD%

n (no. det.)	**0.11 mg/L**	**0.12 mg/L**	**0.13 mg/L**	**0.14 mg/L**	***0.15 mg/L***	**0.16 mg/L**
1	0.1052	0.1145	0.1158	0.1377	0.1485	0.1647
2	0.1056	0.1142	0.1164	0.1384	0.1453	0.1568
3	0.1059	0.1143	0.1156	0.1386	0.1509	0.1595
4	0.1062	0.1142	0.1164	0.14	0.1556	0.1618
5	0.1062	0.1145	0.1164	0.1401	0.1505	0.1643
6	0.1065	0.1148	0.1166	0.1407	0.1571	0.1667
7	0.1067	0.1143	0.1165	0.1406	0.1420	0.1689
8	0.1071	0.1148	0.1168	0.1408	0.1445	0.1712
9	0.1066	0.1142	0.1168	0.1412	0.1470	0.1739
10	0.1065	0.1151	0.1171	0.1412	0.1502	0.1762
$x_{m(sample)}$	**0.1063**	**0.11449**	**0.11644**	**0.13993**	**0.1492**	**0.1664**
σ_{sample}	**0.0006**	**0.00031**	**0.00045**	**0.00125**	**0.00475**	**0.00624**
RSD%	**0.5273**	**0.27451**	**0.38874**	**0.89579**	**3.1872**	**3.74712**

LOD = 0 + 3* 0.00475 = **0.01425 mg/L (1.425 mg/kg CH_2O)**
LOQ = 0 + 10* 0.00475 = **0.0475 mg/L (4.75 mg/kg CH_2O)**

The results obtained for the detection and quantification limit allows establishing the lower limit of the working concentration range at the value of 0.15 mg/L but especially allows the detection and quantification of formaldehyde at lower levels of concentrations. \

3.3. Quantitative results

Results obtained for the quantitative determination of formaldehyde in textile samples by spectrometry and liquid chromatography are very close (Table 2). Therefore, HPLC-MWD

technique can be easily and precisely used as a more modern and efficient alternative to the spectrophotometric method.

Table 2. The result obtained for CH_2O determination in textile samples

Analysis technique	**Formaldehyde concentration (mg/kg)**			
	Sample 1 (Knitted material)	Sample 2 (Knitted material)	Sample 3 (compression garment)	Sample 4 (compression garment)
UV-VIS Spectrometry	4.89	12.35	6.12	12.35
HPLC-MWD	4.74	13.27	5.72	14.05

4. CONCLUSION

Detection and monitoring of formaldehyde in textile materials is a serious concern, considering the toxic effect of this substance on human health. This study presented two reliable methods for the simple and fast quantitative determination of formaldehyde in textile samples. The spectrophotometric method was validated for reliability and precision in routine analysis, confirming that this method is fit for purpose. The chromatographic method was optimized and gave very close quantitative results compared to the spectrophotometric method. HPLC-MWD equipment can thus be safely used for a more rapid, precise and modern determination.

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