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A Gas Chromatographic Procedure for the Determination of Environmental Furfural

Kirpal S. Sidhu

Occupational Health Laboratory, Michigan Department of Public Health, 3500 North Logan Street, P.O. Box 30035, Lansing, MI 48909

Furfural, OCH:CHCH:C CHO is a colorless liquid which turns reddish brown upon exposure to light and air. It is a polar compound and boils at 161.7°C. It is used (a) as a refining solvent for lubricating oils, butadiene, rare earths and metals; (b) as a general solvent for nitrocellulose, cellulose acetate and various dyes; and (c) as an intermediate for tetrahydrofuran, furfural alcohol, phenolic and furan polymers. Furfural is irritant to eyes, skin and mucous membranes. It can be absorbed through skin and is a central nervous system poison (SAX 1975; HAWLEY 1977). The occupational exposure standard for furfural (TAYLOR 1978) is currently established at 5 ppm as a threshold limit value-time weighted average (TLV-TWA). The American Conference of Governmental Industrial Hygienists, Inc. (ACGIH 1981) has recently adopted a threshold limit value of 2 ppm for furfural.

The National Institute for Occupational Safety and Health (NIOSH) has adopted a method for determination of furfural. This method consists of derivatization of furfural with Girard T reagent followed by analysis by high pressure liquid chromatography (TAYLOR 1978). Furfural can be absorbed on activated carbon (GREINKE 1974; CRISP 1980) and the absorbed vapors can be desorbed with carbon disulfide for subsequent analysis by gas chromatography (GREINKE 1974) using the general principles outlined by WHITE et al. (1970). However, the desorption efficiencies (14-69%) of various solvents tested to desorb furfural from carbon particles are lower (GREINKE 1974) than the NIOSH (1977) established criterion that desorption efficiency must be $\geq$ 75%. In view of this drawback, attempts were made to develop a suitable procedure for determination of furfural. The object of this paper is to describe the determination of furfural as developed at this laboratory. This method involves utilization of carbon disulfide plus 2-propanol as a desorbing solvent for underivatized furfural.

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EXPERIMENTAL

Chemicals. Furfural and carbon disulfide were obtained from Baker Chemical Co., Phillipsburg, New Jersey. 2-Propanol was obtained from Fisher Scientific Co., Fairlawn, New Jersey. All chemicals were analytical reagent grade.

Preparation of Furfural Standards. Furfural standards (232 µg/mL to 1160 µg/mL) in carbon disulfide plus 2-propanol (0.1%) were prepared. A standard curve was computed from the data obtained by analyzing these standards.

Adsorption of Furfural on Activated Carbon. Furfural (4 ppm) from a standard environment (50 L) was adsorbed on activated carbon (coconut charcoal tubes, Lot 107, Environmental Compliance Corp., Venetia, Pennsylvania) by sampling 10.0 L of air using personal air sampler (0.515 mL per count, SKC, Inc., Eighty Four, Pennsylvania). Furfural standards (1 ppm to 4 ppm) were prepared by dilution of desorbed furfural with carbon disulfide plus 2-propanol (0.1%).

Gas Chromatography. A gas chromatograph (Beckman GC 72-5) equipped with a flame ionization detector and coupled to a 1-mv recorder with an electronic integrator (Linear Instruments Corp., Irvine, California) was employed. The analytical column used was 3 m x 6 mm i.d. stainless steel packed with 10% Free Fatty Acid Phase (FFAP, Alltech Associates, Arlington Heights, Illinois) on a 60-80 mesh size Chromosorb-P AW (Analabs, New Haven, Connecticut). The analytical conditions were column temperature, 170°C isothermal; flame ionization detector, 250°C; hydrogen flow, 50 mL/min; air flow, 250 mL/min; argon (carrier gas), 60 mL/min; and sample size, 2 µL.

Desorption Efficiency Study. The main object of this study was to compare the efficiency of carbon disulfide alone or carbon disulfide plus 2-propanol to desorb the adsorbed furfural from activated carbon. The effect of duration of storage period on the desorption efficiency of carbon disulfide plus 2-propanol was studied. The efficiency of a solvent to desorb furfural was determined as described previously (SIDHU 1980; SIDHU 1981). The first section of each charcoal tube (100 mg, activated carbon; SKC Lot 107, Environmental Compliance Corp., Venetia, Pennsylvania) was directly injected with furfural. The tubes were immediately stored at 4°C for 1 to 7 days. The activated carbon particles from the first section of each tube were then transferred to 1 mL glass vials (Wheaton Scientific, Millville,

New Jersey) containing 0.5 mL of desorbing solvent. All vials were tightly capped to minimize the losses from evaporation. Furfural was desorbed with the desorbing solvent for 30 min. The contents were thoroughly mixed and agitated 2 to 3 times during the adsorption period. The recovery of furfural was calculated by comparing the results with standard curve. Comparisons between treatments for mean desorption efficiency were made by student's t test (STEEL and TORRIE 1960).

RESULTS AND DISCUSSION

The effect of addition of 2-propanol to carbon disulfide to desorb the adsorbed furfural from activated carbon is shown in Table 1.

TABLE 1. Desorption of furfural from activated carbon by solvents.[a]

Solvent	Determination (n)	Recovery %
Carbon disulfide	6	69.0
Carbon disulfide + 2-propanol (0.1%)	6	85.4[b]

[a] Furfural (580 µg) was adsorbed on 100 mg activated carbon (charcoal tube). Each tube was kept in storage at 4°C for 24 hours.

[b] $P \leq 0.05$.

Addition of 2-propanol to carbon disulfide significantly ($P \leq 0.05$) improved the desorption of furfural (69.0% versus 85.4%). Since furfural is a polar compound, it is reasonable to expect an improvement in desorption efficiency with carbon disulfide plus 2-propanol. The efficiency of carbon disulfide plus 2-propanol to desorb furfural from activated carbon (85.4%) exceeds that of methylene chloride (69%) as reported by GREINKE (1974).

The calibration curve (Figure 1) for furfural indicates it can be analyzed by gas chromatographic identification on 10% FFAP.

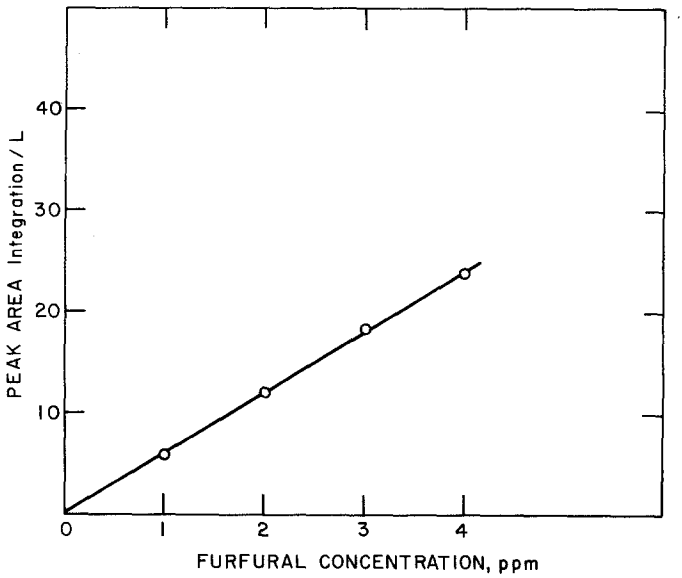

Figure 1. Calibration curve for furfural.

A chromatogram representing the results of analysis of furfural sampled on activated carbon and desorbed by carbon disulfide plus 2-propanol is shown in Figure 2. The retention time for furfural was 7.2 min. The precision (coefficient of variation) for analytical procedure was 4.45% (n = 10). Based on 10 L air sample the calculated limit of detection was 0.1 ppm.

The effect of duration of storage time on the efficiency of carbon disulfide plus 2-propanol to desorb furfural is shown in Table 2. The period of storage under the condition of experiment does not appear to affect the desorption efficiency. This indicates that stability of furfural was not affected by storage up to 7 days. The overall mean desorption efficiency of carbon disulfide plus 2-propanol was 85.2 ± 2.55% (n = 18). This desorption efficiency value meets the NIOSH (1977) established criterion for standard completion program that desorption efficiency must be $\geq$75%.

In conclusion, furfural can be adsorbed on activated carbon and the adsorbed vapors can be desorbed by carbon disulfide plus 2-propanol with an efficiency of 85.2%. Subsequently, the underivatized furfural can be analyzed by a gas chromatographic procedure using 10% FFAP column and the flame ionization detector.

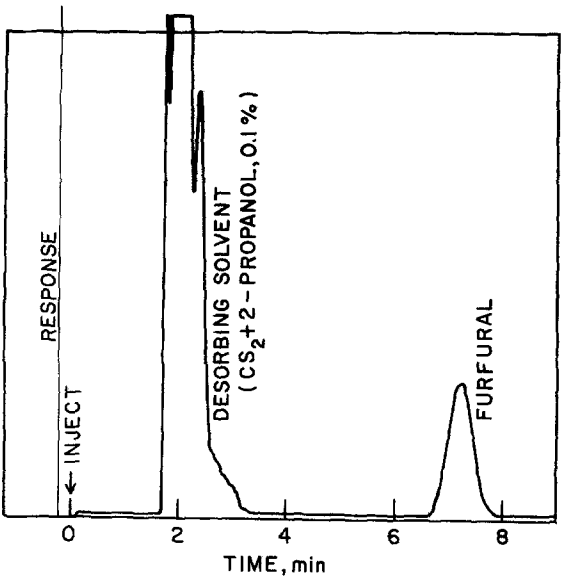

Figure 2. Gas chromatogram of furfural (4 ppm). Volume of air sampled was 10.0 L. The analytical conditions were: column, 10% FFAP on acid washed Chromosorb-P; column temperature, 170°C, flame ionization detector temperature 250°C, carrier gas flow 60 mL/min; and sample size = 2 µl.

TABLE 2. Effect of duration of storage on efficiency of solvent to desorb furfural from activated carbon.[a]

Storage (days)	Determination (n)	Recovery (%)
2	9	86.1 ± 3.94[b]
7	9	84.4 ± 3.44
Overall mean desorption efficiency =		85.2 ± 2.55

[a]Furfural was adsorbed on 100 mg activated carbon. Three levels of furfural (232, 464 and 696 µg per tube were tested in triplicates. It was desorbed with carbon disulfide plus 2-propanol.

[b]Mean ± standard error.

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