IODINE   6005

I$_2$ MW: 253.81   CAS: 7553-56-2   RTECS: NN1575000

| METHOD: 6005, Issue 2 | EVALUATION: FULL | Issue 1: 15 August 1987 |
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OSHA : C 0.1 ppm
NIOSH: C 0.1 ppm; Group I Pesticide
ACGIH: C 0.1ppm
(1 ppm = 10.38 mg/m^3 @ NTP)

PROPERTIES: Solid; d (solid @ 25 °C) 4.93 g/mL;MP 113.6 °C; BP 185.2 °C; VP 40 kPa (0.305 mm Hg; 395 ppm) @ 25 °C; not combustible

SYNONYMS: None

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (alkali-treated charcoal, 100 mg/50 mg)	**TECHNIQUE:**	ION CHROMATOGRAPHY
FLOW RATE:	0.5 to 1 L/min	**ANALYTE:**	iodide ion (I$^-$)
VOL-MIN: -MAX:	15 L @ 0.05 ppm 225 L	**DESORPTION:**	3 mL 10 m$\underline{M}$ Na$_2$CO$_3$
SHIPMENT:	routine	**INJECTION LOOP VOLUME:**	50 µL
SAMPLE STABILITY:	8 days @ 25 °C [1]	**ELUENT:**	10 m$\underline{M}$ Na$_2$CO$_3$; 3 mL/min
FIELD BLANKS:	2 to 10 field blanks per set	**COLUMNS:**	HPIC-AS4A anion separator; HPIC-AG4A anion guard; micromembrane suppressor
MEDIA BLANKS:	6 per sample set + 15 per lot of charcoal	**CONDUCTIVITY SETTING:**	3 µS full scale
		CALIBRATION:	standard solutions of KI in eluent
ACCURACY		**RANGE:**	8 to 200 µg I$_2$ per sample [1]
RANGE STUDIED:	0.74 to 2.1 mg/m^3 [1] (15-L air samples)	**ESTIMATED LOD:**	1 µg I$_2$ per sample [1]
BIAS:	- 5.7%	**PRECISION ($\bar{S}_r$):**	0.071 @ 10 to 30 µg I$_2$ per sample [1]
OVERALL PRECISION ($\hat{S}_{rT}$): 0.085 [2]			
ACCURACY:	± 22.4%		

APPLICABILITY: The working range is 0.05 to 5 ppm (0.5 to 50 mg/m^3) for a 15-L air sample. The method is applicable to 15-min ceiling measurements.

INTERFERENCES: Particulate iodide salts, HI, or organic iodides may give positive interferences, but collection of these compounds on treated charcoal has not been investigated. Iodate, other halogens, nitrate, phosphate, and sulfate do not   interfere.

OTHER METHODS: Better sensitivity (ppb range) has been found using amperometric detection (AS1 column [2] or AG2 and AS2 columns [3]). An AS5 column using 6 m $\underline{M}$ Na$_2$CO$_3$/0.8 m$\underline{M}$ paracyanophenol in 2% acetonitrile as eluent and either conductometric or amperometric detection yielded the best sensitivity [2].

REAGENTS:

1. Deionized, filtered water with specific conductance ≤ 10 µS/cm.
2. Sodium carbonate (Na_2CO_3), reagent grade.
3. Potassium iodide (KI), reagent grade.
4. Iodine (I_2), reagent grade.*
5. Toluene, distilled in glass.
6. Eluent: 10 m$\underline{M}$ Na_2CO_3. Dissolve 4.240 g Na_2CO_3 in 4 L filtered, deionized water.
7. Calibration stock solution, 1000 µg/mL of I^-. Dissolve 0.1308 g KI in filtered, deionized water to make 100 mL solution.
8. Desorption Efficiency (DE) stock solution, 50 µg/µL. Dissolve 500 mg I_2 in toluene to make 10 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends and plastic caps, containing two sections of 20/40 mesh alkali-treated charcoal (Barnebey-Cheney Type 580-19) (front = 100 mg; back = 50 mg) separated by 2-mm urethane foam plug. A glass wool plug and metal retaining spring precede the front section and a 3-mm foam plug follows the back section. Pressure drop ≤ 2.1 kPa across the tube at 1.2 L/min airflow. Tubes are commercially available (SKC No. 226-67, SKC, Inc., Eighty-Four, PA, or equivalent).
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Ion chromatograph (IC), anion separator and guard columns, anion suppressor (page 6005-1), conductivity detector, integrator (optional) and strip chart recorder.
4. File, triangular.
5. Ultrasonic bath.
6. Vials, 20-mL, glass, with PTFE-lined screw caps.
7. Syringes, 3-mL, polyethylene with luer tip.
8. Filters, luer tip, with PTFE filter, 13-mm diameter, 5-µm pore size.
9. Volumetric flasks, 10-, 50-, and 100-mL.
10. Bottles, polyethylene, 100-mL.
11. Pipets, 0.05- to 3-mL.
12. Syringe, 5-µL, readable to 0.1 µL.

SPECIAL PRECAUTIONS: Iodine is a severe irritant to the eyes and respiratory system and, to a lesser extent, the skin [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1.0 L/min for a total sample size of 15 to 225 L.
4. Cap samplers. Pack securely for shipment.
   NOTE: Refrigerate samples if stored longer than 7 days.

SAMPLE PREPARATION:

5. Allow refrigerated samples to equilibrate at room temperature.
6. Score sampler with a file in front of primary sorbent section. Break sampler at score line.
7. Transfer front sorbent section with glass wool plug to vial.
8. Place back sorbent section with foam plugs in separate vial.
9. Add 3.0 mL eluent to each vial. Cap immediately.

10. Agitate vials in ultrasonic bath for 2 min at room temperature.
11. Draw sample extract through 13-mm PTFE filter attached to 3-mL syringe.
    NOTE: All samples, eluents and water flowing through the IC must be filtered to avoid plugging the system valves or columns.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least six working standards.
    a. Add known aliquots of calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark to prepare solutions containing 1 to 60 µg/mL of I^- (equivalent to 1.2 to 72 µg/mL of I_2). Store in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
    b. Analyze working standards with samples and blanks (steps 15 through 17).
    c. Prepare calibration graph [peak height (mm or µS) vs. µg].
13. Determine desorption efficiency (DE) for each lot of charcoal used for sampling in the calibration range. Prepare at least three tubes at each of five levels.
    a. Place treated charcoal from unused front sorbent section in vial. Discard glass wool and backup section.
    b. Inject a known amount (2 to 5 µL) of DE stock solution, or a serial dilution thereof, onto charcoal with microliter syringe.
    c. Cap the vial. Allow to stand overnight.
    d. Desorb (steps 9 through 11) and analyze together with standards (steps 15 through 17).
    e. Prepare a graph of DE vs. µg I_2 recovered.
14. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

15. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 6005-1.
16. Inject sample aliquot. For manual operation, inject 1 to 2 mL of sample to ensure complete rinse of sample loop, or use autosampler.
17. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with eluent, reanalyze, and apply appropriate dilution factor in calculations.

CALCULATIONS:

18. Determine mass, µg (corrected for DE), of analyte 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.
19. Calculate concentration, C, of iodine in the air volume sampled, V (L):

$$C = \frac{1.2 \cdot (W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

where 1.2 = The stoichiometric factor arising from conversion of iodine to iodide on the sampler ($3 I_2 + 6 OH^- \rightarrow 3 H_2O + 5 I^- + IO_3^-$).

EVALUATION OF METHOD:

This method was optimized and evaluated by Southern Research Institute [1] and is based on a method developed by Kim et al. [5]. The method was evaluated over the range 0.74 to 2.11 mg/m^3 iodine in

15-L air samples with a pooled sampling and measurement precision, $\bar{S}_r$, of 0.062. The capacity of the 100-mg charcoal front section was at least 6 mg of iodine vapor. The total variance, $\hat{S}_{rT}$, including pump error, was 0.085. Overall average recovery based on 18 samples, six at each of three levels, was 90.8%. When corrected for desorption efficiency (0.962 in the range 0.0088 to 0.03 mg I_2 per sample), the recovery was 94.3%, representing an insignificant bias. Samples stored at ambient temperature for eight days were stable with recovery of 101.6% and a precision, S_r, of 0.103 based on samples analyzed on day one.

REFERENCES:

[1] Dillon, H. K., M. L. Bryant and W. K. Fowler. Methods Development for Sampling and Analysis of Chlorine, Chlorine Dioxide, Bromine and Iodine: Research Report for Iodine, Contract 210-80-0067, Southern Research Institute, Birmingham, AL, (1983), available as PB83-246595 from NTIS, Springfield, VA 22161 .
[2] The Determination of Iodide by Ion Chromatography, Application Note 37, Dionex Corporation, Sunnyvale, CA (February, 1982).
[3] Han, K., W. F. Koch and K. W. Pratt. Improved Procedure for the Determination of Iodide by Ion Chromatography with Electrochemical Detection, Anal. Chem. 59, 731-736(1987).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[5] Kim, W. S., J. D. McGlothlin and R. E. Kupel. Sampling and Analysis of Iodine in the Industrial Atmosphere, Am. Ind. Hyg. Assoc. J., 43, 187-190 (1981).

METHOD REVISED BY:

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