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# An integrated and fast analysis for formaldehyde residues in consumer goods by ultrasonic assisted extraction

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## ABSTRACT

Determination of free or hydrolysable formaldehyde in consumer goods is an important safety issue and it is addressed by an Ultrasonic assisted extraction (UAE) method. The method studied is found to be an integrated method as extraction and derivatization with 2,4-diphenyl hydrazine (DNPH) all accomplished in one shot employing an aqueous detergent solution. The complete sample preparation for subsequent HPLC analysis was done in 4 min in comparison to the official IULTCS protocol taking 120min. The various influencing factors in UAE of formaldehyde from consumer goods like leather and textiles were studied and reported. Formaldehyde estimation was achieved in various consumer goods with good reproducibility. LOD of 0.3mg $kg^{-1}$ and LOQ of 3mg $kg^{-1}$ were reported.



## KEYWORDS

Determination of formaldehyde in consumer goods;
Ultrasonic assisted extraction of formaldehyde;
Simultaneous extraction and derivatization;
Integrated method of analysis for formaldehyde;
Quick method for formaldehyde.

## INTRODUCTION

Formaldehyde is classified as a substance of high health concern[1] and carcinogenic compound[2-4] but that still remains large in usage in various industries, cosmetics, textiles and leather industries. The finished products of cosmetics including many facial creams, consumer goods of textiles and leather possibly carry residues of formaldehyde. European Union already imposed its ban[5] and there are many official protocols for analyzing formaldehyde in consumer goods[6-7]. Formaldehyde, what is discussed in this study is free or hydrolysable formaldehyde. Although there are official procedures[6-7] they are found with few shortcomings. Of which, some are HPLC based procedures which is the first option as that serve with better reliability from the reason that LC involves detection of formaldehyde in isolation[6-9]. The second option is overwhelmingly photometric procedure[10-15] as is simple but sometimes suffer badly due to the interference by other carbonyls and colouring substances when present in samples. In such conditions the procedure leads to false positive and exaggerated results. The official protocols regardless of HPLC based or otherwise demands 1 hour for extraction followed by atleast 1 hour for derivatization and hence 2 hours of preparation for a sample. The proposed procedure cuts short this 120min to just 4 minutes and also all steps clubbed into one and hence an integrated approach.

Some analytical techniques like Microwave assisted extraction (MAE), Ultrasonic extraction (UAE), Pressurized solvent extraction (PSE) offer scope to develop

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quick procedures for many analytes present mainly in solids. The theory of UAE[16-19], Ultrasonic leaching of analytes[20] and in particular, the one incorporating *in situ* derivatization[21] were reported earlier.

Making use of ultrasonic energy, different approaches were reported for determination of formaldehyde in various types of samples, for example a direct UAE for food [22] which reported 40min for extraction and a long duration of 6hours for derivatization and the next UAE was for consumer goods like textiles[23] while ultrasonic assisted emulsification micro extraction was reported for cosmetics[24]. These last two studies were reported as simultaneous extraction and derivatization based on Ultrasonic technique. L.Chen et.al[23] reported a dynamic ultrasonic assisted extraction coupled on-line derivatization for determination of formaldehyde in textiles. In this study, formaldehyde extracted by ultrasonic means is passed on-line through a DNPH saturated cationic exchange column to achieve DNPH derivatization. I.Lavilla[24] studied Ultrasonic assisted emulsified extraction with simultaneous derivatization using acetyl acetone which is subsequently subjected to centrifugation followed by fibreoptics based UV-VIS micro spectrophotometry for detecting formaldehyde in cosmetic samples. In this study, there were number of factors reported like volume of organic solvent, dispersing solvent, ionic strength, centrifugation time etc. to carefully study and fix, to ensure recovery. A simultaneous extraction and derivatization method involving ultrasonic technique was reported also by J.Huang et.al.[25] for detecting carbonyl compounds in tree leaves but unlike this proposed study, they reported solvents for the extraction and also with a time frame of 1 hour for the entire sample preparation.

In contrast to these last three studies of Ultrasonic assisted simultaneous extraction and derivatization, the proposed study does not involve setting of too many parameters, usage of solvent or having any requirement of additionally prepared column but, found to be a simple and fast approach.

## EXPERIMENTAL

### Reagents

Sodium dodecylsulphate (SDS),2,4-dinitrophenylhydrazine, ortho phosphoric acid of 80% purity were of analytical grade; HPLC-grade acetonitrile were procured from Merck (Mumbai, India). HPLC-grade purity of water was prepared using Milli-Q apparatus of Millipore, (Bedford, MA, USA). Formaldehyde of ISO grade purity was procured from Merck, Darmstadt, Germany and using this, a stock solution of Formaldehyde at 2000 mg $l^{-1}$ was prepared using water of LC grade; from this stock, working standard solutions were prepared daily. The working standards for LC were prepared using appropriate quantities of formaldehyde standard solutions to represent formaldehyde in the range 0.5–10 µg.

### Apparatus

Ultrasonicator Model 275 was procured from CREST Ultrasonics, Trenton, NJ, USA. The model has provision to operate up to 50ÚC with thermostat and has fixed sonicating power of 90W on an average. HPLC consists of pump model Alliance 2695 with Photo diode array detector of model 2996 and operated with Waters Empower2 software version 6.21.00.00. This LC system was procured from Waters Corporation, Milford, MA, USA. Purosphere ($C_{18}$) LC column of 250 x 4.2 mm I.D. with 5 µm particles, was from Merck (Darmstadt, Germany).

### LC analysis

In this study, an isocratic elution programme was used with acetonitrile and water as solvents. 70%Acetonitrile and 30% water was used as mobile phase. The flow rate was 0.80 ml $min^{-1}$. 10µl sample was used for injection and the detection was at 350 nm. The LC analysis time was 10 min.

### Ultrasonic assisted extraction of samples

Textile, Leather samples were reduced to approx.100 to 200 microns using a laboratory mill (some samples that could not be ground were cut into small pieces of approx.1-2sq.mm). 0.1 g of sample thus prepared was weighed and taken in a stoppered 20ml graduated test tube. 5ml 0.1% SDS aqueous extractant was added along with 0.5ml DNPH solution.

Ultrasonicator was set to reach 40ÚC and once found stable, the sample container was placed in the sonicator by ensuring that the water level of the sonicator was above the contents of the sample vessel. Sonication was done for 4min. The contents of the test tube

after cooling to room temperature, transferred to a 10ml volumetric flask, added 4ml of acetonitrile and made up to the mark with LC grade water. The sample was filtered with 0.45µm membrane filter for subsequent LC analysis.

### Spiking studies

The spiking studies was carried by adding formaldehyde standard solutions of appropriate quantities directly to the solid samples of weighed portion and each of them was taken directly for UAE studies. Using Hamilton microlitre syringe, formaldehyde quantities were added to samples in the volumes of 10-25µl as per the following scheme: For spiking, 1mgkg$^{-1}$ spiked studies of samples, 10 µl of 10 µg ml$^{-1}$ was used; for achieving 5mg kg$^{-1}$, 5µl of 100 µg ml$^{-1}$ ; for achieving spiked studies of 10mg kg$^{-1}$ of solid samples, 10 µl of 100 µg ml$^{-1}$ and for achieving 15 mg kg$^{-1}$ spike, 15 µl of 100 µg ml$^{-1}$ were used. Each of these spikes was done to 0.1g of sample directly employed for UAE.

### Official protocol for formaldehyde

This is in accordance with ISO/IUC/IULTCS/EN (or) DIN protocol as almost all are on similar lines[6,7,10]. Leather/ textile samples were cut into fine pieces or milled to a fine size, 2g of sample was weighed and transferred in to a container with lid. 50ml of aqueous detergent solution containing 0.1% sodium dodecyl sulphate was added to the sample. The contents was subjected to leaching of formaldehyde under gentle stirring/shaking at 40°C for 1hr. The contents was filtered off the solid remains and allowed to cool to room temperature. 5ml of the extract was transferred into a 10ml standard volumetric flask, followed by 4ml of acetonitrile and 0.5ml of 0.03% DNPH reagent prepared in concentrated phosphoric acid. If required, water was used to make up to the mark. The derivatization was allowed to proceed atleast for 1 hr but not more than 3 hours. A calibration plot was drawn by using a series of standard formaldehyde solutions in the range of 1.0µg - 10µg (by adding directly in 10 ml volumetric flasks and derivatized similarly). A uniform reaction time was followed for sample and standard solutions.

## SAFETY MEASURES

Formaldehyde is declared as carcinogenic substance and hence it should be handled with all safety measures and precaution; and disposed as per the local regulatory procedures. Detailed safety guidelines should be provided in the work place in the event of any spillage or contact by the analyst.

## RESULTS AND DISCUSSION

### Studies on some influencing parameters

On screening several samples by following official protocol some samples were identified to contain formaldehyde. Of which, a leather sample was found to contain a value of 400 mg kg$^{-1}$ which was the highest among the samples studied and also was well above the permissible limit of 150mg kg$^{-1}$ for formaldehyde. That sample with high content of the analyte was employed for studying the following influencing parameters of UAE.

### The role of SDS in aqueous extractant

SDS was used at 0.1% as found in the official protocol and keeping the extractant identical, influence of UAE was probed. When mere water was employed as extractant in place of aqueous SDS keeping all other conditions identical, the recovery was found to be 71.5%. The comparison was done for the same sample. Actually SDS was included to improve the wetting of hydrophobic surface of samples but, it is found to be additionally serving beneficially in this UAE. Aqueous SDS solution supported better recovery than plain water as extractant; for, it lowered surface tension that helped improving the efficiency of UAE as reported elsewhere[19].

### Influence of volume of aqueous extractant

To study this impact on extraction recovery, the volume of detergent water as extractant was varied from 3ml to 12ml. The volume in the range of 3 to 5ml was found to be good in ensuring a recovery of 99-100%, however when it exceeded 5ml, the extraction recovery dropped below 80%. With the volume of 5ml, the recovery was found to be in the range 99-100% matching that of the reference official method. The influence of volume of extractant on recovery of analyte is shown in Figure 1.

### Influence of sample mass

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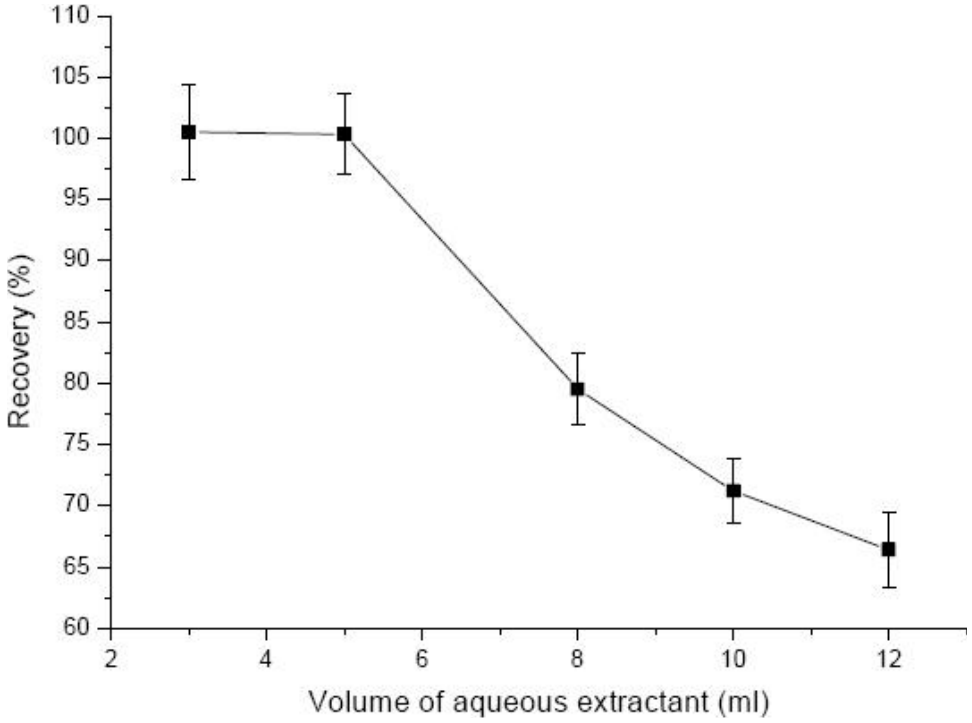


**Figure 1 : Influence of the volume of the aqueous detergent extractant on recovery of formaldehyde.**

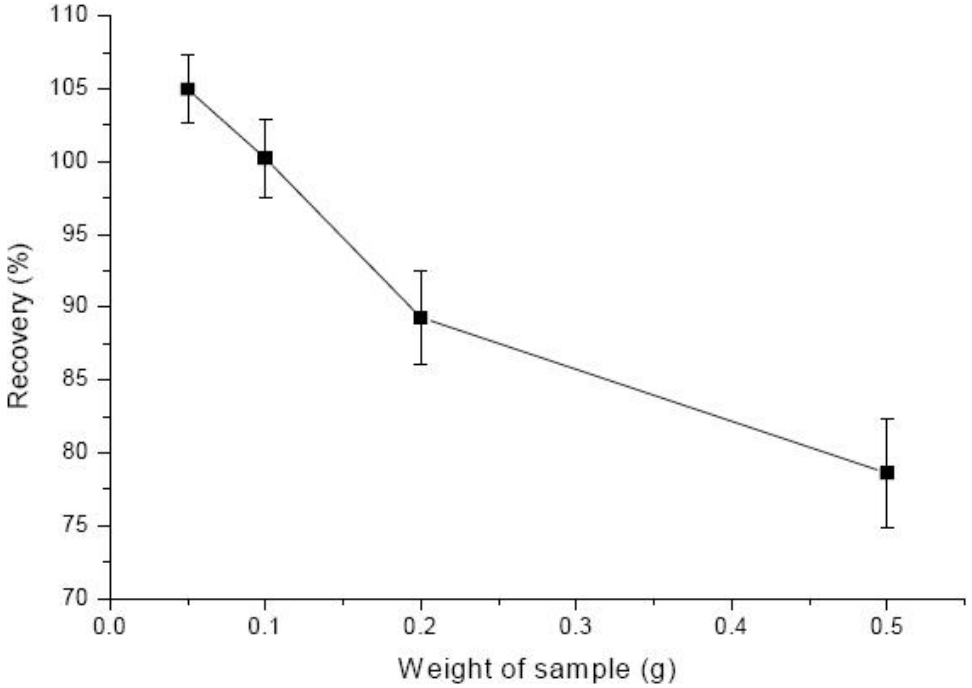


**Figure 2 : Influence of the weight of sample on recovery of formaldehyde.**

To optimize the sample mass with the recovery this study was carried out. For which sample weight from 0.05g to 1.0g was varied in 5ml volume of aqueous extractant along with DNPH derivatizing agent of 0.5ml. The contents were subjected to UAE for 4min. The study revealed that sample of 0.05-0.5g was acceptable however if it exceeded 0.5g, drop in recovery was observed. The sample mass of greater than 0.5g also posed another problem of absorbing good amount of aqueous extractant and hence not preferred. The influence of sample mass on recovery of analyte is shown in Figure 2.

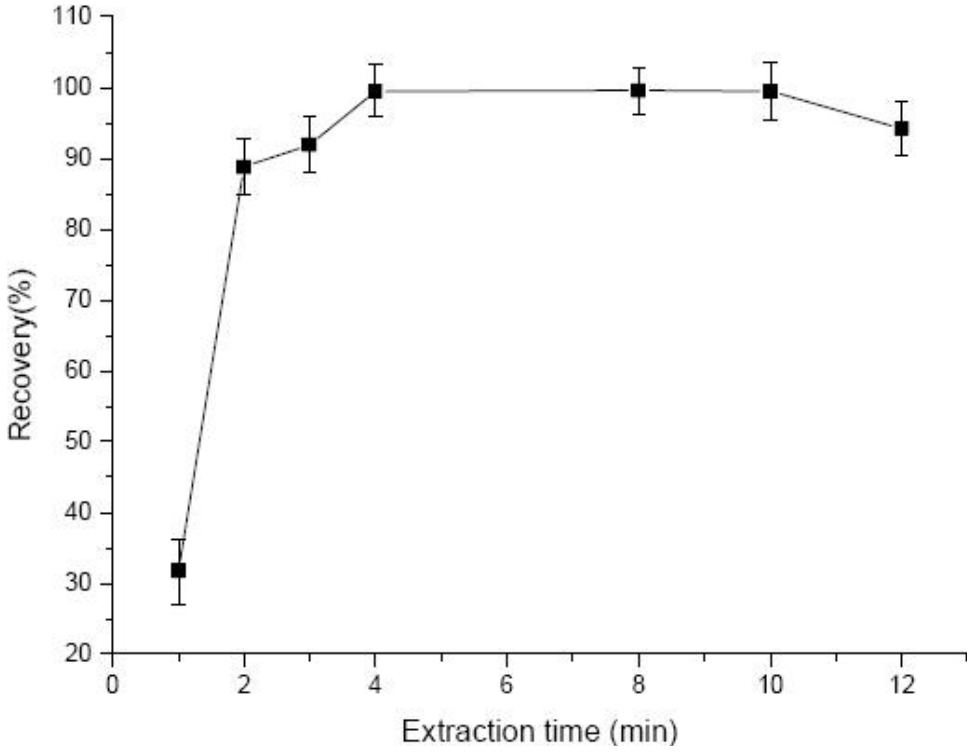


**Figure 3 : Influence of the extraction time of the sample on recovery of formaldehyde.**

**TABLE 1 : Spiked studies to validate the proposed UAE.**

| Nature of Sample | Originally found level of formaldehyde (mg $kg^{-1}$) | Spiked amount (mg $kg^{-1}$) | Total formaldehyde found by the method (mg $kg^{-1}$) | Recovery (%) | RSD (%) (from 6 replicates) |
|---|---|---|---|---|---|
| Leather Textile (cotton) | 10.4 | 1.0 | 11.49 | 100.8 | 1.9 |
| | | 5.0 | 15.35 | 99.0 | 3.2 |
| | | 10.0 | 20.29 | 99.5 | 2.7 |
| | 15.0 | 1.0 | 16.10 | 100.6 | 2.1 |
| | | 5.0 | 19.93 | 98.6 | 3.6 |
| | | 15.0 | 30.50 | 101.7 | 3.4 |

## Influence of extraction time

To study this parameter, 0.1g sample mass was taken in 5ml of water and 0.5ml DNPH derivatizating agent in 20 ml of stoppered test tube. The contents were raised to 40°C and duration of ultrasonication was varied from 1 to 12min. Recovery value was found to exceed 90% right from 3min. However 4 min is considered quite ideal for extraction of solid samples. Figure 3 reveals the trend observed with regard to the extraction time on recovery of analyte in this matrix.

## Vessel factor on recovery of analyte

The contents comprising the optimized volume of aqueous extractant, sample mass and derivatizing agent were found to give good reproducibility of recovery only when slender reaction vessels like a "test tube" were employed. Instead, if beakers, conical flasks or wide-mouthed bottles of comparable volumes used, recovery values were erratic and less. 20 ml stoppered test tubes were found suitable for ensuring good recoveries with reproducibility. This is also in agreement with an earlier report on the influence of vessels on recovery of analyte[26-27].

## Method validation and spiked studies

For method validation, a number of samples were screened for formaldehyde and those samples which were found to be free of formaldehyde or with low values like 20mg $kg^{-1}$ or less (to carry out studies of various spike levels including 1:1) were taken for spiking studies. Formaldehyde standard solutions of concen-

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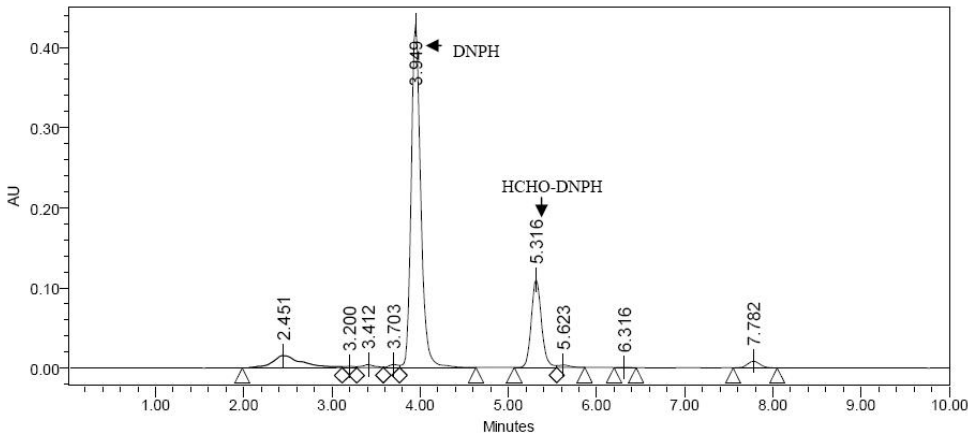


**Figure 4 : HPLC chromatogram of formaldehyde found in a textile (cotton) sample byUAE at λ=350nm. (Rt at 3.94 –DNPH and Rt at 5.31-formaldehyde-DNPH derivative).**

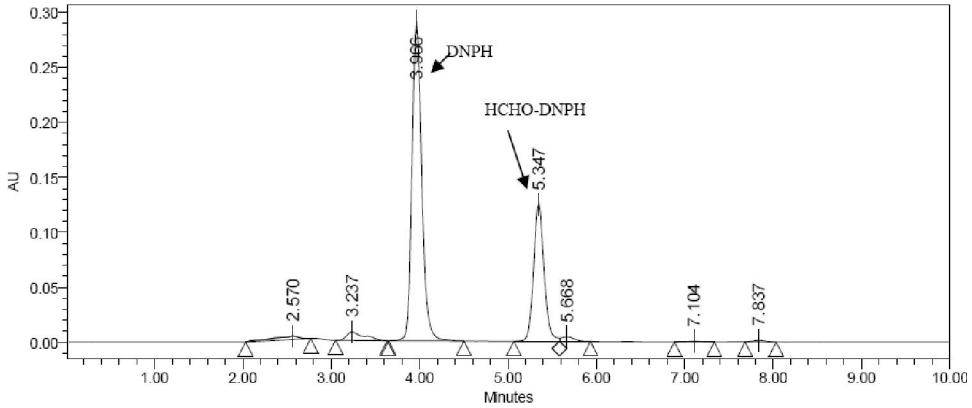


**Figure 5 : HPLC chromatogram of formaldehyde found in a leather sample by UAE at λ=350nm.(Rt at 3.94 –DNPH and Rt at 5.31-formaldehyde- DNPH derivative).**

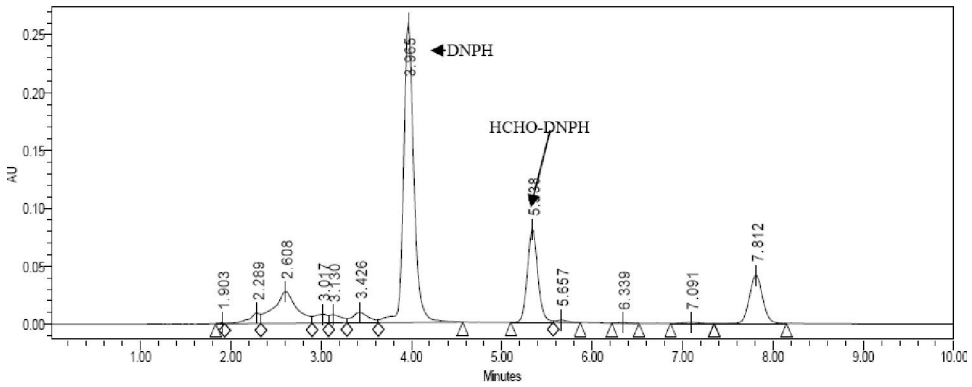


**Figure 6 : HPLC chromatogram of formaldehyde found in an Adhesive tape by UAE at λ=350nm.(Rt at 3.94 –DNPH and Rt at 5.31-formaldehyde-DNPH derivative).**

trations equivalent to 0.02 -1.5µg were directly added to the weighed solid samples so that right from the extraction, the steps were probed. The results along with reproducibility were given in TABLE 1. The recovery values for spiked samples were found in the range of 99– 102% with %RSD values that was a max. of 3.6. The LOD and LOQ values were also calculated on 3 and 10 times the averaged noise value and they were 0.3mg $kg^{-1}$ and 3.0mg $kg^{-1}$ respectively in comparison to the LOD of the Official method which is 0.4mg $kg^{-1}$ and LOQ is 4mg $kg^{-1}$. The linearity for the calibration was 0.9989. This method is found to serve for concentration range of a maximum 450mg $kg^{-1}$ and when this concentration exceeded, the experiment has to be re-

**TABLE 2 : Comparison of formaldehyde estimated in different consumer products by the proposed method and the official IUC method.**

| Nature of Sample | US extraction (mg $kg^{-1}$) | RSD (%) (from 6 replicates) | IULTCS method (mg $kg^{-1}$) | RSD (%) (from 6 replicates) |
|---|---|---|---|---|
| Leather (footwear) | 163.1 | 6.5 | 158.6 | 6.2 |
| Leather (shoe) | 10.4 | 3.0 | 10.3 | 3.6 |
| Textile (cotton shirt) | 112.4 | 3.9 | 113.7 | 3.0 |
| Textile (cotton) | 15.0 | 2.9 | 14.9 | 3.4 |
| Gloves. | 326.5 | 5.7 | 322.3 | 6.4 |
| Chemical (Polymeric resin) | 67.4 | 1.8 | 63.1 | 2.6 |
| Adhesive Tape | | | | |

peated by taking a sample weight of 0.05g.

## Analysis of real samples

A number of samples of consumer goods of leather and textiles and some process-inputs were analyzed by this proposed method and also separately by the official protocol. The results from both the approaches were given in TABLE 2. These results show that the proposed method agrees well with the official method besides being very fast and reproducible as the UAE method found with a maximum of 6.5 % RSD. When repeatability was checked from trials by different analysts the results agreed with %RSD of max.6.1.

Figures 4-6 are produced here for the successful determination of formaldehyde by UAE. Figure 4 is the chromatogram shown for the presence of formaldehyde in a textile sample. Figure 5 is the chromatogram of formaldehyde found in a leather sample and Figure 6 is that for formaldehyde detected in an adhesive sample. The results obtained by UAE for different real samples and their comparable values from the official procedure were furnished in TABLE 2.

## CONCLUSIONS

The proposed UAE method serves as an integrated approach. It may be noted that LOD and LOQ of this proposed method and the official protocol were almost the same; the sample is available at 0.1g per 10ml solution in the case of proposed method while the official method leads to 0.2g per 10ml at the end but there is no noticeable difference in the LOD and LOQ. For, in the proposed method analyte and DNPH reagent are in sufficiently in low concentrations that their reaction is facilitated to completion by ultrasonic energy while in the conventional typed official method it is still to complete. The proposed UAE is found to be in good agreement with the official IULTCS method from the results obtained for scores of samples by doing the samples parallely and data furnished in TABLE 2. Also, it offers to reduce sample preparation time significantly from 120min to 4 min and helps to increase laboratory through put.

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