APPLICATION NOTE

UV/Vis Spectroscopy

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Determination of Formaldehyde Content in Toys and Fabrics Using UV/Vis Spectrometry

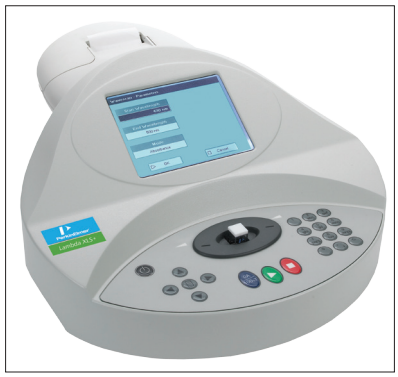

Figure 1. LAMBDA XLS+ UV/Vis spectrometer. Wavelength: 540 nm; Measurement Mode: Absorbance; Cell 10 mm.

Introduction

As product safety regulations for industry are becoming stricter, more testing at lower levels is required for toxic elements or hazardous organic chemicals such as formaldehyde in children's toys/clothing. Formaldehyde resins are used in fabrics to bind pigments to the cloth, as a fire retardant and to provide stiffness. In cotton and cottonblend fabrics they are used to enhance wrinkle resistance and water repellency. They can often be noted by the odor of treated fabric. The types of resins used include urea-formaldehyde, melamine-formaldehyde and phenolformaldehyde. Resins without formaldehyde are typically much costlier. Increases in temperature (hot days) and increased humidity both increase the release of formaldehyde from coated textiles.

Long term chronic exposure or short-term exposure to high concentrations of formaldehyde can lead to cancer. In animal studies, rats exposed to high level of formaldehyde in air developed nose cancer. The European standard EN 71 specifies safety requirements for toys. EN 71, Part 9 contains requirements for organic chemical compoundsin toys and specifies the limit for accessible textile components of toys intended for children under 3 years of age. The limit specified for formaldehyde content is not more than 30 mg/kg or 2.5 mg/L in the aqueous migrate prepared following EN 71, Part 10. EN 71, Part 11, section 5.5.3 specifies a method of analysis.

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Experimental

The analysis was carried out using a PerkinElmer LAMBDA™ XLS+ UV/Vis Spectrometer.

Apparatus and Reagents

Table 1. List of apparatus and reagents used.*

Volumetric flasks, volume 50 mL
Volumetric flasks, volume 100 mL
Hot plate for distillation
Boiling chips
Erlenmeyer flasks, volume 100 mL
Eppendorf® micropipettes
Ammonium acetate, anhydrous
Acetic acid, glacial
Pentane-2,4-dione
Hydrochloric acid, 1 mol/L
Sodium Hydroxide solution 1 mol/L
Starch solution freshly prepared, 2 g/L
Formaldehyde solution, 370 g/L to 400 g/L
Standard iodine solution, 0.05 mol/L
Standard sodium thiosulfate solution, 0.1 mol/L
Water, deionized
Stainless steel tweezers
250 mL glass bottle with flat base, screw neck and PTFE lined rubber septum (Make: Schott Duran)
Magnetic stirrer
*The reagents, chemicals, standards used were of ACS grade.

Pentane-2,4-dione reagent: Dissolved 15 gm of anhydrous ammonium acetate, 0.3 mL glacial acetic acid and 0.2 mL pentane-2,4-dione reagent in 25 mL water and diluted up to the mark in 100-mL volumetric flask with water.

Reagent without pentane-2,4-dione: Dissolve 15 gm of a nhydrous ammonium acetate and 0.3 mL glacial acetic acid in 25 mL water and diluted up to the mark in 100-mL volumetric flask with water.

Formaldehyde stock solution: Transferred 5.0 mL of formaldehyde solution into a 1000-mL volumetric flask and made up to the mark with water.

Standardization of formaldehyde stock solution: 10.0 mL of freshly prepared formaldehyde stock solution was transferred into a conical flask, added 25.0 mL of a standard iodine solution and 10.0 mL of sodium hydroxide solution. The solution was allowed to stand for five minutes. Then the solution was acidified with 11.0 mL of hydrochloric acid and titrated for excess iodine by standard sodium thiosulfate solution. 0.1 mL of starch solution was added when color of the solution became pale straw. After addition of starch solution, immediately the color was changed to deep blue-black. The titration was continued until the color changes from deep blue-black to colorless. Similarly, the blank titration was performed. The difference between titration values of blank and sample was used for calculation of formaldehyde contents in stock solution. The concentration of formaldehyde was found to be 1.99 mg/L.

Formaldehyde dilute standard solution (0.001 mg/mL): 2.5 mL of formaldehyde stock solution was transferred to 50-mL volumetric flask; mixed well and diluted up to the mark with water. 1 mL of this solution was further diluted to 100 mL with water and mixed well.

A series of reference solutions were prepared by pipetting suitable volumes of above formaldehyde dilute standard solution into a 50-mL conical flask as follows

Table 2. Calibration solutions.

	Amounts (mL) Formaldehyde dilute standard solution in 50-mL conical flask	Amount of pentane-2,4-dione reagent (mL)	Concentration (mg/L) of Formaldehyde after making volume to 30 mL with water
Blank	–	5.0	0.0
Reference 1	5.0	5.0	0.167
Reference 2	10.0	5.0	0.333
Reference 3	15.0	5.0	0.499
Reference 4	20.0	5.0	0.667
Reference 5	25.0	5.0	0.833

Absorbance measurement of calibration solutions: Absorbance measurements of calibration reference solutions and blank were done by using water as reference. The calibration curve was constructed by subtracting absorbance value of the blank solution (A2) from each of absorbances obtained from the calibration solutions. Figure 2 shows calibration graph.

Sample preparation: Three different toy samples made up with fabrics were selected for analysis. Sample with surface area of 10 cm^2 was taken and transferred to 250 mL extraction bottle with the help of tweezers. 100 mL of simulant (water, deionized) was added to the sample at 20 °C ±2 °C and the extraction bottle closed. The extraction bottle was kept on a magnetic stirrer for uniform stirring of the solution over the period of 60 minutes. Aqueous migrate was then filtered through a plug of glass wool. 5.0 mL of aqueous migrate was transferred into a 50-mL conical flask followed by addition of 5.0 mL of pentane-2,4-dione reagent and 20.0 mL of water.

Sample reference solution: 5.0 mL of aqueous migrate was transferred into a 50-mL conical flask followed by addition of 5.0 mL of reagent without pentane-2,4-dione and 20.0 mL of water.

These solutions were shaken for about 15 seconds and immersed in a thermostatic water bath at 60 °C ±2 °C for ten minutes followed by cooling for about two minutes in a bath of iced water.

Absorbance measurements were done between 35 minutes and 60 minutes from the time when the conical flasks were placed in a water-bath at 60 °C.

Absorbance measurements of sample solutions were done by using the reference solution as reference (A1).

Calculation of analyte concentration: Calibration curve was prepared manually by taking the absorbance values obtained for calibration reference solutions. To determine the analyte concentration, absorbance value of blank solution (A2) was subtracted from absorbance value of sample solution (A1). The subtracted absorbance value was then read off from the manual calibration curve.

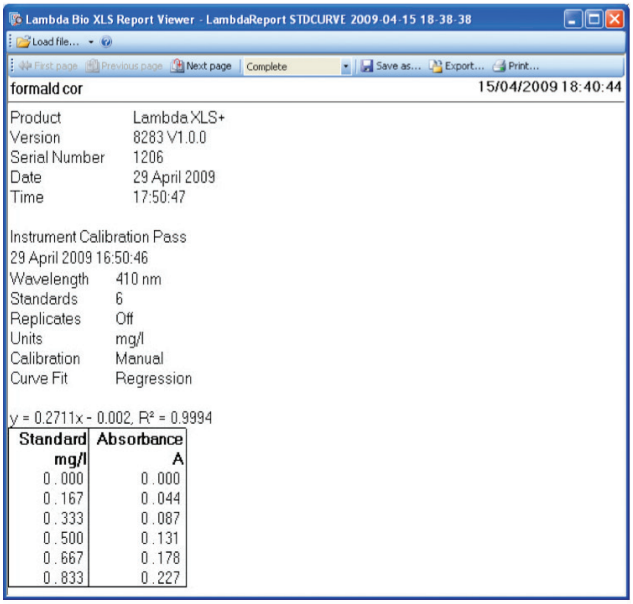

Figure 2. Calibration graph.

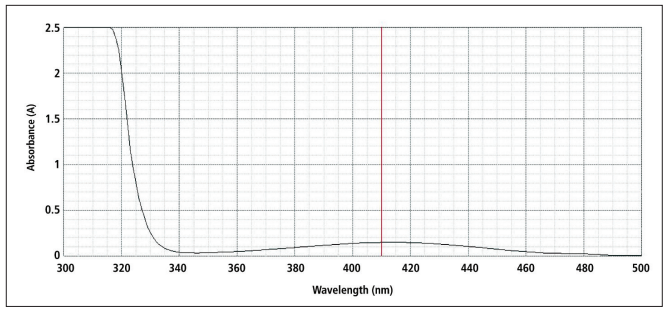

Figure 3. Spectrum of color formed for the determination of 'Formaldehyde' contents.

The formaldehyde content in aqueous migrate was calculated by using following equation,

C_s(mg/L) = C X 5 where,

C_s = concentration of formaldehyde in the sample solution (mg/L)

5 = dilution factor of the sample solution.

Results and discussion

Calibration – linearity:
The six different levels of calibration standards were prepared in the range from 0.167 mg/L to 0.833 mg/L with the reagent blank as first level. Results showed linearity with a good correlation co-efficient of 0.9994. The calibration curve is shown in Figure 2. Figure 3 shows the spectrum of the developed color, confirming the peak maximum at 410 nm.

Method detection limit: 10 replicate reagent blank solutions were prepared to make an estimate of method detection limit. To determine method detection limit, seven replicate aliquots of fortified reagent water (0.1 mg/L) were prepared and processed through entire analytical method. The method detection limit was calculated as follows,

MDL = (t) X (s) where,

t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. [t = 3.143 for seven replicates].

s = standard deviation of replicate analyses.

The method detection limit was found to be 0.0178 mg/L.

Sample analysis: Three different toy samples, as shown in Figure 4, made up of polyester, rayon and synthetic fibers were analyzed as per the procedure given under 'Experimental'. Results obtained in duplicate were averaged and are shown in Table 3. These measurements are below the action level of 2.5 mg/L in the aqueous migrate.

Table 3. Sample analysis results.

Sample	Concentration (mg/L)
Toy 1 (polyester fiber)	0.18
Toy 2 (rayon fiber)	0.25
Toy 3 (synthetic fiber)	Not Detected

Spike recovery studies: A recovery study was performed by spiking 0.5 mg/L concentration in three replicates of the synthetic fiber sample aqueous migrate. The results are summarized in Table 4. As seen in Table 4 the recoveries are good, falling within the usual acceptance range of 80-120% recovery.

Table 4. Replicate spike recoveries.

Sample	% Recovery
Sample 1	113
Sample 2	107
Sample 3	105

Figure 4. Toy samples.

Conclusion

The LAMBDA XLS+ UV/Vis spectrometer can be used to measure formaldehyde contents in fabric toys. The detection limit is sufficient to determine formaldehyde at the level of 30 mg/kg in the original material or 2.5 mg/L in the aqueous migrate solution as specified in the current version of EN-71. Linearity and spike recoveries further validate the performance of this methodology.

References

1. EN 71 Safety of Toys – Part 9, 10, 11 – organic chemical compounds in toys – requirements, limits and sample extraction procedure.
2. 40 CFR, Part 136 Appendix B – Definition and Procedure for the Determination of the Method Detection Limit.

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