GLUTARALDEHYDE 2532

$O=CH(CH_2)_3CH=O$ MW: 100.12 CAS:111-30-8 RTECS: MA2450000

METHOD: 2532, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : no PEL
NIOSH: C 0.2 ppm
ACGIH: C 0.2 ppm
(1ppm = 4.09 mg/m^3 @ NTP)

PROPERTIES: oil; d 0.72 g/mL @ 20 °C; BP 188 °C; MP -14 °C; VP 2.2 kPa (17 mm Hg) @ 20 °C

SYNONYMS: glutaric dialdhyde; 1,5-pentanedial; glutaral; 1,3-diformylpropane

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (silica gel coated with 2,4-dinitrophenylhydrazine HCL, 300 mg/150 mg)	**TECHNIQUE:**	HPLC, UV DETENTION
FLOW RATE:	0.05 to 0.5 L/min	**ANALYTE:**	glutaraldehyde dinitrophenylhydrazone
VOL-MIN:	1 L @ 0.2 ppm	**EXTRACTION:**	3 mL acetonitrile; shaken 2 h
-MAX:	30 L	**INJECTION VOLUME:**	25 µL
SHIPMENT:	routine	**MOBILE PHASE:**	65% acetonitrile/35% water
SAMPLE STABILITY:	at least 30 days @ 25 °C	**FLOWRATE:**	1.5 mL/min
BLANKS:	2 to 10 field blanks per set; 10 to 20 media blanks per set	**COLUMN:**	reverse phase C8, 5-µm particle size (Alltech Altima C8, 5-µm or equivalent)
ACCURACY		**DETECTOR:**	UV at 365 nm
RANGE STUDIED:	none	**CALIBRATION:**	standard solutions spiked onto sampler tubes
ACCURACY:	not determined	**RANGE:**	0.8 to 24 µg per sample
BIAS:	not determined	**ESTIMATED LOD:**	0.3 µg per sample
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined	**PRECISION ($\bar{S}_r$):**	0.007 @ 12 µg per sample; 0.025 @ 1.2 µg per sample

APPLICABILITY: The working range is 0.01 to 0.3 ppm (0.04 to 1.2 mg/m^3) for a 20-L air sample.

INTERFERENCES: Other aldehydes and ketones react with 2,4-dinitrophenylhydrazine but can be resolved using proper HPLC parameters.

OTHER METHODS: OSHA Method 64 [1] uses a glass fiber filter coated with 2,4-dinitrophenylhydrazine and phosphoric acid for collection, with HPLC analysis.

REAGENTS:

1. Glutaraldhyde, 25% (w/v) solution in water (Aldrich D19,930-3 or equivalent).*
2. Water, distilled, deionized.
3. Acetonitrile, HPLC grade.
4. Sodium sulfite, 1.13 M. Prepare fresh immediately before use.
5. Sulfuric acid, 0.02 N.
6. Sodium hydroxide, 0.01 N

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Glass tube, 110 mm long, 6-mm OD, flame-sealed ends and plastic caps containing two sections of silica gel coated with 2,4-dinitrophenylhydrazine HCl. The front section contains 300 mg, the back 150 mg, and sections are retained and separated by small plugs of silanized glass wool. (SKC 226-119 or equivalent).
   NOTE: The hydrochloride salt provides an acid catalyst for the reaction of glutaraldehyde with the dinitrophenylhydrazine. Other acids may be used as catalyst.
2. Personal sampling pump, 0.05 to 0.5 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph (HPLC), UV detector (365 nm), column, and integrator (page 2532-1).
4. Shaker, mechanical.
5. Syringe, 10-mL, disposable.
6. Vials, glass, scintillation, 20-mL, with PTFE-lined caps.
7. Syringes, microliter, readable to 0.1-µL.
8. Flasks, volumetric, various sizes.
9. Pipets, various sizes.
10. Burets, 50-mL.
11. Stirrer, magnetic.
12. pH meter.
13. Beakers, 50-mL.
14. File.

SPECIAL PRECAUTIONS: Glutaraldehyde can irritate the mucous membrane and act on the central nervous system [2]. Work with this compound only in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.5 L/min for a total sample size of 1 to 30 L.
   NOTE: Glutaraldehyde reacts with the 2,4-dinitrophenylhydrazine to form a hydrazone derivative which provides sample stability and UV chromophores for analysis.
4. Immediately after sampling, cap the sample tubes, including blanks, and pack securely for shipment, include 10-20 unused tubes from the same lot to be used for standard preparation.

SAMPLE PREPARATION:

5. Score each sampler with a file in front of the front sorbent section and break the tube at the score line.
6. Remove and place front glass wool plug and front sorbent section (300 mg) in a vial.
7. Transfer back section (150 mg) with remaining glass wool plugs to a second vial.
8. Add 3.0 mL of acetonitrile to each vial. Screw cap tightly onto each vial.
9. Agitate vials in a mechanical shaker for at least 2 h.
   NOTE: The use of ultrasonic bath yields incomplete recovery

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CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range of interest.
    a. Prepare and standardize glutaraldehyde stock solution. (See APPENDIX.) Make serial dilutions of the stock solution with water.
    b. Using a microliter syringe, add known amounts of glutaraldehyde directly onto the DNPH-coated silica gel tubes over the range of interest. Allow the tubes to stand overnight for solvent evaporation and equilibration.
    c. Prepare the standards as described in Steps 5 through 9 and analyze with samples and blanks.
    d. Prepare a calibration graph (peak area or height vs. concentration).
       NOTE: Because the working standards are prepared on media blanks, no additional blank correction or extraction efficiency correction is necessary. Check extraction efficiency occasionally in the range of interest.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

12. Set the liquid chromatograph to manufacturer's recommendations and parameters given on page 5512-1.
13. Inject 25-µL sample aliquot.
14. Measure peak area or height for each UV response. The two isomers of glutaraldehyde are separated using these chromatographic conditions. Sum the peak area or height of both isomers to obtain the total area of height.

CALCULATIONS:

15. Determine the mass, µg, of glutaraldehyde found in the sample front (W_f) and back (W_b) sorbent sections.
    NOTE 1: Corrections for extraction efficiency and blanks are incorporated into the method by using spiked media as standards.
    NOTE 2: If $W_b > W_f/10$, report breakthrough and possible sample loss.
16. Calculate concentration (C) of glutaraldehyde in the air volume sampled in liters (V):

$$C = \frac{(W_f + W_b)}{V}, mg/m^3.$$

EVALUATION OF METHOD:

The pressure drop at 0.2 L/min across representative tubes was 6" H_2O, at 0.5 L/min about 14" H_2O, but at 1 L/min it was about 46" H_2O. This method incorporates the use of spiked media as standards eliminating recovery bias. Mechanical agitation gave better recovery and linearity of the calibration curve ranging from 0.6 to 24 µg per sample. Recoveries from tubes agitated by sonic bath decreased as the concentration increased. Recoveries of glutaraldehyde from the DNPH-coated tubes were determined by spiking 6 tubes each at concentrations of 1.2, 2.4, and 12 µg per sample. After standing overnight to allow the solvent to evaporate, the sorbent was transferred to a vial, 3 mL of acetonitrile was added, and the sample was agitated in a mechanical shaker for at least 1 h. At the same time, 6 more tubes were spiked at each of these concentrations and stored in the laboratory at ambient conditions for 42 days. The data are shown in Table 1.

Table 1. Recovery and Stability Study of Glutaraldehyde

Concentration (µg/sample)	Day Analyzed	Recovery (%)	S_r
1.2	1	95	.028
	42*	100	.014
2.4	1	97	.027
	42	98	.034
12	1	96	.034
	42	98	.023

* Samples stored at 25 °C for 42 days.

A 20-point, 4-concentration curve was used to determine a LOD of 0.24 µg/sample and a LOQ of 0.78 µg/sample. No air samples were generated during this evaluation. Audit samples were prepared with liquid spikes of glutaraldehyde in water added directly onto the DNPH-coated silica gel tube. These audit samples were shipped, stored, and analyzed by an independent laboratory using this method. The results were acceptable with recoveries of about 100% at 1.2 µg per tube, 94% at 2.4 µg per tube, 85% at 12 µg per tube, and <0.3 µg per tube for the blanks [3].

REFERENCES:

[1] OSHA Analytical Methods Manual, Glutaraldehyde, Method 64. OSHA Technical Center, Salt Lake City, UT. U.S. Dept. of Labor (1985).
[2] The Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).
[3] User Check, DataChem Labs, Sequence #7958-J (unpublished, 3/14/94).

METHOD WRITTEN (REVISED) BY:

Charles E. Neumeister, NIOSH/DPSE, and Gordon Hill, DataChem Laboratories, Salt Lake City, UT.

APPENDIX: PREPARATION AND STANDARDIZATION OF GLUTARALDEHYDE STOCK SOLUTION

Dilute 1 mL 25% aqueous glutaraldehyde to 25 mL with distilled, deionized water. Place 10.0 mL 1.13 M sodium sulfite solution in a beaker and stir magnetically. With a pH meter, adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 1.0 mL glutaraldehyde stock solution. The pH should be about 12. Titrate the solution back to its original pH with 0.02 N sulfuric acid. If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, Cs (µg/µL) of the glutaraldehyde stock solution.

$$C_s = 50.06 \cdot \frac{(N_a \cdot V_a) - (N_b \cdot V_b)}{V_s}.$$

where: 50.06 = equivalent weight of glutaraldehyde
N_a = normality of sulfuric acid
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of sodium hydroxide
V_b = volume of sodium hydroxide (mL) used for back titration
V_s = volume of glutaraldehyde stock solution (1.0 mL).