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Original Scientific Paper

Polarography Determination of Free Formaldehyde on Treated Cotton Fabrics

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Application of compounds which, on textile material, release small quantities of formaldehyde makes it necessary to develop an adequate analytical method. Polarography is one of the possible analytical methods to be used. This paper investigates the possibility of using an indirect DC polarographic method *via* semicarbazone, with direct extraction of formaldehyde in the polarographic cell. Such a modified polarographic method is highly sensitive and selective, it makes it possible to measure small quantities of formalhyde, while the maximum sample mass to be measured is around 0.2 g. Disturbances that presumably occur due to the presence of surface active agents on the textile material do not occur in the samples smaller than 0.2 g in 30 ml of the polarographic solution.

INTRODUCTION

Various treatments, involving chemical agents based on *N*-methylol compounds, have been developed for durable-press finishing of cotton. The self-condensation reaction between an *N*-methylol compound and the condensation of *N*-methylol and cellulose are catalytically controlled polymerization reactions that release water. Condensation does not only proceed towards a desirable reaction with cellulose, it also produces a variety of side reactions. During such reactions, various formaldehyde types from various compounds are produced and can later be released. On a treated textile material, formaldehyde can be present in free form; pendant at the end of *N*-methylol

chain; bounded between a cellulose and reactant; or self-condensed with reactant molecules.[1] The biggest analytical problems are the different types of formaldehyde that are formed on the material. It was necessary to find an extraction where analytical condition has no influence on formaldehyde release.

The negative side of such treatments is formaldehyde release from the fabrics treated. Environmental regulations require that the amount of irritants, such as formaldehyde, should be reduced as much as possible. As a consequence, modified DMDHEU (dimethoxydihydroxyethylene urea) containing a low amount of free formaldehyde has been increasingly used.

A spectroscopic method (with 20 h extraction) was usually used for determination of formaldehyde released, which was satisfactory for determination of formaldehyde in the 300–3500 ppm range. Since by 1990 the level of free formaldehyde had been reduced by 95%, as compared to the levels in the 70's, the original method was not sensitive enough. The method was modified in order to be usable for the determination of lower amounts of released formaldehyde.[2] However, the method was still not sensitive enough for precise determination of very low contents of released formaldehyde under 25 ppm.

Several investigators have developed various voltammetric methods for the determination oof free formaldehyde. Using SWV (square wave voltammetry) Yoon was able to determine formaldehyde concentration down to 0.02 μg/ml.[3] Formaldehyde can be reduced electrochemically on a mercury electrode in a methanol solution according to the reaction:

$$H_2C{=}O + 2\ H_2O + 2\ e^- \Rightarrow CH_3OH + 2\ OH^-$$

Boyd and Bambach[4] determined free formaldehyde in biological materials polarographically, and Linhardt[5] determined free formaldehyde in *N*-methylol resins employing a direct reduction in basic solution. However, hydrolysis of compounds can take place during measurements, which can introduce errors. The hydrolysis of these reactive compounds can be suppressed by changing the temperature and pH value of the solution, but it also lowers the accuracy of the measurements, since polarographic waves are deformed.

Direct polarographic reduction of formaldehyde in an acidic medium cannot be used for analytical determination. However, electroactive derivatives are easily obtained by condensing formaldehyde with acid hydrazine, semicarbazide hydrochloride or betaine hydrazide hydrochloride.

Pribyl determined formaldehyde in organic solvents by converting it into a semicarbazide derivative, which is polarographically active and can be precisely determined.[6] The following expression shows the reaction:

$$H_2C{=}O + NH_2{-}NHCO{-}NH_2 \rightarrow H_2C(OH){-}NHNH{-}CO{-}NH_2 \rightarrow$$

$$H_2C{=}NNHCONH_2 + H_2O$$

Semicarbazone formation in the above reaction depends upon the pH value of the solution. Polarographic determination of semicarbazones is considerably more sensitive than direct determination of formaldehyde in neutral or basic solution.

Absenger and Schliefer measured free formaldehyde in *N*-methylol resins employing DC polarography, after converting it into a semicarbazone derivative. Formaldehyde present as *N*-methylol, *N*-methylol-ether or methylene groups, does not interfere under the conditions described.[7] In durable press finishing, free formaldehyde has also been determined by polarography. Polymer agents (additives, softeners) do not deform polarographic waves. Magnesium salts, present as catalysts, do not interfere with polarographic measurements beacuse magnesium is reduced at a more negative potential.[8]

EXPERIMENTAL

Polarographic measurements were done using Polariter PO 4, Electrode Assembly E 65, Drop Life Timer DLT1 – Radiometer Copenhagen. Nitrogen was purified by passing it through a column of active copper (Katalysator R-BASF) at 185 °C, and than rinsed by bubbling it through water.

To get an adequate comparison, free formaldehyde was determined following the AATCC Test Method 112-1982 on the spectrophotometer Unicam SP 1750-Pye Unicam.

The fabric, weighing 120 g/m^2, which had previously been scoured and bleached, was treated in a laboratory padder (Benz), with a pick-up of 70%. DMDHEU and etherified DMDHEU were the two commercial creaseproof resins used, and magnesium chloride was used as a catalyst. Fabric was dried at 105 °C and cured for 4 minutes at temperatures of 130, 140, 150, 160 and 170 °C. The fabric was then left exposed to air for 100 days, which is the optimum period necessary for the material to be ready for testing.[9]

Measuring Procedure

30 ml of the solution was prepared by mixing the semicarbazide hydrochloride solution with McIlvaine buffer in a ratio 1 : 4. This solution had a pH value of 4.6. The solution and a sample of the fabric treated (of 0.2 g maximum) was placed into an electrolytic cell. It was kept there at a constant temperature of 20 °C for a period of 3 hours. Gel solution 0.03 ml (w = 1%) was added prior to polarography and the dissolved oxygen was removed from the solution by passing pure nitrogen through the cell. A saturated kalomel electrode was used as reference electrode.

Polarographic curves were printed under the following conditions:

Printer sensitivity:	7 μA through the whole scale
Range:	0.75 to −1.5 V
Mercury dropping time:	0.6 s
Mercury column height:	400 mm

RESULTS AND DISCUSSION

For comparison, calibrated diagrams have been made, regression analyses calculated, together with a reliability interval at 95% free formaldehyde probability, measured using the spectroscopic and modified polarographic methods (Figure 1).

The purpose of this work is to investigate the possibility of employing polarography to determine the formaldehyde content on a treated textile fabric, by using direct extraction in the polarographic cell. That is why the influence of the pH value of the bath on formaldehyde release from the material treated was investigated first. Results of these measurements can be seen in Figure 2. It can be observed that in the given range of formaldehyde extraction (pH 4.6) no increase in the *N*-methylol compounds occurs.

Release of formaldehyde from the fabric is a slow process. Weakly bound formaldehyde is released first, followed by the hydrolysis of partially formaldehyde. Influence of the extraction duration on the quantity of formaldehyde extracted was investigated to determine the optimum extraction time for formaldehyde. Results of these measurements can be seen in Figure 3. Extraction time of 3 hours was selected, having in mind the sensitivity of the polarographic method.

After a series of measurements, optimal conditions for the polarographic determination of free formaldehyde on treated fabrics were established. Formaldehyde was extracted directly into the polarographic solution from the treated fabric. Figure 4. shows DC polarograms of formaldehyde extracted into the polarographic solution.

For an adequate comparison, free formaldehyde on cotton fabrics treated with DMDHEU and etherified DMDHEU was determined applying the spectrophotometric and polarographic methods. The results obtained can be seen in Figure 5. In the polarographic method (pH 4.6) DMDHEU showed lower values than etherified DMDHEU.

The results show that the modified polarographic method with semicarbazon, due to its high sensitivity, selectivity and reproducibility, is adequate for measuring low free formaldehyde contents on fabrics. The main advantage of this method is that it can determine free formaldehyde in finishes, as well as on the textile materials treated. DC polarography is a sensitive method; hence formaldehyde can be measured at a low content of 1 μg of

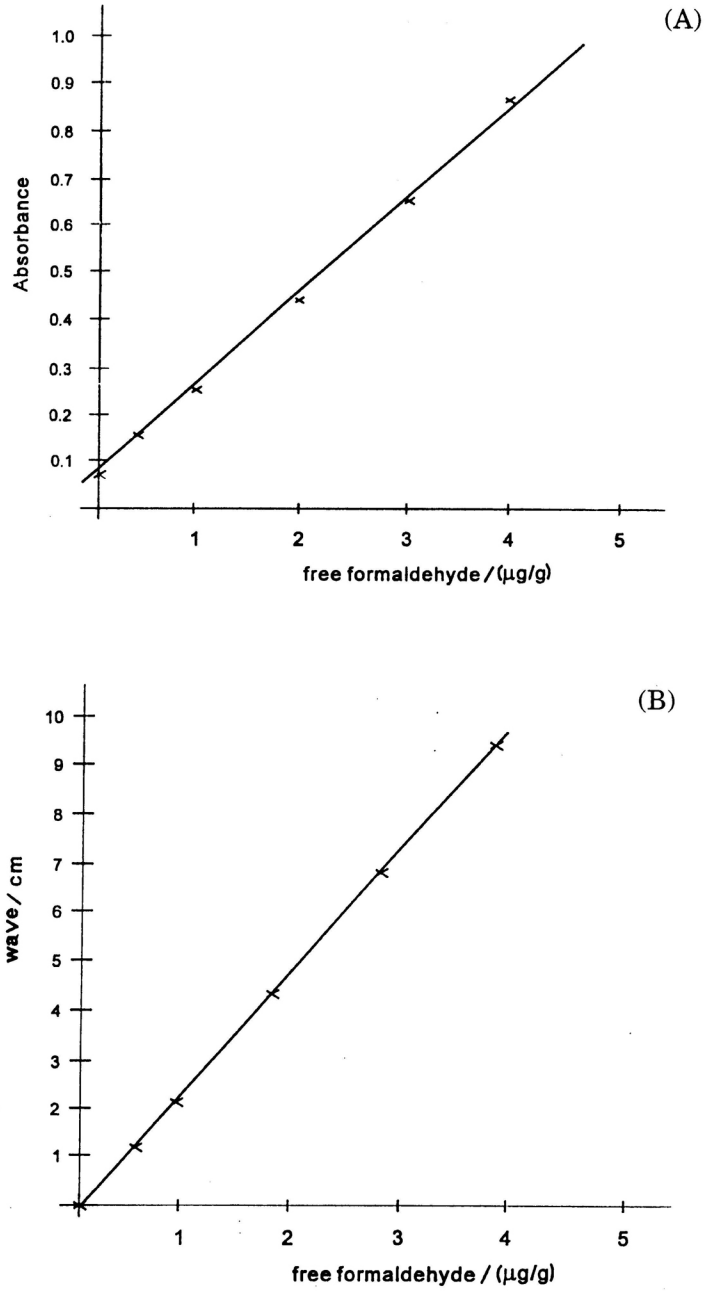

Figure 1. Regression equations of free formaldehyde. (A) Spectroscopic method: acetylaceton solution, absorbance at 412 nm, test tube 1 cm; $y = 0.21\,x + 0.07$, $R = 0.98$. (B) Polarographic method: $y = 3.49\,x - 0.02$, $R = 0.99$.

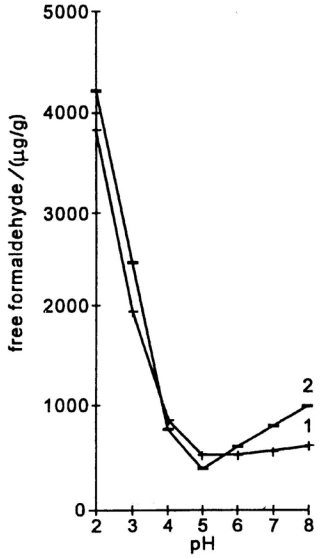

Figure 2. Dependence of formaldehyde release on the pH value of extraction bath, determined by the spectroscopic method: etherified DMDHEU (1), DMDHEU (2).

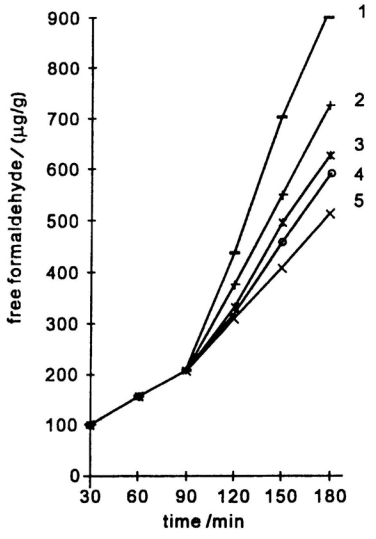

Figure 3. Formaldehyde release from cotton material treated with DMDHEU as a function of condensation temperature determined by the spectroscopic method: condensation temperature 130 °C (1), 140 °C (2), 150 °C (3), 160 °C (4), 170 °C (5).

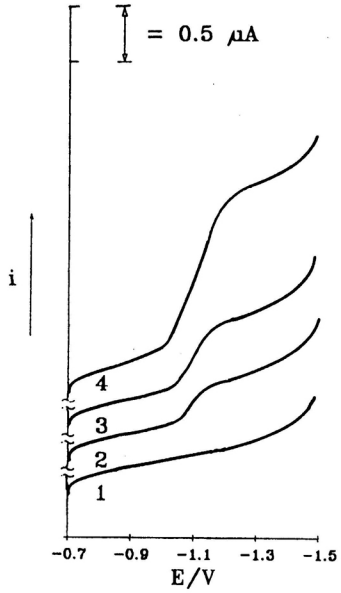

Figure 4. DC polarographic wave of formaldehyde in electrolytic solution (1), electrolytic solution + 0.1 g of samples (2), electrolytic solution + 0.2 g of samples (3), electrolytic solution + 0.2 g of samples + 1 ml formaldehyde solution (w = 20 μg/g) (4).

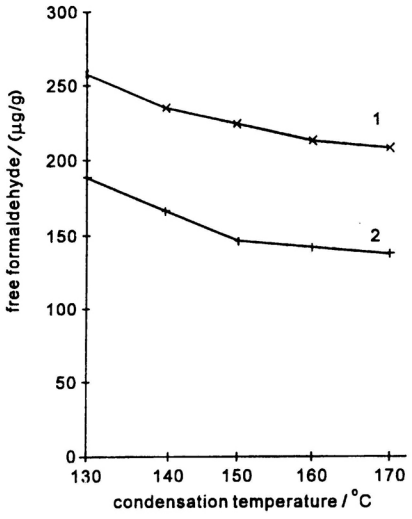

Figure 5. Formaldehyde release as a function of condensation temperature, determined by the DC polarographic method: etherified DMDHEU (1), DMDHEU (2).

formaldehyde on 1 g of fabric, and this sensitivity can be further enhanced by applying other, even more sensitive polarographic techniques. The maximum sample mass for this method can be 0.2 g (because when bigger quantities of textile material are treated, polarographic waves are disturbed). It is supposed that finishing agents have an impact on polarographic curve flattening. Greater masses lead to polarographic wave deformations, which makes the diffusion current as well as polarographic wave height readings impossible. The reason for this lies most probably in a higher content of surface active agents on the fabric.

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SAŽETAK

Polarografsko određivanje slobodnog formaldehida na obrađenomu pamučnom materijalu

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Neki spojevi koji se primjenjuju u obradbi pamučnog materijala oslobađaju male količine formaldehida. Za njegovo određivanje potrebno je razraditi odgovarajuće analitičke metode. Ispitana je mogućnost primjene modificirane DC polarografske metode za određivanje niskih koncentracija slobodnog formaldehida na obrađenim pamučnim materijalima izravnom ekstrakcijom formaldehida u polarografskoj kupelji. Ova osjetljiva i selektivna metoda dopušta mogućnosti mjerenja niskih količina slobodnog formaldehida na uzorcima mase do 0,2 g. Smetnje koje vjerojatno dolaze zbog površinski aktivnih tvari na tekstilnom materijalu, ne pojavljuju se u uzorcima manjim od 0,2 g u 30 mL otopine za polarografiranje.