Determination of Formaldehyde Content in Footwear Samples using a HPLC-UV technique

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Abstract- In this work, the content of formaldehyde is determined in 134 samples from 35 models footwear of which thirteen models correspond to men's footwear, ten models for women, seven models for children and five sport type. The samples were obtained from several parts the finished footwear (court, lining, insole, outsole, accessories) and classified according to: i) the model and ii) type of material: leather and textile. The extraction of formaldehyde from several samples was conducted using 0.1% sodium dodecyl benzene sulphonate as extracting agent, derivatizing with 2,4-dinitrophenylhydrazine and subsequent separation/determination by High Performance Liquid Chomatography(HPLC) with UV detection. The results show that formaldehyde content in the footwear models were in the range of 17.6 to 164 mg/kg for men; 6.74 to 125 mg/kg for women; 17.3 to 157 mg/kg for children and 21.5 to 107 mg/kg for sports. The highest formaldehyde concentrations were found in leather samples, exceeding the permissible limit of 65 mg/kg for adults; while the remaining models for children exceed the permissible limits of formaldehyde in leather 16 mg/kg by children.

Index Terms- Formaldehyde, footwear, leather, textiles, HPLC-UV

I. Introduction

The formaldehyde is a chemical compound used as preservative in a variety of hygiene products, cosmetics, paints textiles[1-3] and tanning or finishing processes for leather[4]. In these last two processes, other substances are used, such as hexavalent chromium salts, azodyes, vegetable tannins, organic solvents and chlorophenols. The toxicity of formaldehyde in humans is well documented and recently the International Agency for Research on Cancer (IARC) classified it as carcinogen in the group 1 [1, 5-9]. The acceptable daily intake established by EPA, is 0.2 mg/kg body weight [3, 10]. The ingestion/contact with large amounts of this pollutant, could cause abdominal pain, dermatitis, vomiting, kidney damage, lung, sinonasal or pancreatic cancer [1, 3, 7, 11-15]. In recent years, the use of formaldehyde has received special attention and a large number of analytical methods have been reported for its detection. Some of them are the high performance liquid chromatography, solid phase extraction, photometric detection of solid-phase micro extraction with isotope dilution including mass spectrometry[1, 5, 11-13]. The most prominent technique is the high performance liquid chromatography. This represent the most powerful separation technique that is available commercially and commonly used in analytical chemistry [1, 2, 7-11, 14-27]. This technique is defined as a physical separation method, in which solutes are separated and distributed between two phases: stationary phase, which remains immobile and a mobile phase, which moves in a definite direction. This technique provides a full range of possibilities of separation of analytes of interest, based on different physicochemical principles. Formaldehyde can be found in different matrices (food, air, cosmetics, paints, leather, textiles, etc.). Prior to separation/detection by HPLC the formaldehyde is commonly derivatized with 2,4-dinitrophenylhydrazine [2, 7-10, 14, 18-31]. In this work is discussed the determination of formaldehyde concentration content in different models of the finished footwear for woman, men, children and sport commercialized in the State of Guanajuato, México.

II. EXPERIMENTAL

2.1. Reagents

The reagents were of analytical grade, tridistilled water (Karal) was used, acetonitrile(Tedia/HPLC-Spectro), 2,4-dinitrophenylhydrazine (Baker), phosphoric acid (Baker), standard solution of formaldehyde (Accustandard, 1000 µg/mL in water), sodium dodecylbenzene sulphonate (Aldrich).

2.2 Instrumentation

The chromatographic separation of formaldehyde, took place in a HPLC Agilent Technologies system, model 1100, using a Eclipse XDB C18 column (250 x 4.6mm, 5 µm), water/acetonitrile (30/70) as mobile phase in isocratic mode to 1.2 mL/min flow rate [17, 21]. Inlet temperature column was of 23°C and the injection volume of 20 µL. The determination was performed using a UV detector at a wavelength of 360 nm [5, 11, 12, 14, 16, 18-20, 22, 23, 26 , 27, 29, 30, 32]. External calibration was performed utilizing nine solutions at different concentrations (0.005; 0.05; 0.10; 0.25; 0.50; 0.75; 1.0; 1.5; 2.0mg/mL) prepared by dilute the standard of formaldehyde to appropriate concentration with tridistilled water/acetonitrile and derivatizing 0.3% 2,4-dinitrophenylhydrazine. The correlation obtained was 0.9992.

2.3 Experimental procedure

A total of 134 samples were analyzed from 35 models footwear: thirteen models corresponding to men's footwear (classified as M1, M2, M3, M4, M5, M6, M7, M8 , M9, M10, M11, M12 and M13), ten models for women (W1, W2, W3, W4, W5, W6, W7, W8, W9, W10), seven models for children (CH1, CH2, CH3, CH4, CH5, CH6, CH7) and five sports type models (S1, S2, S3, S4, S5). The samples analyzed were classified according to: i) the model and ii) type of material: leather and textile. The initial samples were obtained from different parts of footwear: court, lining, insole, outsole and accessories**.**

Saturated solution was prepared by weighing 300 mg of 2,4-dinitrophenylhydrazine and diluting to 100 mL with acetonitrile. It was allowed to stir for 60 minutes, heated to 60 °C and evaporated about 95% the solvent. Allowed to cool and washed twice with acetonitrile and dried in argón atmosphere. Subsequently, a solution 0.3% of 2,4-dinitrophenylhydrazine was prepared by weighing 0.15g completed to 50 mL with concentrated phosphoric acid using the ultrasonic bath for 10 minutes [1, 5, 10, 11, 16, 19, 20, 29, 30]. The solution was stored in amber bottle [32].

The extractant solution was prepared by weighing 1.0g of sodium dodecyl benzene sulphonate and completing the volume to 1000mL with tridistilled water. The method of extraction for the determination of formaldehyde in textiles and leather samples, was performed according to ISO 17226-1:2003 [33] with slight modifications, which consist in: a weight of 2±0.1g of sample (leather or textile) previously cleaned mechanically, was cut into small pieces of 1-2 mm (samples were worked as received) in Erlenmeyer flasks Teflon; were added 50mL of solution 0.1% sodium dodecyl benzene sulphonate pre-heated to 40°C, the samples were capped and heated in water bath at 40°C with stirring for 60 minutes. After this time, immediately were filtered using glass fiber filter.

For the chromatographic determination, the samples were prepared as follows: 1000µL of the filtered extract from each sample were mixed with 800µL of acetonitrile, 100µL of tridistilled water and 100µL of 0.3% 2,4-dinitrophenylhydrazine and derivatizing 60 minutes. All samples were analyzed the same day of preparation.

III. RESULTS AND DISCUSSION

The 35 models of footwear analyzed in this work, correspond to men, women, children and sports. Some of the observed differences are in design, manufacture material (leather or textile) and the different components (cutting, lining, insole, outsole and accessories) for each model.

The elution time obtained in chromatographic separation was 2.78 and 3.59minutes for the 2,4-dinitrophenylhydrazine and formaldehyde, respectively. A similar time was observed in the samples analyzed.

The Table 1 shows the results the formaldehyde determined in 134 samples analyzed, classified according to: a) material (leather or textile) and b) analyzed as part of the footwear (court, lining, insole, outsole or accessories). The total formaldehyde in the models analyzed footwear for men was of 17.6 to 164 mg/kg; for women 6.74 to 124 mg/kg; the children from 17.3 to 157 mg/kg and sport footwear of 21.5 to 107 mg/kg. It is noteworthy that the variability between formaldehyde concentrations found was dependent on factors such as the model (woman, men, children or sport), material (leather or textile) or the part of the footwear (court, lining, insole, outsole or accessories). These results show that higher concentrations of formaldehyde were found in leather samples. Figure 1, presented a scatter diagram with the analytical results for 35 footwear models. It is shown that several footwear models exceed the allowable limit for adults 65mg/kg according Restricted Substances List 2014 [35] of which four models corresponding to children, seven to men, two for woman and one model sports footwear; in the children's footwear all models analyzed exceeded the permissible limit of 16 mg/kg [35].

In Figure 2 is plotted the scatter with the values obtained for 134 total samples analyzed, of which 26 samples were from children's footwear, 33 for women; 54 corresponding for men and 21 samples for footwear sport. It can be seen, that 4 of the samples of footwear for men and a sample for sport footwear exceed the normative value of 65 mg/kg [35]. On the other hand, all samples analyzed in children's footwear surpassed the limit 16 mg/kg [35]. Moreover, taking into account the part footwear analyzed (court, lining, insole, outsole and accessories), the following results were obtained: samples belonging to the court were 38.6% and 18.7%; lining 33.3% and 34.7%; insole 19.3% and 17.3%; outsole 5.3% and 1.3% in leather and textile respectively. In the samples corresponding to accessories was based in laces, ribbons, bias and tapes deriving from 28% textile and 3.5% leather material.

Is important to mention the presence of formaldehyde in the footwear, it is frequently found because most of these manufacture processes use formaldehyde compounds in order to improve the physical properties of these materials[36].

IV. CONCLUSIONS

From 35 footwear models analyzed, 13 models corresponded to men's footwear, 10 for women, 7 for children and 5 sports. Generally the results show that 6.74-50.0 mg/kg formaldehyde were found in the models M1, M4, M8, M10, M12, M13, W3, W7, W9, W11, W13, CH4, S4 and S5; of 50-100 mg/kg in models M3, M7, M9, M11, W2, W4, W10, W12, CH1, CH5, CH6, CH7, CH8, S2 and S3; the 100 to 150 mg/kg in the models M5, M6, W1, CH2, CH3 and S1; and of 150 to 200 mg/kg was found the pattern M2. Based on these results it can be concluded that all models of footwear for children exceed the normative limit 16 mg/kg [35] in leather and textile products for children. Furthermore, for adult, the allowable limit in leather and textile with direct contact is 65 mg/kg [35], being the models M1, M3, M5, M6, M7, M9, M11, W1, CH2, CH3, S1 that exceeded this value.

The highest concentrations of formaldehyde were more frequent found in leather that textile samples and eleven footwear models analyzed exceeded the permissible limit of 65 mg/kg for adult with direct contact, while all models for children exceeded the permissible limits of formaldehyde in leather 16 mg/kg [35].

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Table 1: Content of formaldehyde in footwear models for men, women, children and sport.

	Formaldehyde concentration in different footwear models							
Model	**Men** 17.6-164 mg/kg		**Woman** 6.74-124 mg/kg		**CHildren** 17.3-157 mg/kg		**Sport** 21.5-107 mg/kg	
Material	***Leather***	***Textil***	***Leather***	***Textil***	***Leather***	***Textil***	***Leather***	***Textil***
Court	0.78- 87.5	2.85-22.3	8.32-34.7	1.68-32.0	5.23-44.7	2.78- 4.83	35.1-73.5	1.37- 26.7
Lining	5.82- 83.3	0.55-79.3	8.48-42.1	0.53- 27.4	11.6-35.3	0- 1.26	nd	1.18- 12.9
Insole	8.18- 62.6	1.43-9.37	9.17-10.0	2.94- 5.61	9.11-53.2	1.78- 43.3	nd	2.46 - 44.8
Sole	2.57- 2.95	nd	0 - 2.55	0 - 15.9	nd	nd	nd	nd
Accesories	nd	0.11-4.86	0 - 11.7	1.59- 43.3	nd	3.28- 83.8	nd	0- 3.37

nd: no detected

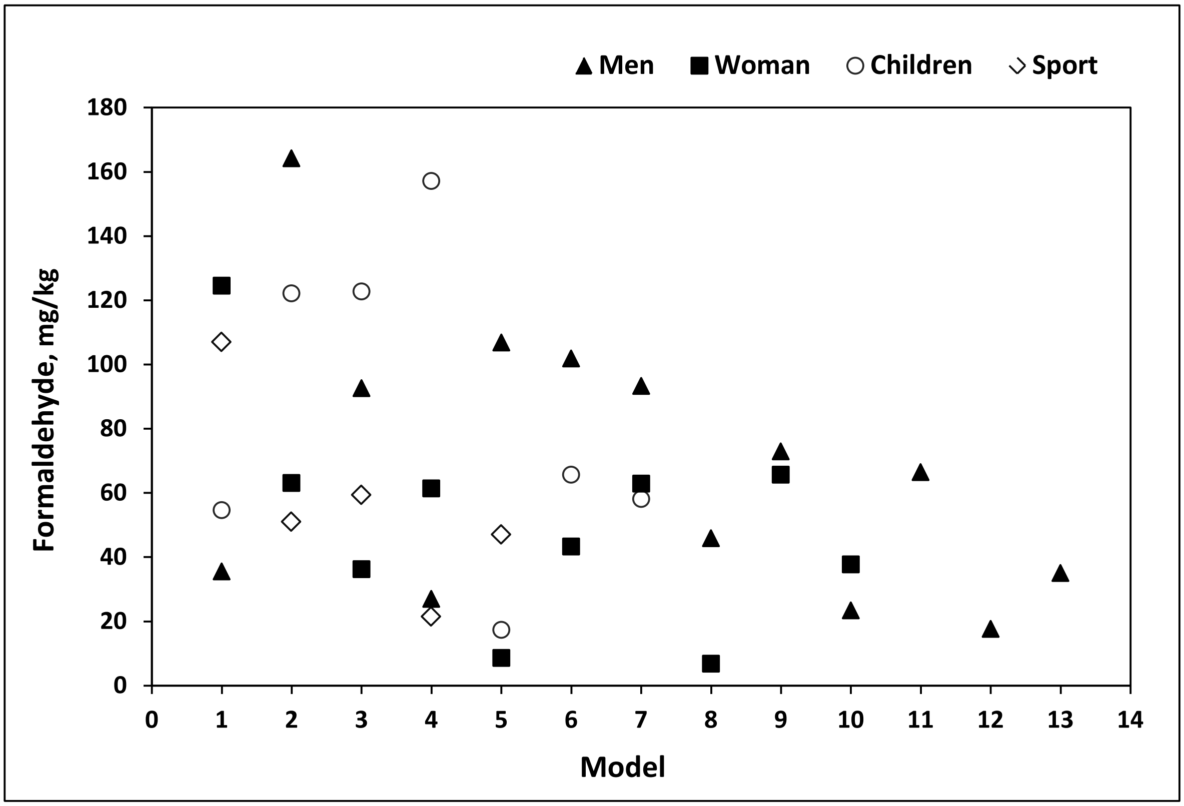

Figure 1: Distribution diagram of formaldehyde content in 35 footwear models analyzed in this work.

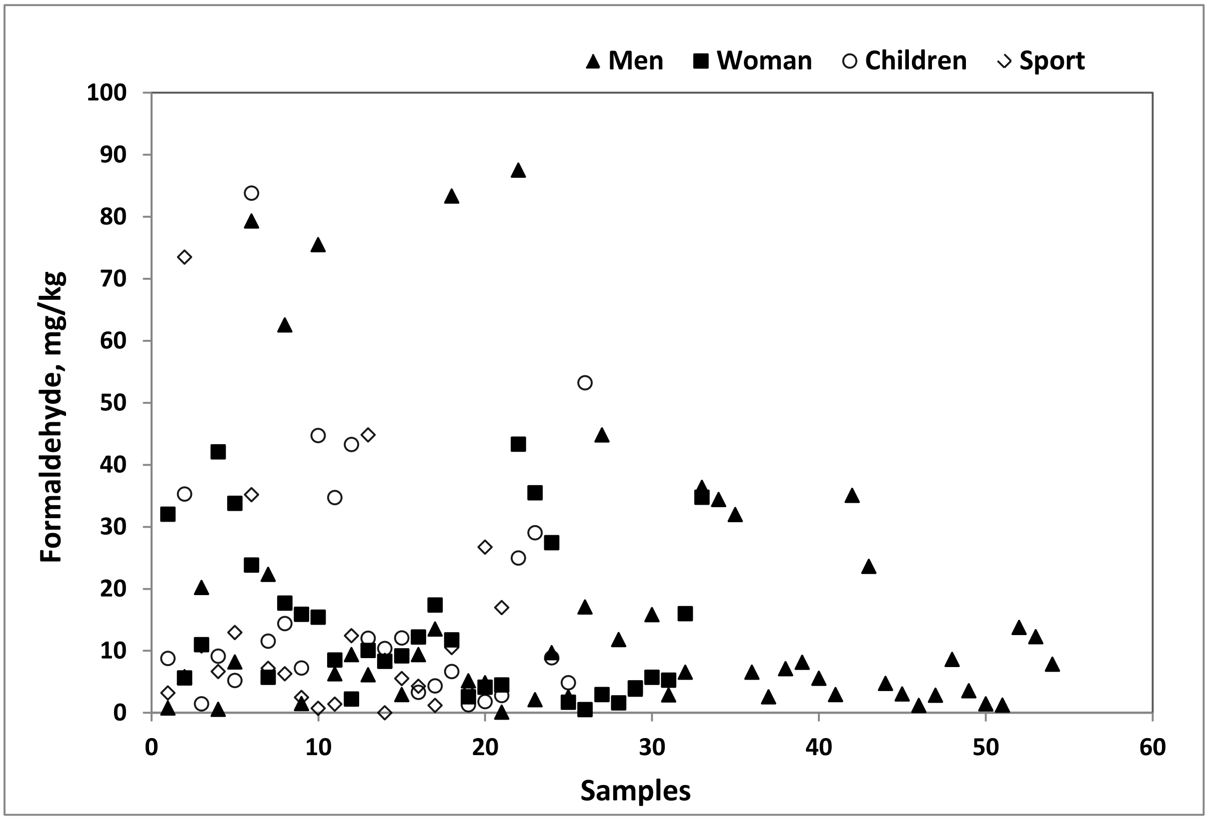

Figura 2: Scatter diagram formaldehyde content in 134 samples analyzed from different footwear models.