

## DIACETYL

2557

C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>

MW: 86.09

CAS: 431-03-8

RTECS: EK2625000

METHOD: 2557, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 March 2003

OSHA: no PEL  
 NIOSH: no REL  
 ACGIH: no TLV

PROPERTIES: yellowish liquid; d = 0.981 g/mL @ 20 °C;  
 BP 88 °C; VP 52 mm Hg @ 20 °C; FP  
 7 °C; flash point 21 °C

SYNONYMS: biacetyl; 2,3-butadione; 2,3-diketobutane; dimethyl diketone; dimethylglyoxal

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	SORBENT TUBE (Anasorb CMS Solid Sorbent Tube, 150/75 mg)	<b>TECHNIQUE:</b>	GAS CHROMATOGRAPHY, FID
<b>FLOW RATE:</b>	0.01 to 0.2 L/min	<b>ANALYTE:</b>	diacetyl
<b>VOL-MIN:</b>	1 L	<b>DESORPTION:</b>	1 mL of acetone/methanol (99:1) on rotary mixer for 1.5 hours
<b>-MAX:</b>	10 L	<b>INJECTION VOLUME:</b>	1 µL
<b>SHIPMENT:</b>	Ship cold (5 °C) and store in dark	<b>TEMPERATURE-INJECTION:</b>	225 °C
<b>SAMPLE STABILITY:</b>	7 days @ 5 °C	<b>-DETECTOR:</b>	250 °C
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>-COLUMN:</b>	35 °C (hold 3 min) to 200 °C (6 °C/min)
<b>ACCURACY</b>		<b>CARRIER GAS:</b>	He (2.8 mL/min)
<b>RANGE STUDIED:</b>	not determined	<b>COLUMN:</b>	capillary, fused silica, 30 m x 0.32-mm ID; 1-µm film, Stabilwax-DA or equivalent
<b>BIAS:</b>	not determined	<b>CALIBRATION:</b>	standard solutions of diacetyl in acetone/methanol (99:1) solvent
<b>OVERALL PRECISION (<math>\hat{S}_{rr}</math>):</b>	not determined	<b>RANGE:</b>	2 to 470 µg/sample
<b>ACCURACY:</b>	not determined	<b>ESTIMATED LOD:</b>	0.6 µg/sample
		<b>PRECISION (<math>\hat{S}_r</math>):</b>	0.018

APPLICABILITY: The working range for diacetyl was 0.057 to 13.4 ppm (0.20 to 47.2 mg/m<sup>3</sup>) for a 10-L air sample.

INTERFERENCES: Any compound with a similar retention time to diacetyl.

OTHER METHODS: None determined.

**REAGENTS:**

1. Diacetyl, chromatographic grade\*
2. Acetone, pesticide grade\*
3. Methanol, pesticide grade\*
4. Helium, pre-purified and filtered.
5. Hydrogen, pre-purified and filtered.
6. Air, compressed, purified, and filtered.
7. Desorbing solvent: acetone/methanol (99:1)
8. Calibration stock solution: Add known amount of diacetyl to desorbing solvent in 10- mL volumetric flask.

\* See SPECIAL PRECAUTIONS

**EQUIPMENT:**

1. Sampler: Anasorb CMS solid sorbent tube (SKC, Inc. # 226-121).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph equipped with FID, integrator, and capillary column with a deactivated glass inlet liner (page 2557-1).
4. Vials, autosampler, 2-mL, amber glass, with PTFE-lined crimp caps.
5. Syringes, 10- $\mu$ L, 25- $\mu$ L, and 1-mL.
6. Pipettes, 3-mL and 5-mL.
7. Volumetric flasks, 10-mL, amber.

**SPECIAL PRECAUTIONS:** Diacetyl is flammable, toxic, and forms explosive mixtures in air. Acetone and methanol are flammable and pose a fire hazard. Work with all chemicals in a well ventilated laboratory safety hood.

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampling tube immediately before sampling. Attach sampling tube to personal sampling pump with flexible tubing.
3. Sample at an accurately know flow rate between 0.01 and 0.2 L/min for a total sample size of 10 L.
4. Cap the samplers with plastic caps, pack in a manner to insure that the samplers are kept in the dark, and are shipped cold (5 °C).

**SAMPLE PREPARATION:**

5. Place the front and back sorbent sections in separate amber vials (due to photosensitivity of diacetyl). Place the glass wool plug preceding the front section into the vial containing the front sorbent section. Discard the urethane foam plugs.
6. Add 1.0 mL of the acetone/methanol (99:1) solvent into each vial. Securely attach crimp caps to each vial.
7. Place each vial on a rotary mixer for 1.5 hours.

**CALIBRATION AND QUALITY CONTROL:**

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
  - a. Add known amounts of diacetyl to the solvent in a 10-mL volumetric flask and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
  - b. Analyze together with samples and blanks (steps 11 and 12).
  - c. Prepare calibration graph (peak area vs  $\mu$ g diacetyl).
9. Determine the desorption efficiency (DE) at least once for each lot of Anasorb CMS used for sampling in the calibration range (step 8).
  - a. Prepare three tubes at each of five levels plus three media blanks.
  - b. Inject a known amount (5 to 20  $\mu$ L) of DE stock solution directly onto the front section of each Anasorb CMS tube with a microliter syringe.
  - c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
  - d. Desorb (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
  - e. Prepare a graph of DE vs  $\mu$ g diacetyl recovered.
10. Analyze a minimum of three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

**MEASUREMENT:**

11. Set gas chromatograph according to manufacturer's recommendations and to the conditions listed on page 2557-1. Inject a 1- $\mu$ L sample aliquot manually using the solvent flush technique or with an autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.

12. Measure peak areas.

**CALCULATIONS:**

13. Determine the mass,  $\mu$ g (corrected for DE), of diacetyl found in the sample front ( $W_f$ ) and back ( $W_b$ ) sorbent sections, and in the average media blank front ( $B_f$ ) and back ( $B_b$ ) sorbent sections.

NOTE: If  $W_b > W_f/10$ , report breakthrough and possible sample loss.

14. Calculate concentration, C, of diacetyl in the air volume sampled, V(L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{mg} / \text{m}^3$$

NOTE:  $\mu\text{g/L} \equiv \text{mg/m}^3$

**EVALUATION OF METHOD:**

This method was developed in response to a request to identify and quantitate possible hazardous chemicals in food packaging facility. Diacetyl, a toxic and reactive compound [2], was identified as a possible suspect chemical in the facility.

Because of the reactivity of diacetyl, several specialized analytical conditions were required during the method development. The use of a deactivated glass inlet liner and a Stabilwax-DA capillary column were required to prevent the reaction of diacetyl in the injection port and with the column which resulted in tailing peaks and decomposition of the analyte. It was further determined that the reactivity of diacetyl could be inhibited or slowed down by storage in the dark at 5 °C. Standards prepared in amber volumetric flasks were stable for a couple days. Even with storage under these conditions, collected samples containing diacetyl were only stable for 7 days (95%). The average DE recovery for diacetyl was 90% over a range from 47 to 470  $\mu$ g [1].

A user check of this method for diacetyl verified that it passed the performance criteria for a NIOSH method. The mean recovery was 103.1% (n=12) with a standard deviation of 4.45%. The precision of an average test result was 9.79% [3].

NOTE: While this method can be used of the sampling and analysis of acetoin, recovery is not optimized and is 65%-70%, which is below the acceptable recovery criteria of  $\geq 75\%$  for NMAM methods [4].

**REFERENCES:**

- [1] Pendergrass SM [2001]. Diacetyl backup data report, unpublished report, NIOSH/DART.
- [2] Aldrich Chemical Company [2000]. Diacetyl, Material Safety Data Sheet (MSDS).
- [3] DataChem [2001]. Diacetyl user check, unpublished.
- [4] Kennedy ER, Fischbach TJ, Song R, Eller PE, Shulman SA [1995]. Guidelines for Air Sampling and Analytical Method Development and Evaluation, Cincinnati, OH: National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication No. 95-117.

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