Spectrophotometric Determination of Formaldehyde Concentration from the Dyed Fabrics in Lahore, Pakistan

Shafiq ur Rehman[*1], Sadaf Javaid[2], Anum Tahir[3], Amna Yousaf[4] ,Sadia Zulfiqar[5], Muhammad Asam Raza[6] ,Fatima Javed[7]
PhD[1], M.Phil[2], M.Phil[3], PhD[4], PhD[5], PhD[6], M.Phil[7]
[1,2,3,5]Department of Chemistry, Faculty of Sciences, University of Central Punjab, Pakistan.
[4,7]Department of Chemistry, Kinnard College for Women Lahore, Pakistan.
[6] Department of Chemistry, University of Gujrat, Pakistan
shafiqchemist@gmail.com, +92(0)3334566845.

Abstract
In the current study formaldehyde determination in fabric was performed 21 fabric samples from local market shops and branded shops. Out of 20 samples, thirteen samples were out of range as per OEKO-TEX standards. Out of all the samples, bed sheets have 316.5 mg/Kg and curtains have 539.7mg/Kg and 771.1 mg/Kg concentration which were collected from local markets and proved to be in the category with the highest risk and children fabric were found within the limits. According to the results, the fabric manufactured in Pakistan has formaldehyde greater in most of the samples than the permissible limits. Maximum concentration of formaldehyde is present in the sample of local market. However, a high level of formaldehyde is also present in branded samples which are undoubtedly a health hazard. From this study it is evident that fabric material manufactured in Pakistan does not meet international quality standards.
Keywords: Formaldehyde, Fabric, dermatology, Toxicity

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Introduction

Formaldehyde causes nose, throat, and eyes irritation, sensitization and dermal allergies on human skin when come in contact [Thompson,2010]. Acute exposure to formaldehyde can be very harmful which may cause irritation, acute poisoning, dermal allergies, allergic asthma, neurotoxicity, cellular change, pulmonary function damage, hemtoxicity, reproductive toxicity and genotoxicity by inducing damage in DNA and chromosomal structure in blood cells. It is also one of the main causes of internal issues related to women. Its higher value can cause time fluctuations in menstrual cycle and dysmenorrheal. It also lowers the blood cells in human body which can ultimately results in blood cancer [Lusting,1967]. Formaldehyde also show reaction with nerve transmitters and nerve proteins which have major function in human body and can cause severe endocrine disruptions [Hyun, 1961].

The patients who have patches of dermatitis on their skin are said to be allergic from that which can be easily recognized that this is due to the high exposure of formaldehyde. Formaldehyde present in different fabrics has a direct contact with skin and may cause irritation in mucous membranes. According to epidemiologic studies, formaldehyde is also the cause of the nasopharyngeal cancer, "strong but not sufficient" evidence of sinus cancer is also found. It may also cause inflammation in respiratory tract which may ultimately cause difficulty in breathing [Hyun, 1961].

Formaldehyde also forms chemical bonds and cross link with the other chemical pollutants present in the environment. If formaldehyde forms a complex with chemical pollutants it can dissociate as free radicals in the presence of sunlight and can be a lot more dangerous than the formaldehyde in the free form, as the radicals have the scavenging effect and are a lot more reactive and as a formaldehyde is an aldehyde it has a strong tendency to react and forms a new compound leading to the either same group of aldehydes or different. As its scavenging properties are harmful on one side while on the other side, they are useful in providing durable press to the fabric [James,2002].

Besides causing minor issues i-e nausea, headache, inflammation it is also a cause of some serious issues for example it can cause the nervous damage by reacting and forming cross linkages with proteins, DNA and fatty acids. As all of these constituents are present in every cell of the body it can cause damage to any of the body cell [Endcrinology,2015].

The permissible exposure limit (PEL) for formaldehyde in all workplaces covered by the Occupational Safety and Health Act is 0.75 ppm measured. This standard includes a 2 ppm short- term exposure limit (STEL). The action level is 0.5 ppm measured over 8 hours [Auctrian,1990].

The formaldehyde resins used in fabric differ from those used in wood industry as the resins used in fabric should provide finishing, crease resistance reagent, anti-wrinkling and anti-clinging properties. For this purpose, nitrogen containing cellulosic fiber resins is used in the textile industry. The resin that is most extensively used for durable press finishes has been dimethyloldihydroxyethyleneurea. The contact with formaldehyde was reduced by the development of non-formaldehyde resins but these resins were of high cost due to which the accepted ones were the formaldehyde-based resins in textile industry [Samuilova, 2005].

Formaldehyde was chosen because of its widespread use in textile as proposed by IARC (international agency of research on cancer). It is used in dying to improve wet fastness, in hardening of caseins fibers and as an anti-wrinkling and anti-clinging reagent etc. [Kong, 2009].

Often it is suggested that washing the fabric will result in the formaldehyde reduction. Some of the studies have revealed that even two washings don't lower the formaldehyde level in fabric [Welch,1988]. Finishing is done mostly by formaldehyde as it provides crease resistance, flame resistance and

dimensional stability. If it is used in a small quantity it may be beneficial rather than being harmful when used in greater quantities [Shiann,1978].

High level of formaldehyde in fabric is the main cause of dermal allergies on human skin. It is the persistent contaminant in environment. The purpose of research is to find the level of formaldehyde in fabric as the fabric is in the direct contact with the skin. It may also be a major cause of diseases if it is detected beyond the permissible limit.

Materials and Methods

The determination of formaldehyde in fabric can be carried out by a number of methods such as water extraction method, HPLC and spectrophotometer. However, the present research work is based on the spectrophotometer. Comparison of transmittance of unknowns to either that of standard solutions, or to those of an internal standard, allows quantitative analysis of the analyte metal in the sample solution.

Preparation of Nash's Reagent

150 g of ammonium acetate was dissolved in about 800 mL of double distilled water, than 2mL of acetyl acetone and 3mL of glacial acetic acid was added in it and made the volume up to 1000 mL in volumetric flask.

Collection of samples

Twenty Samples of fabric were collected from local market, Lahore Pakistan. All of the samples were top knitted, dyed or printed garments.

Preparation of stock solution

1500 mg/L of stock solution of formaldehyde was prepared by diluting 3.8ml of formaldehyde solution to one liter with water and standard dilutions are prepared by this stock solution.
Different dilution was made from the formaldehyde stock solution. The dilutions consist of different concentration of formaldehyde in it. In this experiment dilutions of 0.1 ppm, 0.2 ppm, 0.3 ppm, 0.4 ppm, 0.5 ppm, 0.6 ppm, 0.7 ppm, 0.8 ppm, 0.9 ppm and 1 ppm were made from the standard stock solution.

Preparation and conditioning of test specimen

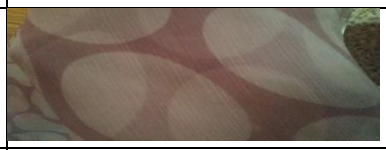
Test specimen should not be conditioned to avoid humidity and pre drying in connection with the conditioning may cause change in the formaldehyde content of the sample. Prior to test store the sample in the container.
From the sample fabric two test specimens were cut off each weighing 2.5g and was placed in a 250ml of stoppered flask and 250ml of water was added. The flask should be stoppered tightly and placed in a water bath at (40 ± 2) °C for (60 ± 5) min. the flask was shaken after every 5 min. Then the solution was filtered into another flask by using a filter paper.

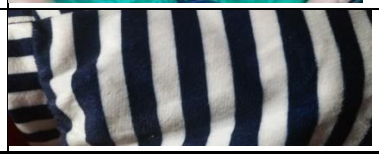
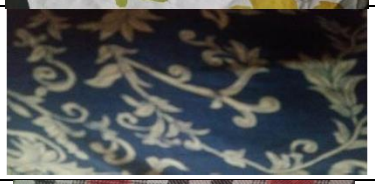
Procedure

1. 5ml of Nash's reagent was taken in a test tube and 5ml of double distilled water was added in it and this was treated as a blank reagent for the analysis on spectrophotometer.
2. 5ml of the diluted standard solution was taken in a test tube and 5ml of Nash reagent was added in it. This was done for solutions off all concentrations i-e 0.1 ppm, 0.2 ppm, 0.3 ppm, 0.4 ppm, 0.5 ppm, 0.6 ppm, 0.7 ppm, 0.8 ppm, 0.9 ppm and 1 ppm respectively. Test Tubes first were kept in the water bath at (40 ± 2) °C for (30 ± 5) min and then at ambient temperature for (30 ± 5) min.
3. The filtered test specimen solution was further diluted by taking 10ml of the test specimen solution and making it up to the mark with 100ml of double distilled water. 5ml of diluted test specimen solution was taken in a test tube and 5ml Nash reagent was added in it. It was shook well. Test tubes were first kept in a water bath at (40 ± 2) °C for (30 ± 5) min and then at ambient temperature for (30 ± 5) min. This was done for all the sample solutions.
4. Solution was warmed in a water bath at (40 ± 2) °C for (10 ± 1) min, then 5 ml of acetyl acetone reagent was added in it, was shaken well and continue to warm the solution in a water bath at (40 ± 2) °C for (30 ± 5) min. the solution was left at room temperature for (30 ± 5) min. the absorbance of all the standard as well as the sample solution was determined. The absorbance for formaldehyde was set at 412 nm on a spectrophotometer.

Results and Discussion

Table 1: Sample Description

ample Code	Picture	Source	Description	Productin Country	Type
A1		Local market	ık printed sample	Pakistan	hildren wear
A2		Local market	on orange sample	Pakistan	omen's wear
A3		Local market	Maroon embroided sample	Pakistan	Curtains
A4		Local market	Brown sample	Pakistan	Sofa fabric
A5		Local market	·d printed sample	Pakistan	omen's wear

A6		Local market	Green printed sample	Pakistan	omen's wear
A7		Local market	ıe printed sample	Pakistan	hildren wear
A8		Local market (mark and lencer)	·een dyed sample	Pakistan	Men's wear
A9		Local market	White printed sample	Pakistan	ed sheet sample
A10		Local market	lue dyed sample	Pakistan	omen's wear
A11		Local market	nted dyed sample	Pakistan	Curtains fabric
A12		Local market	nted dyed sample	Pakistan	Fleece fabric
A13		Local market	Printed sample	Pakistan	omen's wear
B		Branded (Breakout)	ık printed sample	UK	omen's wear
C		Branded (Quiz)	Orange embroided sample	UK	omen's wear
D1		Branded (Gul Ahmad)	Green printed sample	Paksitan	omen's wear
D2		Branded (Gul Ahmad)	rey dyed sample	Pakistan	Men's wear

E		Branded (Ahmad fabrics)	nted dyed sample	Pakistan	omen's wear
F1		Branded (Khaadi)	nted dyed sample	Pakistan	omen's wear
F2		Branded (Khaadi)	nted dyed fabric	Pakistan	Women's wear

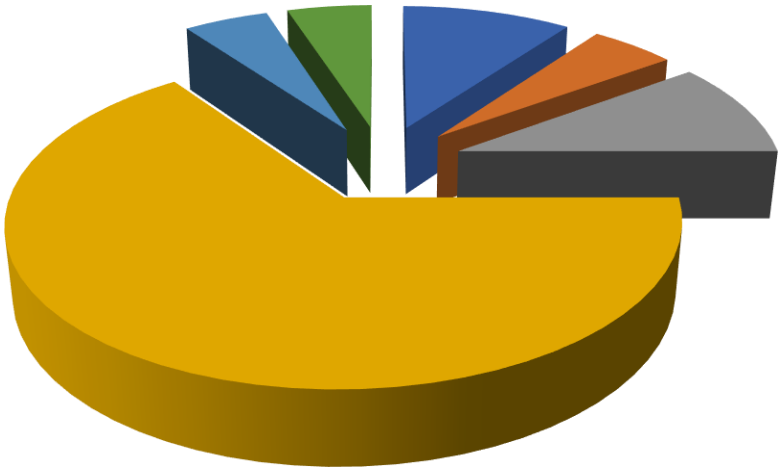


Figure 1: Percentage of sample Brands

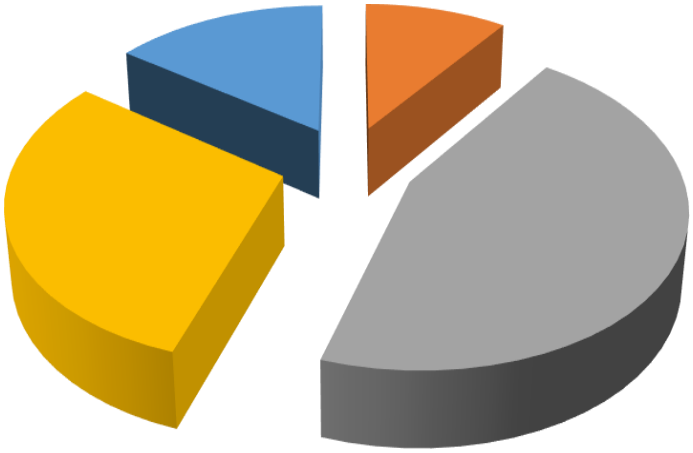


Figure 2: Age group distributions

Absorbance of samples

Table 2: Formaldehyde concentration in different samples

Sr. No.	Sample	Sample No.	ıcentration (mg/kg)	tandard Values (mg/kg)
1	Children	A3	539.7	≤ 16ppm [32]
		A11	771.7	≤ 16ppm
2	20-22 Years	B	8.6068	≤ 75ppm [32]
		C	60.368	≤ 75ppm
3	Adults (30 onwards)	A2	62.5	≤ 75ppm
		A6	165.148	≤ 75ppm
		A10	265.1	≤ 75ppm
		A13	309.1	≤ 75ppm
		D1	54.768	≤ 75ppm
		D2	223.8	≤ 75ppm
		E	58.7	≤ 75ppm
		F1	124.90	≤ 75ppm
		F2	164.908	≤ 75ppm

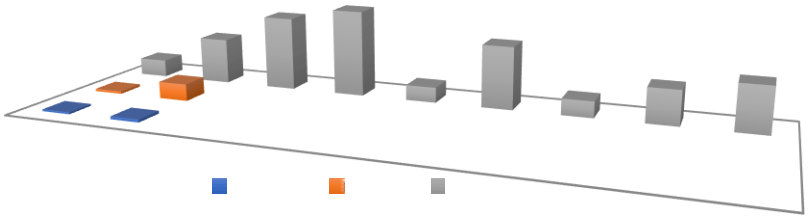


Figure 3: Fabric samples of people of different age groups

Table 3: Formaldehyde in samples of direct as well as indirect contact

Sr. No.	Sample	Sample No.	ıcentration (mg/kg)	Standard Values (mg/kg)
1.	direct contact (Curtains)	A3	539.7	≤ 300ppm
		A11	771.7	≤ 300ppm
2.	Direct contact	A4	782.32	≤ 75ppm
		A9	265.1	≤ 75ppm
	(Fleece and Bed sheets)	A12	316.5	≤ 75ppm

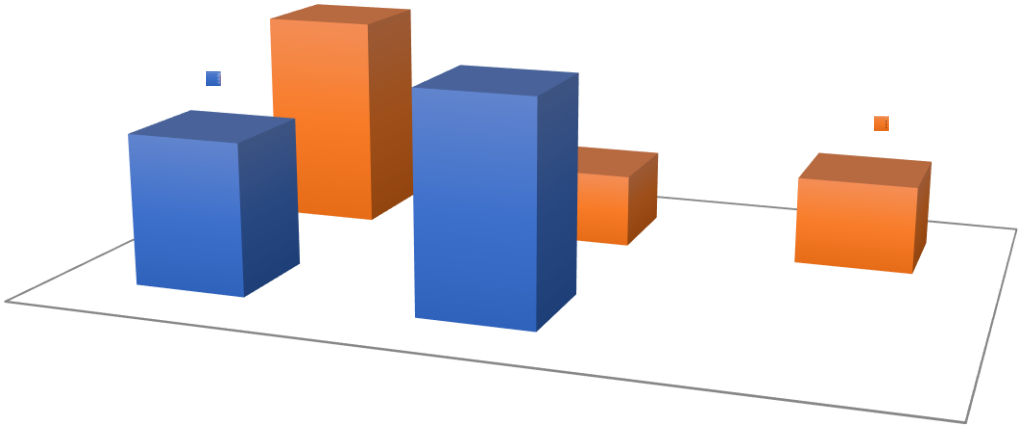


Figure 4: Fabric samples with direct and indirect contact

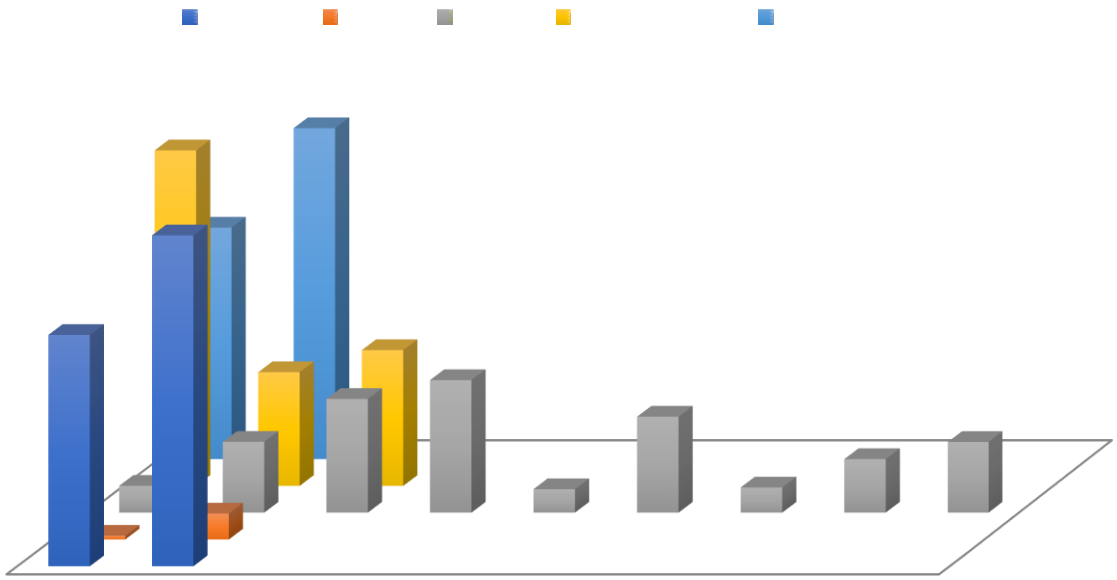


Figure 5: Comparison of concentration of all fabric samples

Formaldehyde concentration in different fabric samples was determined including samples with direct as well as indirect contact with human body. The samples with direct contact include clothes for wearing of children as well as adults, bed sheets and fleece. The samples with indirect contact include curtains. The fabric of children was especially tested because there skin is more sensitive as compared to adults and hence may be more prone to allergies as compared to adults [7].

In this study, total of 20 samples of fabric of different brands and nature were selected. Thirteen samples are collected from local market. Out of which, two samples were of children among age of 12-15, two samples were of bed sheets, two sample of curtain, one sample of fleece and 7 samples of women wear were selected. Formaldehyde in the samples of children were under permissible limits i-e. 6.512 mg/kg and 9.9028 mg/kg which depict that it's not harmful to use as the standard set by OEKO-TEX for children is ≤ 16ppm.

The eleven other samples from the local market were out of the permissible limits which includes all other fabric other than the children. The fabric which was in indirect contact (curtains) were out of permissible limits i-e 539.7 mg/kg and 771.7 mg/kg while its permissible limit is ≤ 300ppm. The formaldehyde in these samples is extremely high which means formaldehyde concentration in fabric was not checked before its delivery in local market.

The fabric of local market which was in direct contact i-e bed sheets and women wear were also out of permissible limits. The concentration of formaldehyde in fabric of two bed sheets and fleece were 782.32

mg/kg, 265.1 mg/kg and 316.5 mg/kg respectively which indicates that the fabric was not tested. The other samples of women wear of local market were also out of range and the concentration of formaldehyde in the fabric sample of women wear were 62.5ppm, 81.164ppm,
165.148 mg/kg, 241.404 mg/kg, 249.4 mg/kg and 309.1 mg/kg but the permissible limit for fabric in direct contact is ≤ 75ppm [11-22]. In this fabric formaldehyde compounds or resins might have been used without any consideration of permissible limits not only during the process but also after the complete finishing of the fabric. So, government should undertake steps for proper investigation of the fabric of local market as well.

Two of the samples were taken from breakout and quiz (International Brand). The formaldehyde in both of these samples were under permissible limits i-e 8.6068 mg/kg and 60.368 mg/kgwhich indicates that the fabric was tested before sending it into the market.

Two of the samples were taken from Gul Ahmad which is a known brand working in Pakistan. One of the samples was of women wear while the other was of men's wear. The formaldehyde in women's fabric was under permissible limits i-e 54.768 mg/kg while in men's fabric it was 223.8 mg/kg. This indicated that formaldehyde concentration vary from fabric to fabric and also depends upon dyes which are applied. The sample of women's wear was soft which indicates that less formaldehyde was present but the sample of men wear was thick. For the anti-shrinking properties more formaldehyde would have been added to the men's fabric to make it more durable [8].

One sample was taken from Ahmad Fabrics which is also a well-known brand for women and men's working in Pakistan. The fabric taken from Ahmad Fabrics was used in making t- shirts for men. But formaldehyde was in limit i-e. 58.7 in the sample making it safe to use. The formaldehyde may actually be little in this fabric or formaldehyde may have been replaced by some other compound or resin such as melamine formaldehyde or urea formaldehyde etc.

Khaadi is also a brand which sponsors women wear in Pakistan. The fabric taken from Khaadi was out of permissible limits i-e. 124.90 mg/kg and 164.908 mg/kg. Formaldehyde is used in fabric to provide permanent press, anti-cling, anti-static, anti-wrinkle and anti-shrink finishes. For this purpose formaldehyde might have been used in excess in these fabric samples making it harmful to use.

At least 20 samples were taken, some of them were branded and some were taken from the local market. Out of these twenty samples thirteen samples were out of range all others were safe to use and had formaldehyde under the permissible limits. Government should take strict measures for the checking of formaldehyde in fabric as it is very dangerous for human health.

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