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The Determination in Air of Selected Low-Molecular Weight Aldehydes as Their Oxazolidines by Capillary Gas Chromatography

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The sampling of 2-furaldehyde, pentanedial, and pentanal from air has been accomplished using sorbent tubes containing 120-mg and 60-mg beds of XAD-2 coated with 10 percent 2-(hydroxymethyl)piperidine. Samples were collected at ca. 50 cm³/min for a maximum of 4 hours for 2-furaldehyde, ca. 80 cm³/min for a maximum of 8 hours, or ca. 200 cm³/min for minimum of 15 minutes for pentanedial and ca. 40 cm³/min for a maximum of 4 hours for pentanal. The oxazolidines, formed by reaction of the 2-(hydroxymethyl)piperidine with the aldehydes, were desorbed from the sorbent with 2 ml of toluene. Recovery from the sorbent was essentially quantitative for the aldehydes, and the resulting solution was analyzed by gas chromatography using a fused-silica capillary DB-5 column. Typical limits of detection ranged from 0.2–0.6 µg/sample for 2-furaldehyde, pentanedial, and pentanal. Pooled relative standard deviations for sets of 18 samples were 7.6 percent (3–41 mg/m³) for 2-furaldehyde, 8.7 percent (1–8 mg/m³) for pentanedial, and 7.3 percent (9–374 mg/m³) for pentanal. During storage at ambient conditions, samples were stable for up to 5 weeks for pentanedial, 4 weeks for pentanal, and 2 weeks for 2-furaldehyde. The method is able to measure pentanedial at its ceiling value of 0.7 mg/m³ with a relative standard deviation of 9.1 percent. Kennedy, E.R.; Gagnon, Y.T.; Okenfuss, J.R.; Teass, A.W.: The Determination in Air of Selected Low-Molecular Weight Aldehydes as their Oxazolidines by Capillary Gas Chromatography. Appl. Ind. Hyg. 3:274–279; 1988.

Introduction

The potential for occupational exposure to aldehydes exists in a number of industries.[1–3] Reported health effects due to exposure to these compounds have ranged from irritation to suspect carcinogenicity.[4,5] To help in limiting worker exposure to these compounds, Threshold Limit Values (TLVs)[6] have been established for a number of aldehydes. These cover a wide range of concentrations, extending from 0.1 ppm (0.25 mg/m³) for acrolein to 100 ppm (180 mg/m³) for acetaldehyde.

Because of their reactive nature, aldehydes have been difficult to sample and analyze. Many researchers have taken advantage of this reactivity in the development of reagent-containing sampling devices.[7–10] Many of these methods use either impingers or noncommercially available sorbent tubes. Work in our laboratory has centered on the use of reactive sorbents for the collection and stabilization of aldehyde samples. The equations of the reactions which serve as the basis for these sampling methods are shown in Figure 1. Successful methods for formaldehyde[11] and acrolein[12] have resulted from this work. The major advantages of these methods are long-term sample stability and commercial availability of the sorbent tubes.[13] Further modification of the acrolein method by researchers at the Occupational Safety and Health Administration Laboratory, Salt Lake City, Utah, has allowed simultaneous determination of both formaldehyde and acrolein.[14]

The aim of our work was to explore this sampling and analysis technique further and to develop a method which would have the necessary specificity for the analysis of multiple aldehydes and long-term sample stability. Because of the suspect carcinogenicity of formaldehyde, the use of pentanedial (glutaraldehyde; TLV-Ceiling, 0.7 mg/m³) may become more prevalent in the health care industries as a sterilant. Thus, it was an important aldehyde to consider for investigation. The use of 2-furaldehyde (furfural; TLV-TWA, 8 mg/m³) as a chemical intermediate and solvent also made it a compound for consideration. Other low molecular weight aldehydes, such as propanal (no limit), 2-butenal (crotonaldehyde; TLV-TWA, 6 mg/m³), 2-methylpropanal (isobutyraldehyde; no limit), and pentanal (valeraldehyde; TLV-TWA, 175 mg/m³) were also considered. Previous work with acetaldehyde had shown this compound to have limited capacity on the coated sorbent approach used in this method.[12]

Experimental

Chemicals

2-(Hydroxymethyl)piperidine was obtained from Aldrich Chemical Company (Milwaukee, WI) and was recrystallized from isooctane three times before use to remove impurities. Since the

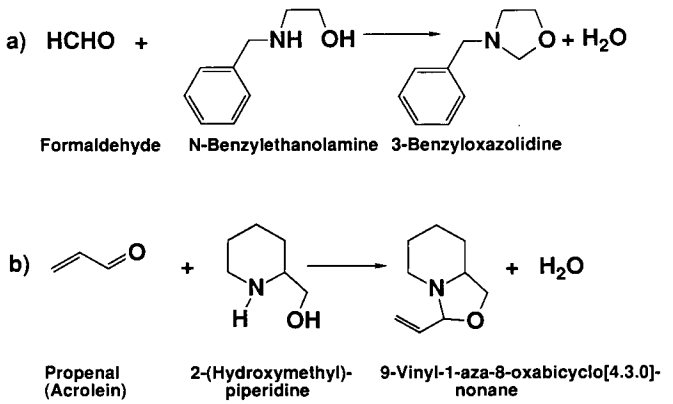

FIGURE 1. Equations for the reaction of a) 2-benzylaminoethanol with formaldehyde and b) 2-(hydroxymethyl)piperidine with acrolein.

2-(hydroxymethyl)piperidine is hygroscopic, this recrystallization allowed the 2-(hydroxymethyl)piperidine dissolved in the isooctane to be decanted from the oily residue of 2-(hydroxymethyl)piperidine contaminated with water. Anhydrous magnesium sulfate was obtained from Fisher Scientific (Cincinnati, OH); 2-furaldehyde was obtained from Aldrich Chemical Company; and pentanedial (25% aqueous, Grade I) was obtained from Sigma Chemical Company (St. Louis, MO). Toluene and isooctane were obtained from Burdick and Jackson Laboratories, Inc. (Muskegon, MI).

Oxazolidine Preparation

Anhydrous magnesium sulfate (2–4 g) was added to 10 mmol of 2-(hydroxymethyl)piperidine in 20 ml of toluene in a round-bottom flask. Aldehyde (11 mmol) in 20 ml of toluene was added dropwise over 1 hour with stirring. Excess aldehyde was added to ensure complete conversion of 2-(hydroxymethyl)piperidine to oxazolidine. Since water was formed from the reaction of the aldehydes with the 2-(hydroxymethyl)piperidine, the magnesium sulfate helped drive the reaction to completion. For the synthesis using pentanedial, 2.4 mmol of dialdehyde was added to 4.8 mmol 2-(hydroxymethyl)piperidine to prevent extensive formation of the mono-oxazolidine derivative. Four to five grams of anhydrous magnesium sulfate were added to the reaction flask to dry the solution because pentanedial was added as a suspension of 1 ml of 25 percent aqueous pentanedial solution in 10 ml of toluene.

After stirring overnight, the magnesium sulfate was removed by filtration; the solvent and any excess aldehyde were removed by rotary evaporation at 70°–90°C and high vacuum (133 Pa). The remaining viscous oil was the oxazolidine product. The oxazolidines were stored at 0°C to prevent decomposition. Purity was determined by capillary gas chromatography using 10:1 split injections of 0.01–0.05 μL of the undiluted oil. Chromatography columns and conditions are described in the Instrumentation Section. All derivatives were found to be ca. 85–95 percent oxazolidine based on peak area results. With pentanedial, even though precautions were taken to favor formation of the bis-oxazolidine derivative, approximately 15 percent of the product was the mono-derivative.

All derivatives were analyzed by gas chromatography/mass spectrometry. Exact mass data were collected for the pentanal and pentanedial derivatives. Additionally, the derivative of pentanal was analyzed by gas chromatography/fourier transform infrared (GC/FT-IR) spectroscopy. Presented below for each derivative are the aldehyde precursor, the name of the derivative, and the mass and infrared spectral data:

- 2-Furaldehyde; 9-furyl-1-aza-8-oxabicyclo[4.3.0]nonane; mass spectrum, m/e (relative intensity), 192 (100), 163 (50), 128 (26), 95 (45), 81 (20), 69 (14).
- Pentanal; 9-butyl-1-aza-8-oxabicyclo[4.3.0]nonane; mass spectrum, m/e (relative intensity), 182 (7.0), 152 (4.6), 126 (100), 110 (11.3), 98 (37) (exact mass data: M—H, 182.1521, calculated for $C_{11}H_{20}ON$, 182.1543; M—C_4H_9, 126.0914, calculated for $C_7H_{12}ON$, 126.0917); IR (vapor at 280°C), cm^{-1}, 2945 (strong), 2874 (medium), 2781 (medium), 1455 (weak), 1383 (weak), 1339 (weak), 1265 (weak), 1203 (weak), 1133 (medium), 1075 (weak), 1028 (medium).
- Pentanedial; 9,9′-trimethylenebis(1-aza-8-oxabicyclo[4.3.0]nonane); mass spectrum, m/e (relative intensity), 293 (0.4), 263 (2.8), 196 (4.5), 166 (2.3), 152 (10), 141 (7), 126 (100), 110 (16), 98 (10.5), (exact mass data [field desorption], M—H 293.2208, calculated for $C_{17}H_{29}O_2N_2$, 293.2229; M—$C_{10}H_{18}ON$ 126.0931, calculated for $C_7H_{12}ON$, 126.0918).

Instrumentation

The gas chromatographic analyses were performed on a Varian 3700 Capillary Gas Chromatograph equipped with a split/splitless injector, a flame ionization detector, a Varian Model 8000 Autosampler, and a Varian CDS-111 data system. The CDS-111 data system was used only for gas chromatograph oven-temperature programming and autosampler control; chromatographic data were collected and analyzed on a Hewlett-Packard 3357 Laboratory Automation System. The following fused silica capillary columns (J&W) were used: 10-m by 0.25-mm i.d. coated with 1.0-μm film of DB-5 (column A); 30-m by 0.25-mm i.d. coated with 1.0-μm film of DB-5 (column B).

Electron-impact mass spectra (70 eV) were obtained by gas chromatography/mass spectrometry on a VG 7070HS mass spectrometer interfaced to a Hewlett-Packard 5840 gas chromatograph. Infrared spectra were obtained by GC/FT-IR spectroscopy on a Nicolet 60SX fourier transform infrared spectrometer interfaced to a Hewlett-Packard 5880 gas chromatograph with a Nicolet 60GC gas chromatograph interface maintained at 280°C. Gas chromatographic conditions used for these analyses were those described in the Analysis section.

An AID Model 590 Organic Vapor Monitor was used as an independent method for some of the pentanal generation experiments. This system was calibrated using standard atmospheres prepared in Tedlar bags.

Sampling

Samples were generated using a generation system described previously.[11] Aqueous solutions of 2-furaldehyde (6.7 mg/ml) and pentanedial (4 ml of 25% aqueous pentanedial/100 ml; 10 mg/ml) were prepared and vaporized via syringe pump injection into a heated injection block in the generator system. Neat pentanal was vaporized via the same technique. Samples were collected from the generator at 50–60 cm^3/min using calibrated critical orifices (Langer Jewel Bearing, Rolla, ND) or at 40, 80, or 200 cm^3/min using Sipin Model SP-1 sampling pumps (New York, NY).

Aldehydes were trapped from the air samples on ORBO-23 sampling tubes (Supelco, Inc., Bellefonte, PA). Each sampling tube consisted of a 120-mg sorbent bed, followed by a 60-mg backup bed, of 10 percent 2-(hydroxymethyl)piperidine on XAD-2 contained in a 10-cm by 4-mm i.d. glass tube.

To assess the efficiency of the sorbent for collection of the

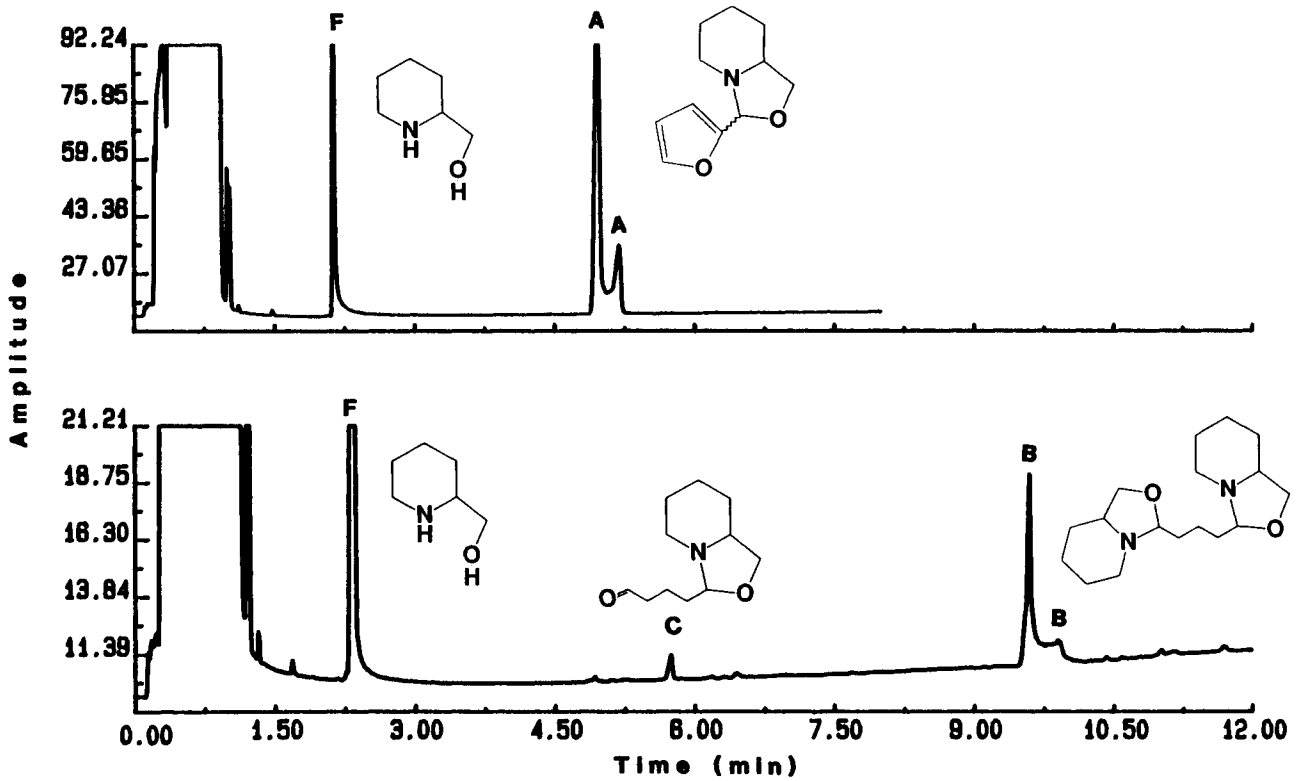

FIGURE 2. Sample chromatograms of 2-(hydroxymethyl)piperidine (F) and the oxazolidines of 2-furaldehyde (A, 96 ng injected), pentanedial (B, 12.3 ng injected), and mono-derivative of pentanedial (C) (analysis conditions: column A, 70°C for 1 min, program at 20°C/min to 270°C and hold for 3 min).

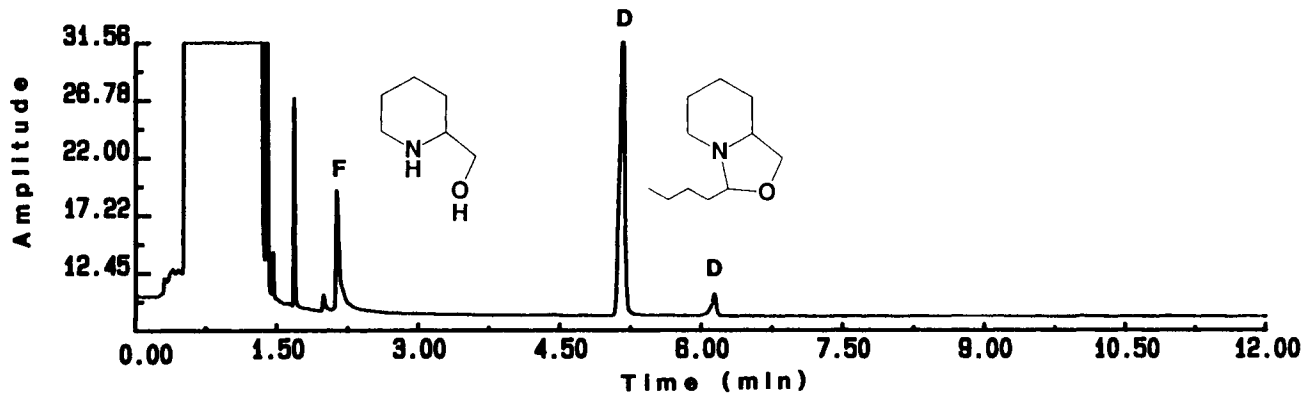

FIGURE 3. Sample chromatogram of 2-(hydroxymethyl)piperidine (F) and the oxazolidine of pentanal (D, 9.4 ng injected) (analysis conditions: column B, 70°C for 0.5 min, program at 50°C/min to 120°C, hold for 2.5 min, program at 20°C to 160°C and hold for 6 min).

aldehydes, breakthrough studies were conducted. Generated atmospheres of the aldehydes (36 mg/m^3 for 2-furaldehyde; 2 and 14 mg/m^3 for pentanedial) were sampled with the commercial sorbent tubes containing only the 120-mg primary section. The sorbent bed was backed up by additional ORBO-23 tubes, which were changed every hour during sampling. Results from the analysis of these backup tubes were indicative of aldehyde breakthrough.

Analysis

Each 120-mg or 60-mg section of each sampler was placed in a 4-ml screw-cap vial, to which 2 ml of toluene was added. The vials were capped and placed in an ultrasonic bath for 30 min. One microliter of each solution was then injected into a gas chromatograph using the splitless injection technique and a split vent time of 0.5 min. Conditions for analysis were 2-furaldehyde and pentanedial, column A, 70°C for 1 min, program at 20°C/min to 270°C and hold the 3 min; pentanal, column B, 70°C for 0.5 min, program at 50°C/min to 120°C, hold for 2.5 min, program at 20°C/min to 160°C and hold for 6 min (alternate program: 70°C for 0.5 min, program at 50°C/min to 120°C, hold for 2.5 min, program at 10°C/min for 12 min, 240°C).

The procedure was calibrated using standard samples prepared from aldehyde and sampling medium. Except for pentanedial, standard samples were prepared by adding 1–10 μL of 0.1 to 10 mg/ml of the aldehyde in toluene to 120 mg of sampling medium in 4-ml screw-cap vials. After sitting 8–12 hr, these standard samples were analyzed with the unknowns as described above. All data in this report are given as the free aldehyde and not as the oxazolidine derivative. Standards for all aldehydes, including pentanedial, were prepared in triplicate and covered the expected range of the samples to be analyzed.

Standard samples for pentanedial were prepared by adding 2–10 μL of an aqueous solution of 10 mg/mL pentanedial to 120-mg portions of sampling medium. This solution, prepared by dilution of 1 ml of 25 percent aqueous pentanedial to 25 ml with distilled deionized water, was standardized as follows: the pH of 10 ml of freshly prepared 1.13 M aqueous sodium sulfite solution was adjusted to pH 8.5–9 with either sulfuric acid or sodium hydroxide; the exact pH value was recorded as the initial pH. One milliliter of the diluted pentanedial solution was then added to the sodium sulfite solution, causing an increase to pH 11–12. This solution was then titrated back to the initial pH with 0.02 N sulfuric acid. The pentanedial concentration was equal to the equivalent weight of pentanedial (50.07 g/equivalent) times the volume of titrant used times the normality of the titrant divided by the volume of the pentanedial solution being standardized (1.0 ml).

Results and Discussion

Both the 10-m and 30-m DB-5 columns (columns A and B) resolved the oxazolidines of pentanal, 2-furaldehyde, and pentanedial from each other and from excess 2-(hydroxymethyl)piperidine. Optimized analysis conditions are represented in chromatograms shown in Figures 2 and 3. With pentanedial, it was necessary to use the shorter 10-m column, since decomposition of the oxazolidine derivative of this compound was observed on longer columns. The DB-5 columns did give a major and a minor peak for each of the oxazolidines studied due to resolution of the pairs of mirror-image isomers (enantiomers) arising from the multiple asymmetric centers in each oxazolidine. The oxazolidine from pentanedial contains four asymmetric centers and has the possibility of 8 dl or meso stereoisomers. From the chromatogram (Figure 2), it is obvious that not all isomers are resolved.

Even though the ratio of the two enantiomeric peaks for a given oxazolidine remained fairly constant, calibration curves were constructed using the combined peak area for each oxazolidine to compensate for the incomplete chromatographic resolution of isomers. These calibration curves were linear over the range of 1–100 ng/μL. Samples exceeding the upper limits for the calibration curves were diluted. The limit of detection for each aldehyde was determined using calibration curve data. For each set of samples, calibration curves were prepared and plotted with their upper and lower 95 percent confidence intervals. The limit of detection was then calculated based on the y-intercept of the calibration line plus the 95 percent confidence limit.[15] From this point on the y-axis, a horizontal line is calculated to intersect with the lower 95 percent confidence interval for the calibration data. This x-value of this intersection point is the limit of detection. This procedure is graphically represented in Figure 4. Using this procedure, the detection limit will change depending on the number of low-concentration standards used for the calibration curve, since the confidence intervals may be tighter at the lower levels when additional low-level standards are included in the calibration data. This is also a very conservative way of expressing detection limit, and levels below this limit may be detectable. The detection limit, for the aldehydes studied, ranged from 0.6 to 9.2 μg/sample for 2-furaldehyde, 0.2 to 6.8 μg/sample for pentanedial, and 0.4 to 4.6 μg/sample for pentanal.

TABLE I. Recoveries from Aldehyde-Spiked Coated Sorbent

Aldehyde	Limits of Detection[A] (μg per sample)	Quantity (μg per sample)	Recovery[B] (%)
2-Furaldehyde	0.6–9.2	16.0–160	94 ± 2.9
Pentanal	0.4–4.6	2.0–509	102 ± 6.9
Pentanedial	0.2–6.8	8.5–85	118 ± 2.0[C]

[A]Limits of detection calculated based on calibration data.[15] See text for further description.
[B]Average recoveries reported with the 95% confidence limits. Calibration curves were based on standard solutions of the authentic oxazolidine.
[C]Standards were approximately 85% pure. Data are uncorrected for this impurity.

Recovery of the aldehydes from the coated sorbent was studied by spiking 120-mg portions of the reagent-coated sorbent in 4-mL vials with a toluene solution of the aldehyde of interest. The sorbent was stored 8–12 hr at ambient temperature and then analyzed with standard solutions prepared from the authentic oxazolidines. Recoveries with their 95 percent confidence limits

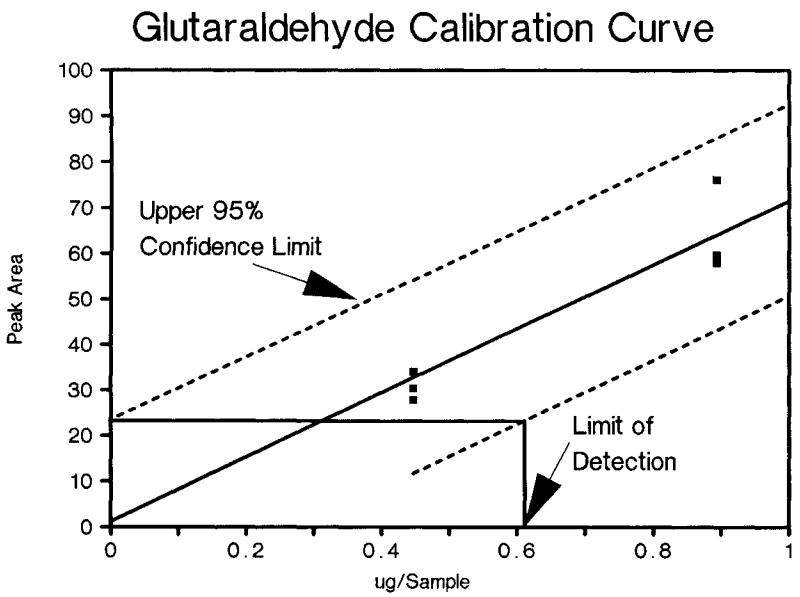

FIGURE 4. Graphic representation of Limit of Detection determination. A horizontal line is calculated from a point equal to the sum of the y-intercept of the calibration line and the 95% confidence limit. The x-value for the intersection of this horizontal line with the lower 95% confidence interval is taken to be the Limit of Detection.[15]

TABLE II. Results of Sorbent Breakthrough Study (80% relative humidity)

Compound	Flow Rate (cm^3/min)	Conc. (mg/m^3)	Breakthrough to 5% of Challenge Conc. Time (min)	Vol. (L)
2-Furaldehyde	80	39	180	14
Pentanedial	80	24	>480	> 38
	200	2	>480	>100

are reported in Table I. In the case of pentanedial, the standard could only be synthesized in an approximately 85 percent pure form, with the remainder of the product being the adduct of single molecules of pentanedial and 2-(hydroxymethyl)piperidine. Calculations were performed assuming 100 percent purity for the standard, which resulted in the apparent excess recovery of this compound. If this impurity is taken into account, then the recovery is essentially quantitative.

Breakthrough data are summarized in Table II. The data from the breakthrough studies suggest that, to ensure effective collection of the aldehydes, the following sampling parameters should not be exceeded: pentanedial, 80 cm^3/min for 8 hr (39 L) or 200 cm^3/min for 30 min (6 L); 2-furaldehyde, 50 cm^3/min for 4 hr (12 L). Recommended flow rates and sampling volumes for each analyte listed above were arbitrarily reduced below the values used for breakthrough studies to further decrease the probability of breakthrough during sampling. Breakthrough work with pentanal was performed using an infrared monitor which gave questionable results. With this compound, flow rates between 30 and 65 cm^3/min were studied in the precision and accuracy experiment (Table III). Based on the results of this experiment, a flow rate of 40 cm^3/min for 4 hr (10 L) was recommended for pentanal.

In addition to pentanedial, 2-furaldehyde, and pentanal, the analyses of 2-methylpropanal (isobutyraldehyde), propanal, and 2-butenal (crotonaldehyde) were investigated with limited success. The oxazolidines of formaldehyde and acrolein were included as potential interferences in the analyses for the other aldehydes. The oxazolidines of these additional five aldehydes were resolved from each other on the DB-5 column, but the oxazolidine of acrolein was not resolved from the propanal derivative. The oxazolidine of formaldehyde was found to elute under the 2-(hydroxymethyl)piperidine peak and did not pose a problem. During sorbent capacity evaluation, 2-methylpropanal, propanal, and 2-butenal were found to have capacity limitations severe enough to prevent successful method development.

Precision and accuracy of the method for pentanedial, 2-furaldehyde, and pentanal were assessed by generating known concentrations of the aldehydes in air and sampling the atmosphere with the sorbent tubes. Approximately six samples were collected for each aldehyde at each of three concentration levels. Twelve additional samples were collected at the lowest level to assess sample stability during long-term storage. All sorbent-tube samples were analyzed as described in the experimental section. The generator concentration was determined independently[8] and concurrently with the Miran IA infrared spectrometer (2-furaldehyde, pentanedial, and pentanal) or the AID Model 590 Organic Vapor Monitor (pentanal). With pentanal, an additional two sets of data were collected at the higher levels. With pentanedial, an additional two sets of samples were collected at ca. 200 cm^3/min for 15 and 30 min at 0.8 mg/m^3. Results from the analyses of all these samples are summarized in Table III. Although it was desirable to generate concentrations in the range of 0.1 to over 2 times the TLVs,[6] this was experimentally difficult due to leakage of the aldehyde solutions from the syringe pump. In some instances, the actual concentrations generated did not match those calculated from syringe pump output. Attempts to compensate for the syringe leakage often resulted in concentrations greater than expected.

Overall precision for each analyte was calculated by pooling the relative standard deviations (RSDs) from each of the three sets of long-term samples. The pooled RSDs were 7.6 percent over the range of 3–41 mg/m^3 (16–640 µg/sample) for 2-furaldehyde, 8.7 percent over the range of 1–8 mg/m^3 (18–180 µg/sample) for pentanedial, not including the short-term samples, and 7.3 percent over the range of 9–374 mg/m^3 (127–3860 µg/sample) for pentanal. Short-term samples for pentanedial had RSDs of 9.1 percent for the 15-min set and 8.8 percent for the 30-min set. Recoveries were essentially quantitative for all aldehydes. Pentanal samples collected at 134 mg/m^3 and 214 mg/m^3 gave indications of sample breakthrough with 2–7 percent of the analyte found on the backup sections. These results indicated the sensitivity of the sampling chemistry to flow rate and the need to stay within recommended sampling limits.

Since pentanedial has a ceiling limit of 0.7 mg/m^3, it was necessary to evaluate the method for the collection of this compound at this level for a 15-min sampling time. Because the sorbent tubes had good capacity for pentanedial, as indicated in the breakthrough experiment, a flow rate of 200 cm^3/min was used for the 15-min sampling periods. A concentration of 0.8 mg/m^3 was generated as measured by an independent method. Two sets of six samples each were taken with the coated-sorbent tubes for 15 min and 30 min. Results were 0.8 ± 0.1 mg/m^3 (109 ± 10% relative recovery) for the 15-min samples and 0.7 ± 0.1 mg/m^3 (96.1 ± 8.4% relative recovery) for the 30-min samples. There was no indication of analyte breakthrough onto the backup section of the sorbent tube.

TABLE III. Aldehyde Method Accuracy Summary

Aldehyde	Flow Rate Range (cm^3/min)[A]	Reference Conc. (mg/m^3)[B]	Found Conc. (mg/m^3)[B]	Results as % of Reference Conc.
Pentanedial	53–79[C]	0.9 ± 1.1	0.8 ± 0.1	89
	52–63[C]	1.5 ± 0.1	1.5 ± 0.1	100
	52–64[C]	7.0 ± 1.8	8.0 ± 0.6	115
	139–205[D]	0.8	0.8 ± 0.1[E]	100
	138–191[F]	0.8	0.7 ± 0.1	96
Pentanal	47–63	8.5 ± 1.2	8.8 ± 1.2	104[G]
	47–65	10.8 ± 1.7	10.3 ± 1.4	95[G]
	47–64[H]	134.0 ± 26.1	131.0 ± 5.4	98
	46–63[I]	214.0 ± 53.8	239.0 ± 13.8	112
	30–42	189.0[J]	194.0 ± 8.0	103
	30–41	380.0[J]	374.0 ± 39.4	99
	53–76	2.8 ± 0.5	2.6 ± 0.1	93
2-Furaldehyde	53–64	9.5 ± 1.1	9.9 ± 0.2	104
	53–64	45.0 ± 1.7	41.0 ± 2.0[K]	91

[A]Samples were collected for 4 hr except where noted.
[B]95% confidence interval given.
[C]Samples were collected for 6 hr.
[D]Samples were collected for 15 min.
[E]Average of 5 samples.
[F]Samples were collected for 30 min.
[G]Average of 3 samples.
[H]Samples were collected for 5 hr.
[I]Samples were collected for 3 hr.
[J]Concentration determined independently by integration of AID 590 continuous monitor signal.
[K]Breakthrough onto the sampler backup section was noted in all samplers but did not exceed 15%.

TABLE IV. Aldehyde Sample Stability Summary[A]

Aldehyde	Reference Conc. (mg/m³)	Measured Concentration[A] of Samples Stored For 1 week (mg/m³)	2 weeks (mg/m³)	5 weeks (mg/m³)
Pentanedial	0.9 ± 1.1	0.8 ± 0.1	0.8 ± 0.1	0.8 ± 0.2
Pentanal[B]	8.5 ± 1.2	8.8 ± 0.1	9.2 ± 0.7	8.9 ± 1.6[C]
	10.8 ± 1.7	10.3 ± 1.4	—[D]	11.5 ± 1.3[C]
2-Furaldehyde	2.8 ± 0.5	2.6 ± 0.1	2.7 ± 0.1	1.4 ± 1.0

[A]Results are presented with their 95% confidence limits. Average of 6 samples.
[B]Pentanal samples were taken at two different concentrations. Storage results are based on the average of three samples at each concentration.
[C]Samples were stored for only 4 weeks.
[D]Samples were lost due to analysis problem.

Long-term storage data, presented in Table IV, indicated that both pentanedial and pentanal could be stored for at least five weeks and four weeks, respectively, at room temperature without loss of sample integrity. 2-Furaldehyde could only be stored for a maximum of two weeks at room temperature before significant sample decomposition occurred.

Summary and Recommendations

A sampling and analysis method exhibiting precision and accuracy within established criteria[16] has been presented for 2-furaldehyde, pentanedial, and pentanal. Samples were collected on commercially available sorbent tubes consisting of 120-mg and 60-mg beds of XAD-2 resin coated with a 10 percent loading of 2-(hydroxymethyl)piperidine. Samples stored at ambient temperature were stable for two weeks with 2-furaldehyde, five weeks with pentanedial, and four weeks with pentanal. The method does have the ability to measure pentanedial at its ceiling limit of 0.7 mg/m³.

For analysis, the samples were desorbed with toluene to give a solution of the oxazolidines, formed from the reaction of the aldehydes collected with the reagent on the sorbent. The solution was analyzed by gas chromatography on either a 10-m or a 30-m fused silica DB-5, 0.25-mm i.d. capillary column and with flame-ionization detection. The 10-m column was preferred for the analysis of the pentanedial derivative, since it reduced decomposition of the derivative on the column. Based on the observed limits of detection and maximum recommended sample volumes, the method should be able to detect concentrations of 0.02 mg/m³ (8-hr sample at 80 cm³/min) and 0.2 mg/m³ (15-min sample at 200 cm³/min) for pentanedial, 0.05 mg/m³ (4-hr sample at 50 cm³/min) for pentanal, and 0.06 mg/m³ for 2-furaldehyde (4-hr sample at 40 cm³/min).

The sampling and analysis of other aldehydes (propanal, isobutyraldehyde, crotonaldehyde) was attempted using similar conditions. Resolution of the oxazolidines of these compounds was successful using the DB-5 columns, but sorbent capacity for these compounds was so low as to preclude efficient sampling.

In field applications, maximum sampling rates must be observed, since the kinetics of the reaction control the collection efficiency of the sorbent. These rates are 80 cm³/min for 8 hr or 200 cm³/min for 30 min for pentanedial, 50 cm³/min for 4 hr for pentanal, and 40 cm³/min for 4 hr for 2-furaldehyde.

The sampling and analytical procedures described in this report will be included in the *NIOSH Manual of Analytical Methods* as individual methods for glutaraldehyde (pentanedial), furfural (2-furaldehyde), and valeraldehyde (pentanal).[17–19]

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