NH_3 MW: 17.03 CAS: 7664-41-7 RTECS: BO0875000

METHOD: 6015, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 50 ppm
NIOSH: 25 ppm; STEL 35 ppm; Group III pesticide
ACGIH: 25 ppm; STEL 35 ppm
(1 ppm = 0.697 mg/m^3 @ NTP)

PROPERTIES: gas; MP -77.7 °C; BP -33.4 °C; explosive range 16 to 25% v/v in air; vapor density 0.6 (air = 1)

SYNONYMS: none

SAMPLING

SAMPLER:	SOLID SORBENT TUBE (sulfuric acid-treated silica gel) A 0.8-micron MCE prefilter may be used to remove particulate interferences.
FLOW RATE:	0.1 to 0.2 L/min
VOL-MIN:	0.1 L @ 50 ppm
-MAX:	96 L
SHIPMENT:	routine
SAMPLE STABILITY:	not determined
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
ACCURACY:	not determined
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined

MEASUREMENT

TECHNIQUE:	VISIBLE ABSORPTION SPECTROPHOTOMETRY
ANALYTE:	indophenol blue
EXTRACTION:	20 mL deionized water
COLOR DEVELOPMENT:	EDTA antiprecipitant, phenolate coupling agent, nitroprusside intensifier, hypochlorite.
WAVELENGTH:	630 or 660 nm
CALIBRATION:	standard solutions of ammonium chloride in deionized water
RANGE:	1.5 to 20 µg per sample [1]
ESTIMATED LOD:	0.5 µg per sample [1]
PRECISION ($\bar{S}_r$):	not determined

APPLICABILITY: The working range is 0.2 to 400 ppm (0.15 to 300 mg/m^3) for a 10-L air sample. This method is applicable to STEL measurements.

INTERFERENCES: None identified.

OTHER METHODS: This method is based on the sampling procedure of Method S347 [2], the automated analytical procedure of EPA Method 350.1 [3], and Standard Methods 417G [4]. NIOSH Method 6701 [5] was less sensitive, employing a passive liquid sorbent badge for collection followed by ion chromatography. NIOSH Method P&CAM 205 [6] used impinger collection and Nessler's reagent for manual colorimetric analysis. OSHA has both impinger collection with ion specific electrode analysis (ID-164) [7] and sulfuric acid-impregnated beaded carbon collection followed by ion chromatography analysis (ID-188) [8].

REAGENTS:

1. Water, distilled and deionized. Special precaution must be taken to ensure that distilled water is free of ammonia, by passing it through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Regenerate the ion exchange column according to the instructions of the manufacturer.
   NOTE: All solutions must be made using ammonia-free water.
2. Sulfuric acid, conc., reagent grade.
3. Phenol.
4. Sodium hydroxide, reagent grade.
5. Brij-35.
6. Ammonium chloride.
7. Chloroform.
8. Sulfuric acid 5 N. Air scrubber solution (AAII). Carefully add 140 mL of concentrated sulfuric acid to approximately 500 mL of ammonia-free distilled water. Cool to room temperature and dilute to 1 L with ammonia-free water.
9. Sodium phenolate. In a 1-liter flask, dissolve 83 g phenol (or 80 mL 90% liquid phenol) in 500 mL distilled water. In small increments, cautiously add with agitation, 32 g NaOH (96 g 50% NaOH for TRAACS). Periodically cool flask under water faucet. When cool, dilute to 1 L with distilled water. Filter if necessary. Store in amber glass bottle. For AAII add 0.5 mL Brij-35.
10. Sodium hypochlorite solution: Dilute one volume of a bleach solution containing 5.25% NaOCl (such as "Clorox") with an equal volume of deionized water. Available chlorine level should approximate 2 to 3%.
11. Disodium ethylenediamine-tetraacetate (EDTA) (5%): Dissolve 50 g EDTA (disodium salt) and six pellets NaOH in 1 L of deionized water. (For TRAACS, dissolve 41 g EDTA, 1 g 50% NaOH, and 3-6 mL Brij-35.)
12. Sodium nitroprusside (0.05% $Na_2Fe(CN)_5NO \cdot 2H_2O$): Dissolve 0.5 g sodium nitroprusside in 1 L deionized water (or 1.1 g for TRAACS).
    NOTE: Sodium nitroprusside solution is light-sensitive. Store in and use from a brown bottle.
13. Calibration stock solution (100 mg NH_3/L): Dissolve 0.3144 g anhydrous ammonium chloride, NH_4Cl, dried at 105 °C, in deionized water, and dilute to 1 L. Add 1 mL chloroform as a preservative.

EQUIPMENT:

1. Sampler:
   a. Prefilter (to remove particulate interferences): 37-mm cellulose ester membrane filter (0.8-µm pore size) supported by stainless steel screen in two piece cassette filter holder.
   b. Sulfuric acid-treated silica gel sampling tubes. Glass tube with both ends unsealed and fire-polished, 6.0 cm long with a 6-mm O.D. and a 4-mm I.D. containing two sections of 20/40 mesh sulfuric acid-treated silica gel (200 mg front/100 mg back) separated by a 2-mm portion of glass wool. Plugs of silylated glass wool are placed at the ends of the tube. The pressure drop across the tube must be <13 inches of water at a flow rate of 0.2 L/min (see APPENDIX). The glass tubes should be rinsed and dried with acetone before packing. The tubes are capped with plastic caps. Tubes are commercially available.
2. Personal sampling pump calibrated, 0.1 to 0.2 L/min, with flexible tubing.
3. Technicon AutoAnalyzer Unit (AAII) (or TRAACS 800 equivalent) consisting of an autosampler, and analytical cartridge (AAII), proportioning pump, colorimeter equipped with 15-mm, 30-mm, or 50-mm tubular flow cell and 630- to 660-nm filters, a data collection system, and recorder.
4. pH Meter and pH electrode.
5. Plastic vials, 80-mL or 50-mL.
6. Polyethylene centrifuge tubes.
7. Magnetic stirrer and stirring bars.
8. Pipets: delivery type of convenient sizes.
9. Volumetric flasks: 1-L and 50-mL and other convenient sizes for preparing standard solutions.
10. Stopwatch.
11. Manometer.

SPECIAL PRECAUTIONS: Phenol is both corrosive and poisonous from ingestion, inhalation, or absorption through the skin [10]. Avoid skin contact and inhalation of vapors. Sodium hydroxide, sulfuric acid, and sodium hypochlorite (bleach) are all corrosive. Avoid contact with skin or inhalation of vapors. Chloroform is believed to be carcinogenic [10], with reports of mutagenic and teratogenic effects in animals. Handle in a hood and avoid skin contact. Sodium nitroprusside (sodium nitroferricyanide) is highly toxic. Use extreme caution to avoid ingestion or inhalation of dust.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.1 and 0.2 liter/minute for a total sample size of 0.1 to 96 L.
3. Cap the sampling tubes with plastic (not rubber) caps immediately after sampling.
4. Pack securely for shipment.

SAMPLE PREPARATION:

5. Remove the plastic caps. Transfer the front and back sections of sulfuric acid-treated silica gel to separate 80-mL vials. Discard glass wool plugs. Analyze the two sections separately.
   NOTE: Firm tapping of the tube may be necessary to effect complete transfer of the sulfuric acid-treated silica gel.
6. Add 20 mL of ammonia-free deionized water to each vial. Cap and shake vigorously. Desorption is complete in 45 minutes. Adjust the pH of each sample to 5.0 to 6.5 with sodium hydroxide.
   NOTE: Analyses should be completed within one day after the ammonia is desorbed.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.05 to 1 µg/mL. Using the stock solution, prepare standards such as the following in 100-mL volumetric flasks (prepare fresh daily):
   a. Add known amounts of calibration stock solution to deionized water in 100-mL volumetric flasks and dilute to the mark. Prepare fresh daily.

NH_3, µg/mL	mL Stock Solution/100 mL
0.05	0.05
0.10	0.10
0.20	0.20
0.40	0.40
0.80	0.80
1.00	1.00

   b. Analyze working standards together with samples and blanks (steps 9 through 12).
   c. The instrument automatically generates calibration graph (peak height versus concentration). Sample concentrations will be printed out directly from this graph.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibrating graph is in control.

MEASUREMENT:

9. For a working range of 0.05 to 1.0 µg NH_3/mL, set up the manifold as shown in Figure 1 for AAII and as shown in Figure 2 for TRAACS. Higher concentrations may be accommodated by sample dilution.
10. Allow both the colorimeter and the recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding deionized water through the sample line.
11. For normal conditions use a 30 or 40/hour 2:1 cam with a common wash for the AAII. For the TRAACS use a sampling rate between 90 and 120/hour with a 3:1, 4:1, or 5:1 sample/wash ratio.
12. Arrange ammonia standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples. Begin analysis.

CALCULATIONS:

13. Read NH_3 concentration (µg/mL) found in sample front (W_f) and back (W_b) sorbent sections directly from the instrument printout.
14. Calculate the concentration (C) of NH_3 in the volume, V (L), of air sampled from the sample solution concentrations, W_f and W_b (µg/mL), multiplied by the appropriate solution volumes, V_f and V_b (mL):

$$C = \frac{W_f V_f + W_b V_b}{V}, \text{ mg/m}^3.$$

REFERENCES:

[1] DataChem Laboratories report for NIOSH Seq. 7482-L (NIOSH/DPSE, unpublished, May 20, 1992).

[2] NIOSH Manual of Analytical Methods, 2nd ed., Volume 5, S347, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

[3] Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 Revised March 1983, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

[4] Standard Methods for the Examination of Water and Wastewater, 16th ed., 1985, APHA, AWWA, WPCF.

[5] NIOSH Manual of Analytical Methods, 3rd ed., Method 6701, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 84-100, February 1984.

[6] NIOSH Manual of Analytical Methods, 2nd ed., Volume 1, P&CAM 205, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[7] "Ammonia in Workplace Atmosphere" Method ID-164, Inorganic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah.

[8] "Ammonia in Workplace Atmosphere" Method ID-188, Inorganic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah, (April, 1988).

[9] The Merck Index, 11th Edition, 7206 Phenol, 2141 Chloroform, Merck & Co., Inc., Rahway, NJ (1989).

[10] 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 #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

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APPENDIX: PREPARATION OF SULFURIC ACID-TREATED SILICA GEL

1. Place 6 g of 20/40 mesh silica gel in 250-mL beaker.

2. Add 15 mL 0.4 N sulfuric acid to the beaker. Stir the mixture, and cover the beaker with a watch glass.

3. Heat the silica gel-acid mixture in a fume hood with a Bunsen burner to a very gentle boil. Evaporate approximately one-half of the liquid.

4. Place the covered beaker in a drying oven at 120 °C until the remainder of the water has been evaporated.

5. The prepared acid-treated silica gel should flow freely and not adhere to the beaker. Store in silica gel in a desiccator until ready for use.

FIGURE 1 (AAII)
Ammonia Manifold

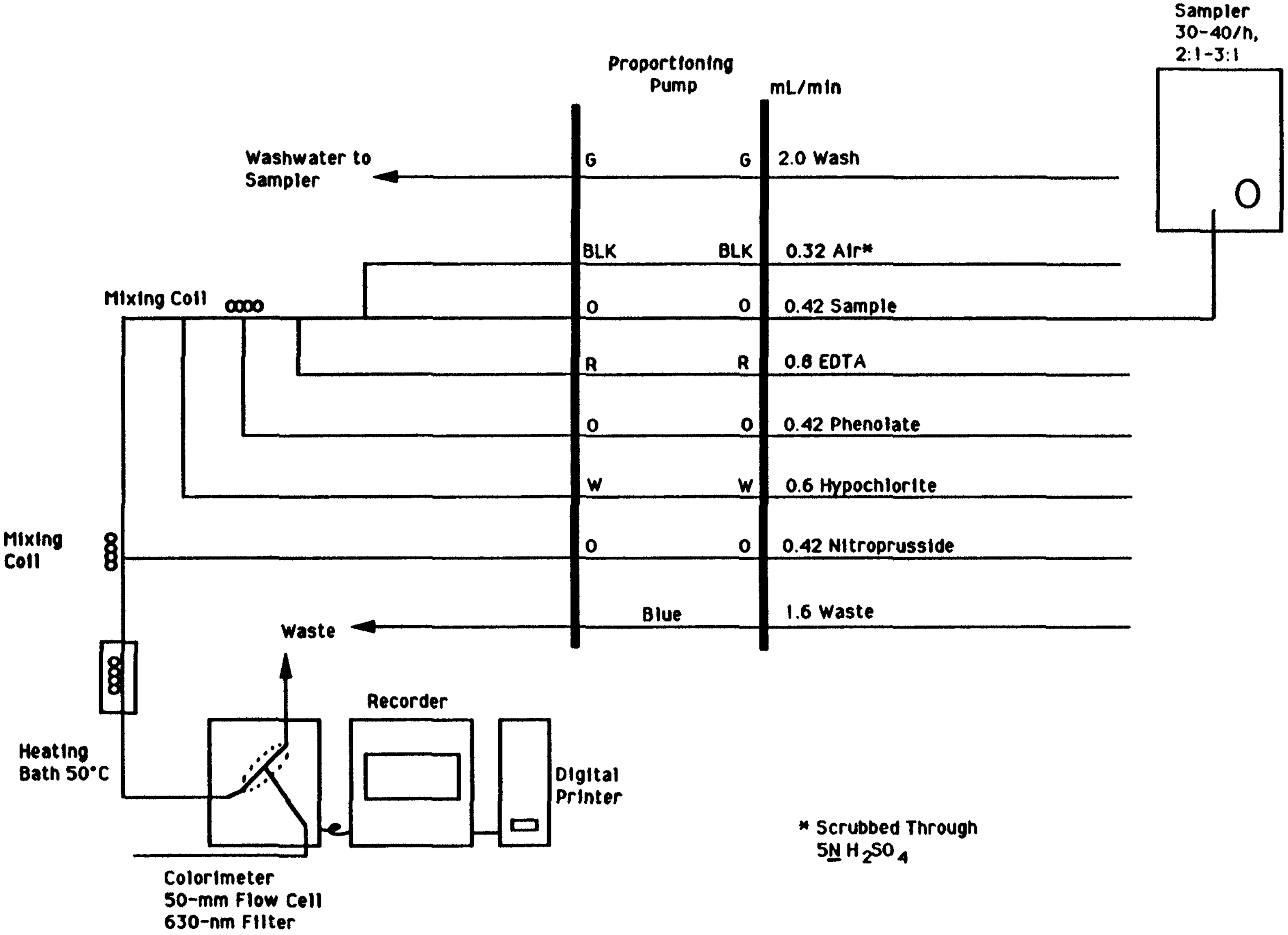
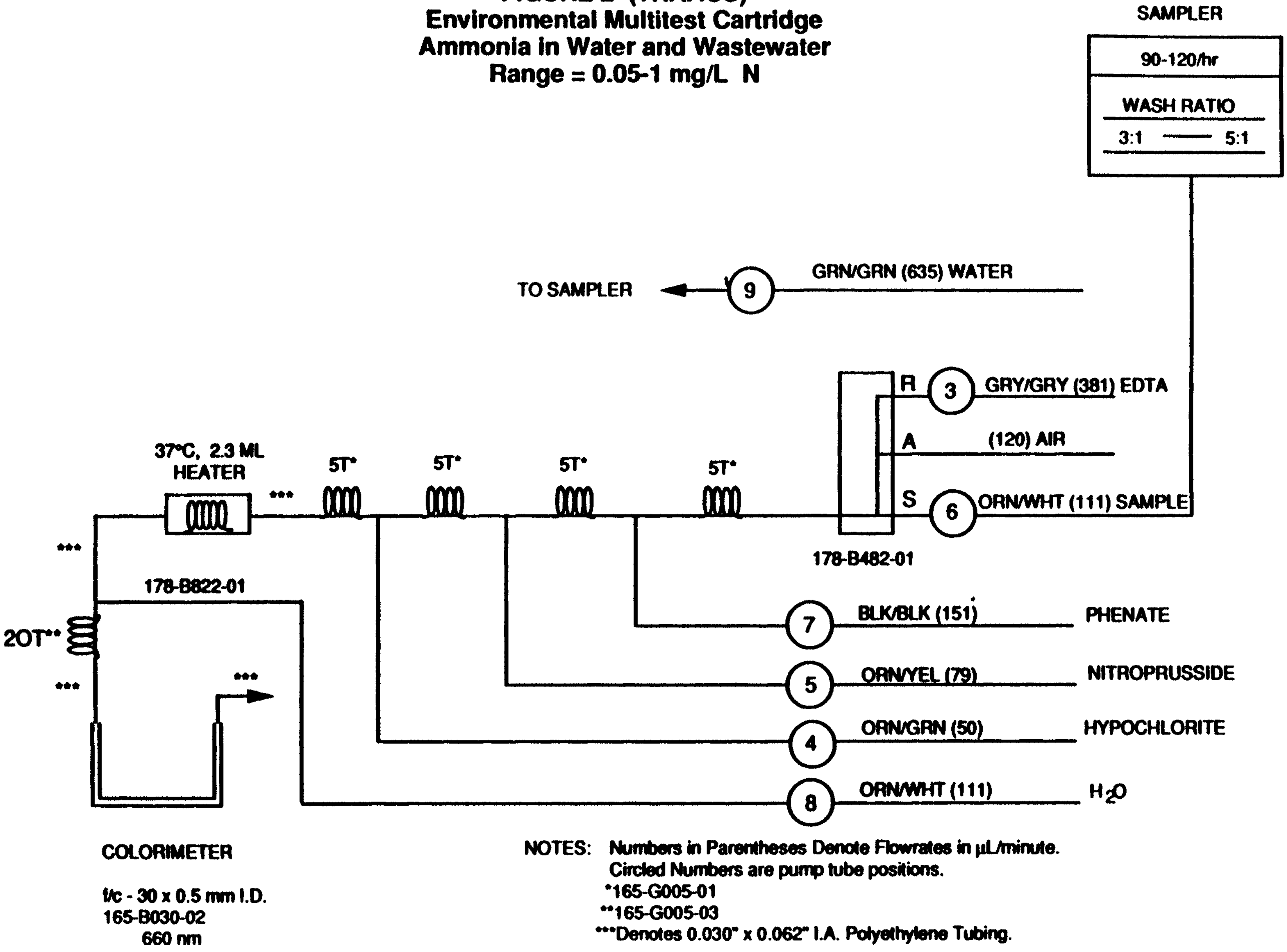


FIGURE 2 (TRAACS)
Environmental Multitest Cartridge
Ammonia in Water and Wastewater
Range = 0.05-1 mg/L N



NOTES: Numbers in Parentheses Denote Flowrates in µL/minute.
Circled Numbers are pump tube positions.
*165-G005-01
**165-G005-03
***Denotes 0.030" x 0.062" I.A. Polyethylene Tubing.