Validation of an analytical method using UV / VIS spectrophotometry, for the quantification of free formaldehyde in textiles and application in the analysis of garments sold in the Colombian market

Validación de un método analítico mediante espectrofotometría UV/VIS, para la cuantificación de formaldehído libre en textiles y aplicación en el análisis de prendas comercializadas en el mercado colombiano

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Abstract

Formaldehyde has been reported as a carcinogen by the International Agency for Research on Cancer (IARC), it has also been reported that low levels of formaldehyde can cause skin, eye and nose irritation. Formaldehyde is used as a component in resins, in cotton fabrics as an anti-wrinkle and anti-shrink finishing product. In the Colombian textile market, this type of toxic substance is not controlled. In this work an analytical method was validated by Ultraviolet/Visible spectrophotometry for the detection and quantification of free formaldehyde in textile products, for which an analytical method was adapted, taking as reference the ISO 14184-1:2011 standard and the following were obtained: results: a correlation coefficient of 0.999991 indicating that the method is linear, it was also observed that the analytical method has the ability to recover 99.34 % ± 0.951 % of the formaldehyde content in cotton fabrics, in addition to the coefficient variation of 0.354983 % indicates the reproducibility of the method, whose limits of detection and quantification were 0.4073 mg/L and 1.358 mg/L of free formaldehyde respectively. In the trials on samples marketed in the Colombian market, formaldehyde was quantified in 46 of the 62 samples analyzed.

Keywords: textiles; pollutants; allergies; Ultraviolet / Visible spectrophotometry; free formaldehyde; OEKO-TEX® Standard 100.

Resumen

El formaldehído ha sido reportado como cancerígeno por la Agencia Internacional para la Investigación del Cáncer (IARC), también se ha reportado que niveles bajos de formaldehído pueden producir irritación en la piel, los ojos, la nariz. El formaldehído, se emplea como componente en resinas, en tejidos de algodón como producto de acabado antiarruga y antiencogimiento. En el mercado textil colombiano, este tipo de sustancias tóxicas no son controladas. En este trabajo se validó un método analítico mediante espectrofotometría Ultravioleta/Visible para la detección y cuantificación de formaldehído libre en productos textiles, para lo cual se adaptó un método analítico, tomando como referencia la norma ISO 14184-1:2011 y se obtuvieron los siguientes resultados: un coeficiente de correlación de 0,99991 que indica que el método es lineal, también se observó que el método analítico tiene la capacidad de recuperar el 99,34 % ± 0,941 % del contenido de formaldehído en telas de algodón, además el coeficiente de variación de 0,354983 % indica la reproducibilidad del método, cuyos límites de detección y cuantificación fueron de 0,4073 mg/L y 1,358 mg/L de formaldehído libre respectivamente. En los ensayos sobre muestras comercializadas en el mercado colombiano, se cuantificó formaldehído en 46 de las 62 muestras analizadas.

Palabras clave: textiles; contaminantes; alergias; espectrofotometría Ultravioleta/Visible; formaldehído libre; OEKO-TEX® Standard 100.

Introduction

Formaldehyde is a colorless gas at normal conditions of pressure and temperature, soluble in water, commercialized with the name formaldehyde in aqueous solutions of concentration around 40%. Formaldehyde is used as a preservative in a large number of cosmetic and household products due to its broad spectrum of antimicrobial action, in addition to having a large number of industrial applications.

According to the US Agency for Toxic Substances and Disease Registry (ATSDR), low levels of formaldehyde can irritate the skin, eyes, nose, and throat (ATSDR, 1999). On the other hand, in 2004 it was classified by the International Agency for Research on Cancer (IARC) within group 1 of chemical substances, which classifies it as carcinogenic in humans (Kawakami, Maruo, Nakagawa, and Saito, 2015). In Colombia, formaldehyde is among the 33 agents recognized as carcinogenic (Araque, Casas, and Herrera, 2013).

Formaldehyde is a common cause of allergic contact dermatitis. The frequency of sensitivity to this allergen in the United States (approximately 8 % -9%) is higher than in Europe, where studies of patch test results have reported a frequency between 2 % and 3%. In Spain, the frequency is 1.61 % (García-Gavín *et al.*, 2011; Scheman *et al.*, 2008). However, there has been a trend towards a decrease in the frequency of formaldehyde sensitivity since 1980, this is due in part to the replacement of formaldehyde with formaldehyde releasers in cosmetics, toiletries and the introduction of resins for textile finishes. they release low amounts of formaldehyde. Formaldehyde releasers are substances that release formaldehyde as they decompose or that may contain trace amounts of formaldehyde remaining after the synthesis of these substances. (Latorre, Silvestre, and Monteagudo, 2011).

Formaldehyde-releasing resins are widely used in the textile industry, mainly cotton garments, viscose, linen and their blends with synthetic fibers, since the cellulosic fibers tend to wrinkle after washing, due to the swelling of the fibers by the moisture absorption. The incorporation of a polymeric finish in the pores of the fibers prevents the water molecules from being absorbed into the fiber. On the other hand, there are other resins that generate a multifunctional cross-linking reaction between the resin and the hydroxyl groups of the cellulose molecules, which will eventually hinder the swelling of the fiber and therefore it's folding (Frosch, Menné, and Lepoittevin, 2006).

The disadvantage of these anti-wrinkle resins is that they tend to release formaldehyde, due to subsequent degradation of the resin during storage, during use due to sweat and acid washing or with chlorine

(Peng, Yang, and Wang, 2012; Yao, Wang, Ye, and Yang, 2013). Said resins are also a common cause of contact dermatitis since they mainly affect the areas of the skin in contact with the textile such as the inside of the thighs, neck, and areas prone to greater sweating such as the armpits, the groin, folds of the elbow and behind the knees (De Groot and Maibach, 2010; Cohen, Hatch, Maibach, and Pratt, 2001). Studies conducted in the United States and Israel have identified patients who have allergic reactions to contact with garments due to exposure to these releasing resins, either due to formaldehyde released or by contact with the resin. In a study in Israel (Lazarov, 2004), 40 out of 644 tested individuals (6.2 %) reacted to one or more than six formaldehyde-based textile resins tested. In a previous study, the authors found an incidence of 5.9 % among 286 patients, also in Israel (Lazarov, Trattner, Abraham, and David, 2002). Prevalence rates of sensitivity due to formaldehyde-releasing resins in North America in the 1990s ranged from 5.0 % to 7.2 % (Marks *et al*., 2000; Marks *et al*., 2003). Since 2001, rates have been stable at a level a little over 2 % (Zug et al., 2009; Warshaw *et al*., 2008; Pratt *et al*., 2004).

The first formaldehyde-based resins used for textile finishes released large quantities of this substance, thus causing allergic dermatitis in contact with garments. Between 1950 and 1960, levels of 5000 to 12,000 ppm (0.5-1.2 %) of formaldehyde were reported in rayon and cotton garments manufactured in Europe and concentrations of 750 ppm (0.075 %) of formaldehyde in garments. manufactured in the United States at the same time (De Groot and Maibach, 2010). Over time, resins have been developed that release a smaller amount of formaldehyde, but with the same effect on fiber. The most commonly used resin is based on modified dimethylol dihydroxy ethylene urea, which releases less than 50 ppm of formaldehyde (Schindler, and Hauser, 2004, Frosch *et al*., 2006).

The limit of free formaldehyde in garments that will produce clinical dermatitis is unknown. In some experiments (Fisher, Kanof and Biondi, 1962), it is suggested that garment contact dermatitis will occur only when textiles contain more than 750 ppm of free formaldehyde, but these levels have been discussed, since in studies with Formaldehyde-releasing substances in cosmetics concentrations that can lead to dermatitis are <200 ppm (De Groot and Maibach, 2010).

The content of formaldehyde and other harmful substances in different textile products has been regulated for more than twenty years in the European Union, Japan and the United States, which has allowed to control the use of harmful substances, such as formaldehyde in textile processes. The international association Oeko Tex, groups representatives of 14 textile research institutes in the world, has set as maximum limits of permitted concentration of formaldehyde <300 mg/kg in clothing that does not come in contact with the skin, <75 mg/kg in clothing in contact with the skin and <16 mg/kg in clothing for babies (OEKO TEX, 2016). In Colombia, the content of formaldehyde in garments is not regulated since there is no awareness of its effect on health and few laboratories at the national level offer services for the quantification of this substance in textile products.

In 2007 in the European Union a study was carried out in which the formaldehyde present in samples sold in this market was quantified and it was found that 10 % of all the samples (23 samples of 221) released more than 30 mg/kg of formaldehyde. The highest value was 162.5 mg/kg. 11 % of the samples destined for direct contact with the skin (20 of the 183 samples, including pillowcases and sofa cushion covers) exceeded the 30 mg/kg limit established by Decision 2002/371 / EC of the Commission (eco-label). About 3 % of the samples also exceeded the 75 mg/kg limit set by the Oeko-Tex 100 for articles in contact with the skin. 5 of 46 (11 %) garments for babies under two years of age showed a release of formaldehyde higher than 20 mg/kg (OEKO TEX, 2016, Piccinini, Senaldi, and Summa, 2007).

The quantification of free formaldehyde in textiles can be carried out through various analytical methods. The chronotropic acid method is a semiquantitative method that is based on a chemical reaction between chronotropic acid and free formaldehyde that results in the formation of a purple color, the problem is that other aldehydes and ketones can also react with the acid, resulting in a yellow discoloration that may interfere with the test (Gryllaki- Berger, Mugny, Perrenoud, Pannather, and Frenk, 1992). It can also

be quantified indirectly by HPLC high-efficiency liquid chromatography with ultraviolet detection. Several modifications have been published around this method in different matrices, but in all of them a derivatization with dinitrophenylhydrazine or other chromophoric agents must be carried out (Gryllaki-Berger *et al*., 1992; Wahed, Razzaq, Dharmapuri, and Corrales, 2016; Rezende, by Souza Santos Cheibub, Pereira Netto and de Carvalho Marques, 2017). In the acetylacetone method, formaldehyde reacts with acetylacetone in the presence of ammonium to produce 3,5-diacetyl-1,4-dihydropyridine (DDL), which absorbs light at a length of a wave of 412 nm and can be quantified spectrophotometrically (Fregert, Dahlquist, and Gruvberger, 1984). This method is the one suggested in several international standards ISO 14184-1: 2011, JIS-L1041 (International Organization for Standardization, 2011; Standard, 2011), since it provides simple operation, with high sensitivity and reproducibility (Kawakami *et al*., 2015).

In the present work, an analytical method was validated by ultraviolet / visible spectrophotometry for the detection and quantification of free formaldehyde in garments commercialized in the Colombian market, taking as reference the ISO 14184-1: 2011 standard, which indicates that a extraction of free formaldehyde in the garment with water at 40 °C and constant agitation, after the extract is added acetylacetone in ammonium acetate solution in order to produce 3,5-diacetyl-1,4-dihydropyridine (DDL), which absorbs light at a wavelength of 412 nm and allows indirectly quantifying formaldehyde spectrophotometrically (International Organization for Standardization, 2011).

Materials and methods

Reagents

37 % formaldehyde, glacial acetic acid, 98 % pure grade ammonium acetate, type I water, 110 mm 5A cellulose filter paper.

Equipment

Water bath with temperature control, orbital shaker with temperature control and agitation, UV/Vis spectrophotometer with a spectral range between 190 and 900 nm.

Extraction and quantification of formaldehyde

The quantification of free formaldehyde in textiles is done taking as reference the ISO standard 14184-1:2011.

Nash reagent: Dissolve 150 g of ammonium acetate in approximately 800 mL of type I water, add 3.0 mL of glacial acetic acid and 2.0 mL of acetylacetone, pour into a 1000.0 volumetric balloon. mL and is filled with water type I. Before using, let it stand for a minimum time of 12 hours. The final solution should be kept in a dark bottle for a maximum of 6 weeks, since the sensitivity may vary slightly over a long period of time.

Sample treatment: Cut the fabric sample into squares approximately 0.5 cm x 0.5 cm in area and weigh 2.5000 ± 0.0001 g in a clean and dry 250 mL Erlenmeyer flask, add 100, 0 mL of type I water, the Erlenmeyer is covered with aluminum foil and taken to an orbital shaker at 40 ± 2 °C, for one hour and 150 rpm. At the end of this time, the sample is allowed to cool to room temperature and is filtered on a volumetric flask of 100.0 mL. 5.0 mL of the filtrate is measured in a capped test tube and 5.0 mL of Nash reagent is added, the test tube is shaken and immersed in the water bath at 40 ± 2 °C for 30 minutes. ± 5 min, at the end of this time the solution is allowed to cool and stand for 30 ± 5 min more at room temperature. Finally, the absorbance is measured at a wavelength of 412 nm, which is the wavelength of maximum absorbance of 3,5-diacetyl-1,4-dihydropyridine (DDL).

Validation parameters

As validation parameters, were evaluated those indicated in the International ICH Harmonization Conference: linearity, specificity, precision, intermediate precision, accuracy, the limit of detection and quantification (Guideline, 2005).

Linearity: Standard solutions of concentrations between (0.56462 and 12.099) mg / l of formaldehyde were prepared from the formaldehyde solution certified at 37 %. These concentrations were chosen because they were within the limits established for the spectrophotometric method for compliance with Lambert-Beer law and for the absence of distortion in the spectrum. For the reading in the spectrophotometer, 5 mL of each of the standard solutions was poured into a capped test tube and 5.0 mL of Nash reagent was added, in order to form the substance colored Subsequently the tubes were shaken and immersed in a water bath at 40 ± 2 °C for 30 ± 5 min, after this time the solutions were allowed to cool and stand for 30 ± 5 min more at room temperature. Finally, the absorbances were measured at a wavelength of 412 nm. The following parameters were evaluated as linearity acceptance criteria: coefficient of variation of the response factors (f) ≤ 5 %, correlation coefficient (r) ≥ 0.990, adjusted coefficient of determination (r2) ≥98.01 %, hypothesis test for the slope (b) ≠ 0, hypothesis test for the intercept (a) = 0.

Specificity: As an acceptance criterion, it was evaluated that no interferences were presented by components of the matrix, degradation products or related compounds for first-order kinetics in relation to the analyte (degradations greater than 5 % and lower than 30 %).

Matrix interference: In order to evaluate the influence of matrix degradation analytes on the spectrophotometric reading of formaldehyde, the procedure of treating the fabric samples described prior to a commercial cotton garment was carried out until approximately two liters of extract. For each degradation test, 90.0 mL of the extract was measured and for the reading in the spectrophotometer the formaldehyde derivatization treatment was carried out and the absorbance data was taken at a wavelength of 412 nm.

Degraded analyte interference: In order to evaluate the influence of degraded formaldehyde on the spectrophotometric reading thereof, the procedure of treating the fabric samples described above was carried out on a commercial cotton garment, until obtaining approximately two liters of extract, said extract was added formaldehyde in an amount equivalent to 1.8 mg/L of formaldehyde in solution, since this is the concentration that is expected to be measured in an extract of a garment containing 75 mg/kg of cloth, which is the maximum limit allowed for clothing in contact with the skin, according to the OEKO-TEX® Standard 100 standard (OEKO TEX, 2016). For each degradation test, 90.0 mL of the extract was measured and for the reading in the spectrophotometer the formaldehyde derivatization treatment was carried out and the absorbance data was taken at a wavelength of 412 nm.

Degradation treatments

Interference by acid hydrolysis: 5 mL of a 1N hydrochloric acid solution is added, it is subjected to heating in a water bath at 70 ± 5 °C for one hour, it is left to cool, it is neutralized with 5 mL of a hydroxide solution of sodium 1N, the volume is adjusted to 100.0 mL with type I water and homogenized.

Interference by basic hydrolysis: 5 mL of a 1N sodium hydroxide solution is added, heated in a water bath at 70 ± 5 °C for one hour, allowed to cool, neutralized with 5 mL of a 1N hydrochloric acid solution, the volume is adjusted to 100.0 mL with type I water and homogenized.

Thermolysis interference: Heat in a water bath at 80 ± 5 °C for two hours, allow to cool, adjust the volume to 100.0 mL with type I water and homogenize.

Interference by photolysis: It is exposed to ultraviolet light for 24 hours.

Oxidation interference: 5 mL of 1 % V/V hydrogen peroxide is added, it is heated in a water bath to 70 ± 5 °C for 30 minutes, allow to cool, adjust the volume to 100.0 mL with type I water and homogenize.

Accuracy: According to the Oeko-Tex® Standard 100, the maximum allowed concentration of formaldehyde in garments that will be in contact with the skin is 75 mg/kg, for which a sample of raw cotton cloth was enriched with said concentration, without no preliminary process (OEKO TEX, 2016). Six samples of the enriched cloth were then weighed and subjected to the sample treatment described above. As an acceptance parameter to evaluate the accuracy, the coefficient of variation of the percentage of recovery of formaldehyde in the doped sample was evaluated, which must be ≤ 2 %.

Intermediate Precision: Three samples of raw cotton cloth were enriched, without any preliminary treatment with concentrations of 16 mg/kg, 75 mg/kg and 90 mg/kg. These concentrations were evaluated since they are the maximum limits allowed in international regulations for garments in direct contact with the skin and in baby garments. The enriched fabrics were treated in triplicate according to the sample treatment procedure described above. A repeatability and reproducibility (R & R) study was carried out among analysts. As an acceptance parameter, it was evaluated that there are no significant statistical differences among analysts in relation to the estimates obtained among the samples evaluated in the study (R & R).

Accuracy: Three samples of raw cotton fabric were enriched with concentrations (80 %, 100 %, and 120 %), taking as a reference the maximum allowed concentration of 75 mg/kg, equivalent to concentrations of 60 mg/kg, 75 mg/kg and 90 mg/kg. The enriched fabrics were treated in triplicate according to the sample treatment procedure described above.

The average recovery percentage was evaluated for the three concentrations, which should be 100 % ± 2 %, for a protection factor of 95 %, equivalent to a k = 1.96.

Limit of detection (LD) and quantification (LC) (Table 9): The average response of 10 blank readings (noise, Nash reagent solution without formaldehyde) was estimated and that value multiplied by 3 for the LD and for 10 for the LC.

Analyzed samples

The content of free formaldehyde was analyzed in triplicate, in garments sold in different chain stores in the city of Medellín, Colombia.

Statistic analysis

The acceptance criteria for each of the validation parameters were calculated using the software STATGRAPHICS Centurion XVI, version 16.1.18.

Results and Discussion

Validation parameters

Linearity

Analysis of response factors

In Table 1 it is observed that the lowest P-value of the tests performed is equal to 0.146055. Because the P-value for this is greater than or equal to 0.05, the idea that the Response Factor comes from a normal distribution with 95 % or more confidence can not be rejected.

Table 1. Normality test corresponding to the parameter response factors of the concentrations evaluated for the calibration curve

Proof	Statistical	Value-P
Estadístico W de Shapiro-Wilk	0,912043	0,146055

Source: the authors.

As seen in Figure 1 and Table 2; with a confidence level of 95 %, the data corresponding to the parameter excluding response factors atypical, are adjusted to a normal probability distribution, because the P-Value is greater than 0.05, which allows estimating the value of dispersion corresponding to the coefficient of variation with a result of 4.03 %.

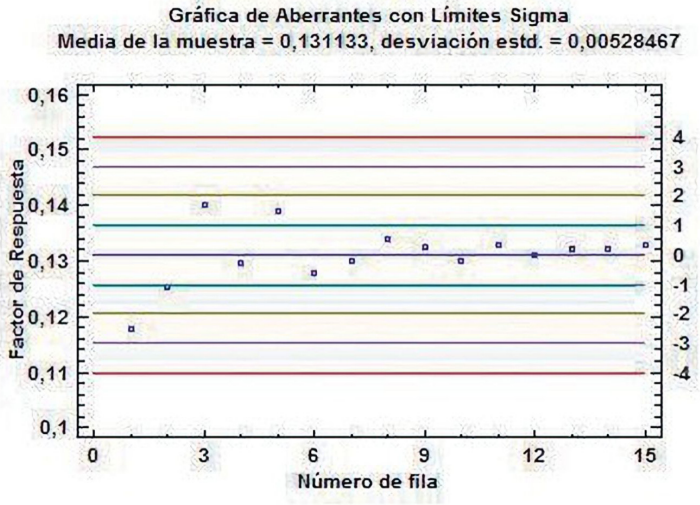

Figure 1. Graph of behavior corresponding to the parameter response factors of the concentrations evaluated for the calibration curve
Source: the authors.

Table 2. Statistical summary corresponding to the parameter response factors of the concentrations evaluated for the calibration curve

Recuento	15
Promedio	0,131133
Desviación estándar	0,00528467
Coef. de variación	4,03002%
Mínimo	0,11772
Máximo	0,140025
Rango	0,0223048
Sesgo estandarizado	-1,29625
Curtosis estandarizada	1,88967

Source: the authors.

Lineal regression model

The data are adjusted to a linear regression model which describes the relationship between the variables Absorbance and formaldehyde concentration in mg / L (Figure 2).

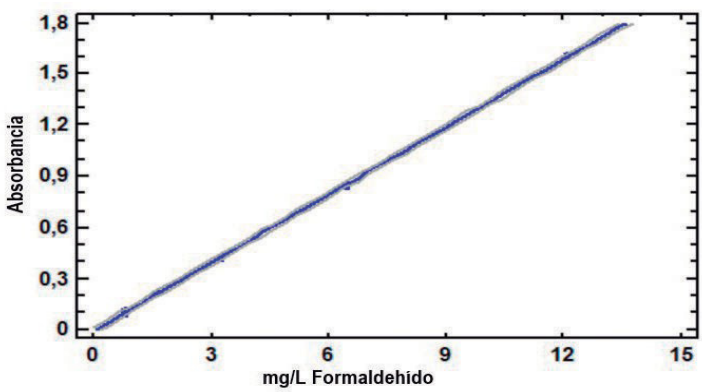

Figure 2. Linear regression for formaldehyde quantification
Source: the authors.

Table 3 shows the slope and intercept values for the linear equation, the equation of the fitted model Absorbance = -0.00304564 + 0.132572 * mg/L formaldehyde.

Table 3. Summary results in a linear regression model for the quantification of formaldehyde

	Dear from	Error	Estadístico	
Parameter	Least Squares	Standard	T	Value-P
Intercept	-0,00304564	0,00312642	-0,974162	0,3478
Pending	0,132572	0,000492177	269,359	0,0000

Source: the authors.

According to the analysis of variance of the linear regression model for formaldehyde quantification (Table 4), the P-Value of the model is less than 0.05 there is a statistically significant relationship between the variables Absorbance and formaldehyde concentration in mg/L with a 95.0 % confidence level.

Table 4. Analysis of variance of the linear regression model for formaldehyde quantification

Source	Sum of squares	GL	Middle Square	Reason-F	Value -P
Model	4,46085	1	4,46085	72554,44	0,0000
Residue	0,000799276	13	0,0000614827		
Lack of Adjustment	0,000262109	4	0,0000655272	1,10	0,4141
Pure Error	0,000537167	9	0,0000596852		
Total (Corr.)	4,46165	14			

Source: the authors.

Correlation coefficient = 0.999991

R-Square = 99.9821 %

R-Square = 99.9807 %

The standard error of est. =0.00784109

The adjusted R-squared statistic with degrees of freedom indicates that the linear model explains 99.9807 % of the variability obtained in the Absorbance with respect to the concentration of formaldehyde in mg/L. The correlation coefficient is equal to 0.999991, indicating a relatively strong relationship between the variables. The standard error of the estimate shows that the standard deviation for the residuals is 0.00784109.

Hypothesis tests for slope and intercept

Null hypothesis: intercept = 0.0

Alternative hypothesis: intercept not equal 0.0

Statistical t calculated = -0.974162

Value-P = 0.3447755

Do not reject the null hypothesis for alpha = 0.05.

Since the P-value in the hypothesis test for the intercept is greater than 0.05, the null hypothesis is accepted, which indicates that the intercept is statistically equal to zero.

Null hypothesis: slope = 0.0 Alternative hypothesis: slope not equal 0.0

Statistical t calculated = 269.359

P-value = 0.0

Reject the null hypothesis for alpha = 0.05.

Since the P-value in the hypothesis test for the slope is less than 0.05, the alternative hypothesis is accepted, which indicates that the slope is statistically different from zero.

Specificity

Figure 3 shows that the matrix interference and associated impairments do not present a percentage response greater than 1 %. In Figure 4 it is observed that the analyte-matrix associated degradations present first-order degradations, no degradation is less than 5 %, nor more than 30 %.

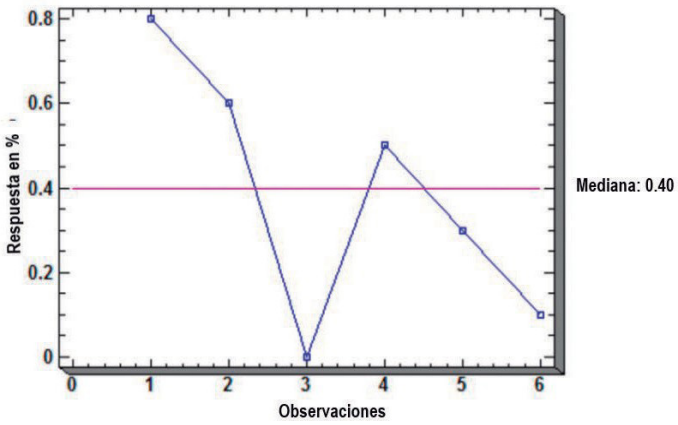

Figure 3. The behavior of the interferences associated with matrix degradations on the formaldehyde response
Source: the authors.

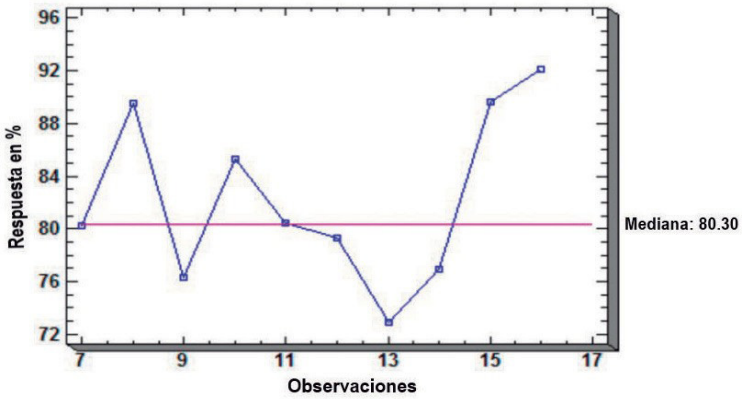

Figure 4. The behavior of the response associated with the interferences of degradations of (analyte (formaldehyde) - matrix)
Source: the authors.

Precision

Table 5 shows that the P-Value is greater than 0.05, indicating with a confidence level of 95 % that the data obtained can be assumed as coming from a normal probability distribution. In Table 6 it is observed that the coefficient of variation obtained is 0.354983 %. Figure 5 shows that all the data are distributed in a range of two standard deviations above and below the nominal value, which indicates the reproducibility of the analytical method.

Table 5. Normality test corresponding to the precision test of the formaldehyde response

Proof	Statistical	Value-P
Estadístico W de Shapiro-Wilk	0,951246	0,767548

Source: the authors.

Table 6. Statistical summary corresponding to the precision test of the formaldehyde response

Average	93,7133
Standard deviation	0,332666
Variation coefficient of variation	0,354983%
Minimum	93,28
Maximum	94,22
Rank	0,94

Source: the authors.

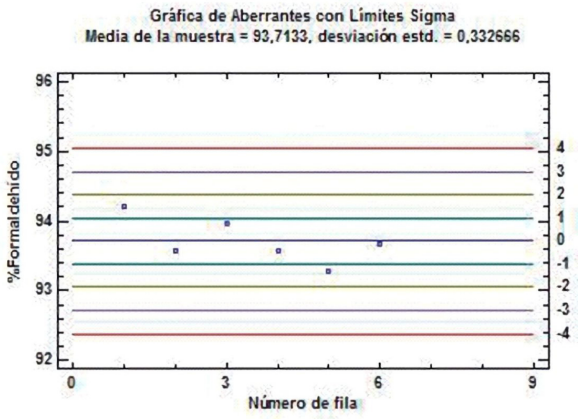

Figure 5. Behavior corresponding to the precision test of the formaldehyde response
Source: the authors.

Intermediate precisión

In Figure 6 and Table 7, it is observed that the 35.80 % of the variability obtained in the study (R & R) is provided by the analyst's repeatability (precision in the replicates of the samples prepared by concentration level), 50.25 % Reproducibility, and 13.95 % Interaction Analyst* Sample. The percentage of the total variation is 1.07378 %, which indicates that the analysts present a statistically equal performance because the said percentage of the total variation is less than 10 %, which can be observed more clearly in Figure 7.

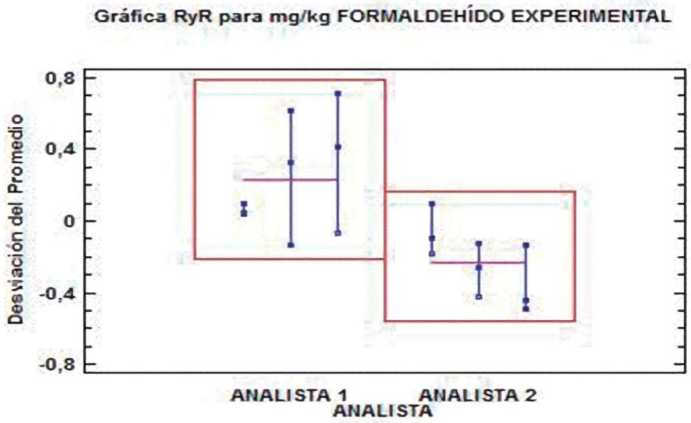

Figure 6. The behavior of deviations from formaldehyde concentration results obtained by analysts at three levels of concentration
Source: the authors.

Table 7. Summary study of repeatability and reproducibility (R & R)

Measurement	Sigma	Percentage	Variance	Percentage of	Porcentaje
Unity	estimated	Total Variation	estimated	Contribution	from (R&R)
Repeatability	0,250836	0,642431	0,0629185	0,00412717	35,80
Reproducibility	0,297201	0,761179	0,0883283	0,00579394	50,25
Interaction	0,156609	0,401101	0,0245264	0,00160882	13,95
(R & R)	0,419253	1,07378	0,175773	0,0115299	100,00
Parts	39,0425	99,9942	1524,32	99,9885	
Total Variation	39,0448	100,0	1524,49		

Source: the authors.

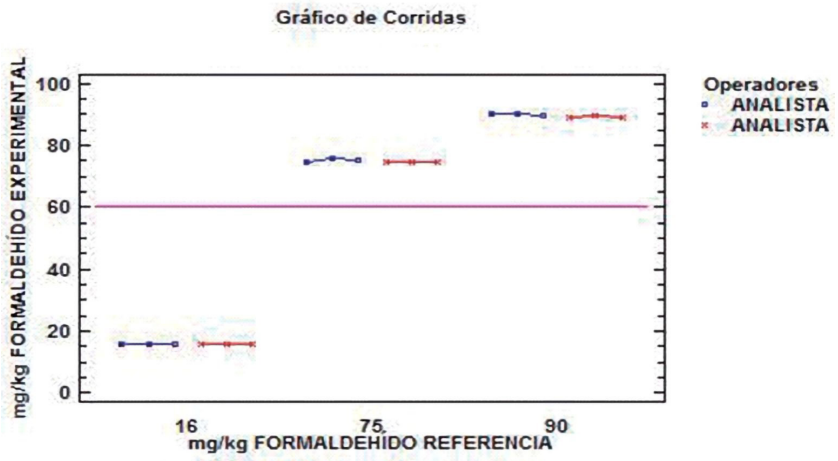

Figure 7. The behavior of the analysts in relation to the formaldehyde concentration results obtained in the three concentration levels
Source: the authors.

Accuracy

Table 8 shows that the P-Value is greater than 0.05, which allows us to estimate the data as coming from a normal probability distribution. With a confidence level of 95 %, it can be inferred that 95 % of the data will be between 97.0372 % and 101.643 %. The analytical method for the quantification of free formaldehyde has the capacity to recover 99.34 % ± 0.941 % (Figure 8).

Table 8. Normality test for the data obtained in recovery in %

Proof	Statistical	Value-P
Estadístico W de Shapiro-Wilk	0,912043	0,146055

Source: the authors.

Normal

Normal Tolerance Limits for% Recovery

Límites de 95.0 % tolerance for 99.73 % of the population

X bar +/- 4,82,785 sigma

Higher: 101,643

lower: 97,0372

Figure 8 shows that the control limits are covered by the specification limits with results for the short-term potential and real capacity indexes of 1.52 and 1.02 respectively.

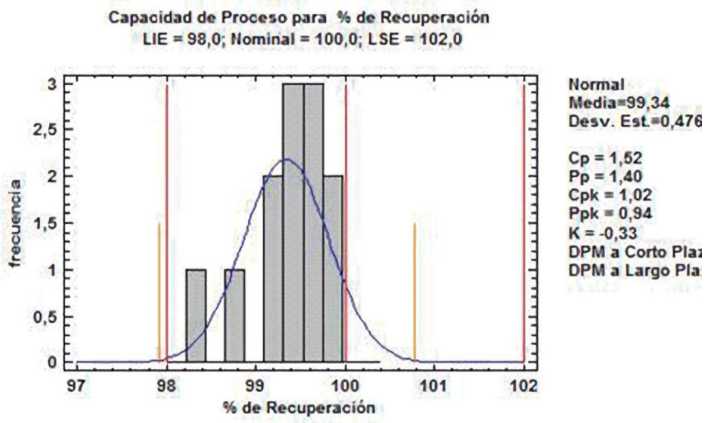

Figure 8. Short-term capacity indices for the percentage of formaldehyde recovery
Source: the authors.

Limit of detection (LD) and limit of quantification (LC)

Table 9 shows the limits of detection and quantification of the validated analytical method for the quantification of free formaldehyde in textiles.

Table 9. Limits of Detection and Quantification for the spectrophotometric quantification of Formaldehyde

LD (mg/L of Formaldehyde)	0,4073
LC (mg/L of Formaldehyde)	1,358

Source: the authors.

Analyzed commercial samples

Table 10 shows the results of free formaldehyde analysis in 62 samples sold in the Colombian market. Concentrations between 0.2 and 86.7 mg/kg of formaldehyde were found.

Table 10. Formaldehyde content (mg/kg) in commercial samples analyzed, by a validated method

SAMPLE	FORMALDEHYDE CONCENTRATION (mg/kg)	STANDARD DEVIATION (mg/kg)
Sample 1	ND	NA
Sample 2	ND	NA
Sample 3	86,7	0,3
Sample 4	72,1	0,4
Sample 5	4,3	0,3
Sample 6	ND	NA
Sample 7	8,6	0,9
Sample 8	9,3	0,9
Sample 9	21,3	0,7
Sample 10	3,7	0,5
Sample 11	12,3	0,5
Sample 12	0,2	0,5
Sample 13	13,4	0,1
Sample 14	15,6	0,1
Sample 15	15,6	0,1
Sample 16	17,7	0,1
Sample 17	15	0,1
Sample 18	29,1	0,1
Sample 19	21,8	0,1
Sample 20	22,2	0,3
Sample 21	29,9	0,3
Sample 22	11,5	0,1
Sample 23	5,8	0,2
Sample 24	43	0,1
Sample 25	25,4	0,8
Sample 26	9,6	0,1
Sample 27	45,7	0,3
Sample 28	5	0,1
Sample 29	8,1	0,2
Sample 30	ND	NA
Sample 31	16,9	0,1
Sample 32	36,4	0,8
Sample 33	28,6	0,1

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Continued from the previous page

Sample 34	36,7	0,1
Sample 35	27,7	0,2
Sample 36	61,6	0,5
Sample 37	8,15	0,3
Sample 38	ND	NA
Sample 39	ND	NA
Sample 40	ND	NA
Sample 41	ND	NA
Sample 42	ND	NA
Sample 43	ND	NA
Sample 44	ND	NA
Sample 45	ND	NA
Sample 46	ND	NA
Sample 47	ND	NA
Sample 48	39,6	0,1
Sample 49	8,4	0,1
Sample 50	4,7	0,5
Sample 51	25,1	0,2
Sample 52	25,1	0,9
Sample 53	26,3	0,3
Sample 54	26,3	0,4
Sample 55	11,4	0,8
Sample 56	5,1	0,9
Sample 57	4,3	0,9
Sample 58	14,9	0,3
Sample 59	14,9	0,1
Sample 60	38,7	0,1
Sample 61	ND	NA
Sample 62	ND	NA

ND: Not Detectable, NA: Not Applicable
Source: the authors.

Conclusions

The limits of detection and quantification of this analytical method were 0.4073 mg/L and 1.358 mg/L of free formaldehyde respectively, which means that the validated method allows detecting a minimum amount of formaldehyde 16.2 mg/kg of cloth and allows a minimum quantification of 54.3 mg/kg of cloth, which indicates that this method allows formaldehyde to be quantified below the maximum allowed limit for garments, in direct contact with the skin, which is formaldehyde 75 mg/kg cloth. While, for baby garments, this method is adequate to detect formaldehyde from its maximum allowed limit, which is 16 mg/kg of fabric.

The validated analytical method for the quantification of free formaldehyde allowed to quantify concentrations between 0.2 and 86.7 mg/kg in 74 % of samples sold in the national market and only one of the 62 samples

analyzed exceeded the maximum limit allowed for Garments in direct contact with the skin of 75 mg/kg according to OEKO TEX. The concentrations found in the domestic market were similar to those reported in Japan in 2015 from 2 to 89 mg/kg of formaldehyde in commercial garments (Kawakami *et al*., 2015) and those reported in the United States by the Office of Public Accountability. The government in 2010 for national garments of 75.4 mg/kg of formaldehyde (States and Accountability, 2010). In this same study, concentrations of up to 206 mg/kg of formaldehyde were reported in garments from China, India, Indonesia, Pakistan, and Thailand. The levels of formaldehyde reported from all these countries are above the levels reported in the European Union, which were 30 mg/kg (Piccinini *et al*., 2007), this demonstrates the success of more than fifteen years of regulation. In Colombia, greater control is required over the presence of this type of substances in garments, since their harmful effects on human health are demonstrated, which is even more worrisome in children's clothing and clothing intimate use.

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