APPENDIX A

SUGGESTED OPERATING PROCEDURE FOR
DETERMINATION OF ACRYLONITRILE
EMISSIONS FROM STATIONARY SOURCES

Formula: $H_2C=CHCN$
Molecular Weight: 53.06
Boiling Point: 77 °C
Density: 0.806 g/mL

1. PRINCIPLE

1.1. Principle. A gas sample is extracted from the effluent of the stack. The dissolved acrylonitrile (AN) is measured using a nitrogen selective thermionic ionization detector.

2. APPARATUS

2.1. Sampling. The sampling apparatus is shown in Figure 1. Component parts are described below. The method specifies a sampling rate of 50 mL/min over a 1 hour period with samples collected in replicates of four or more.

2.1.1. Probes. Stainless steel, 1/8 inch outer diameter, 15-20 feet in length.

2.1.2. Impingers. One 25 mL midget impinger per probe. Impingers with either glass frits or standard tips may be used.

2.1.3. Tubing and Interconnections. TFE Teflon tubing, 1/4" OD x 3/16" ID x 1/32" wall. About 5 inches is needed for each impinger inlet and outlet. Teflon Swagelok unions and fittings, 1/4", are required for all direct connections to the

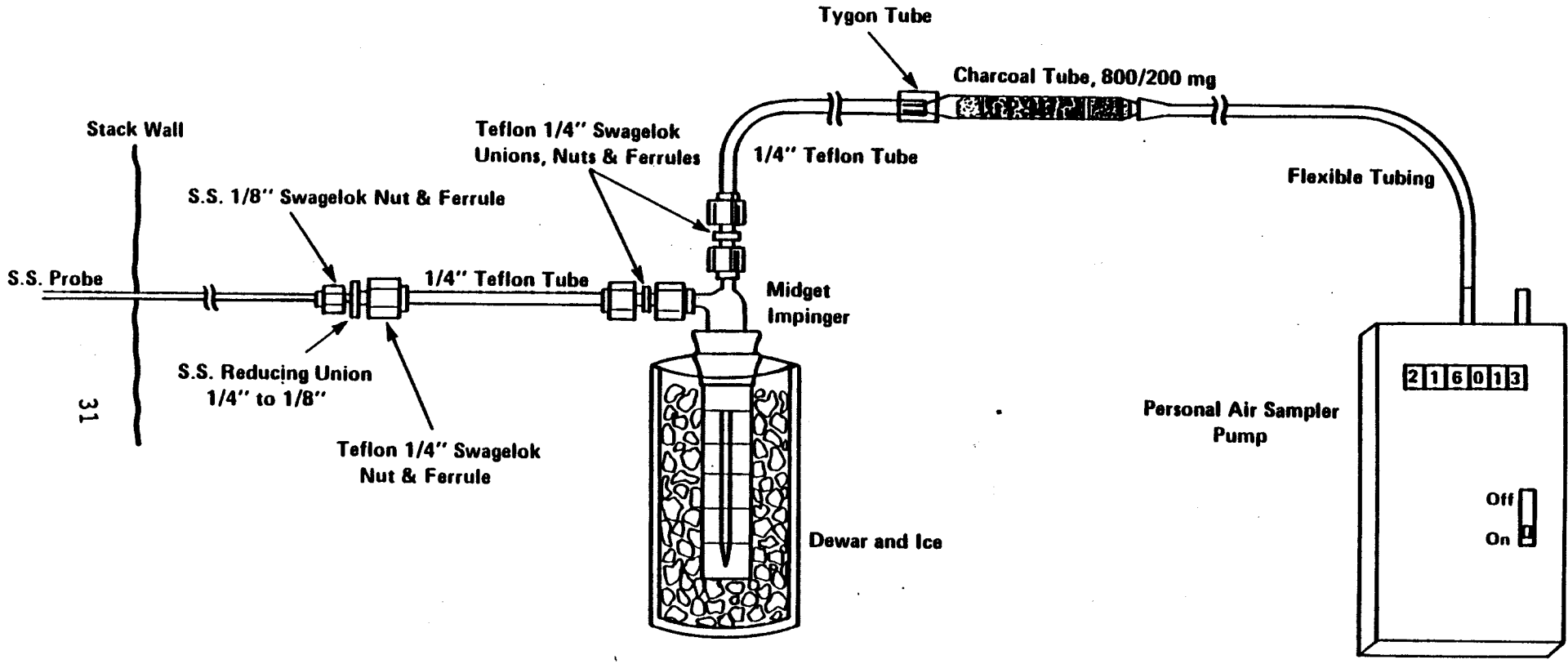

Figure A-1. Acrylonitrile sampling apparatus.

impingers. The probe must be connected to the impinger inlet line with a 1/8" to 1/4" stainless steel reducing union with 1/8" nut and ferrule on the probe and 1/4" Teflon nut and ferrule on the impinger inlet tube.

2.1.4. Sorbent Tubes. 800/200 mg coconut charcoal. Sorbent tubes must be connected to the impinger outlet with a short length of Tygon tubing (about 1 inch) in such a manner that the tip of the charcoal tube extends snuggly into the end of the Teflon tube. The Tygon tube has an inner diameter just large enough to allow it to be placed simultaneously over the outside of the impinger outlet and the charcoal tube without slipping off or leaking.

2.1.5. Pump. Diaphragm pump with flow rate adjustable from 50-200 mL/min. Pump must be a constant volume sampler with a pump stroke counter.

2.1.6. Mercury Thermometer. For measuring ambient temperature. Temperature of gas exiting pump chamber is assumed to be at ambient temperature (a good approximation).

2.1.7. Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 1 mm Hg. In some cases, the barometric pressure may be obtained from a nearby National Weather Service station. Corrections for differences in elevation between the weather service station and sampling location may be applied at the rate $\pm$ 2.5 mm Hg per $\pm$ 30 m difference in elevation.

2.1.8. Dewar Flasks. Thermally insulated Dewar flasks sufficiently large (about 350 mL) to accommodate impinger and crushed ice.

2.2. Sample Recovery.

2.2.1. Storage Bottles. Glass vials, 35 mL, for each impinger sample. Vial caps must be lined with Teflon.

2.2.3. Disposable Pasteur Pipets. 5 3/4 inch borosilicate glass pipets with bulbs for solvent rinsing of impingers.

2.3. Analysis.

2.3.1. Standard Vials and Flasks. Glass vials, 1.7 - 2.0 mL, with Teflon-lined caps. Class A volumetric microflasks, 1 mL ($\pm$ 0.01 mL) and 5 mL ($\pm$ 0.02 mL), for preparing calibration

standards.

2.3.2. Sample Vials. Glass vials with Teflon caps for use in extracting sorbent tubes. 10 mL vials are needed for front section, 5 mL vials are needed for backup section. See also Sections 2.2.1. and 2.3.1.

2.3.3. Microsyringes. Appropriately sized syringes, 5 μL and 100 μL, for use in preparation of calibration standards and samples for analysis.

2.3.4. Gas Chromatograph.

2.3.4.1. Column and Injector. Wall-coated J&W DB-WAX capillary column, crosslinked and bonded. Column temperature program: 60 °C (hold 3 min), 5 °C/min to 100 °C (hold 1 min). Column dimensions: 30 m x 0.25 mm, 0.5 μm film. Carrier gas: 1.3 mL/min measured at 60 °C. Split mode of injection using microliter syringe with 2" needle into wide-bore (4 mm) glass liner with flow inverter near the end. Liner is used without packing material. Split ratio: approximately 60:1. Injector temperature: 250 °C. Alternate analytical column: DB-WAX wide bore capillary column, crosslinked and bonded. Column temperature program: 50 °C (hold 4 min), 8 °C/min to 110 °C (hold 3 min). Column dimensions: 30 m x 0.55 mm, 1μm film. Carrier gas: 5.6 mL/min measured at 50 °C. Split/splitless mode of injection; splitless period 1.2 seconds followed by helium purge at 120-160 mL/min. AN elutes after about 4 min and the internal standard after about 9 min.

2.3.4.2. Detector. Flameless thermionic nitrogen/phosphorous selective detector uilizing an electrically heated bead containing rubidium salt positioned just above the detector jet with a low H_2/air ratio. Detector sensitivity and stability is highly dependent on bead temperature and its relative position above the jet. Make adjustments as necessary to obtain the optimum sensitivity and stability. Detector temperature: 240 °C. Detector hydrogen: 6.5 mL/min. Detector air: 85 mL/min. Makeup gas: helium at 30 mL/min.

3. REAGENTS

The highest purity reagents should be used, particularly in the preparation of calibration standards.

3.1. Sampling.

3.1.1. Methanol. Capillary GC grade methanol for use as impinger solvent. Each impinger shall be filled with 25 mL of solvent. Allow an additional amount for rinsing and quantitative transfer of sample to storage vials.

3.2. Sample Recovery.

3.2.1. Methanol with 2% formic acid. A prepared solution of capillary GC methanol containing 2% v/v formic acid for use in extracting charcoal tubes.

3.3. Analysis.

3.3.1. Acrylonitrile. The highest purity available (Aldrich, 99 + %) for use in preparation of calibration standards. Shall contain 35-45 ppm 4-methoxyphenol to inhibit AN polymerization.

3.3.2. Valeronitrile (M.W. 83.13, b.p. 139-141, d. 0.795). Very high-purity valeronitrile (Aldrich, 99%) to be used as an internal standard in the samples during laboratory analysis.

3.3.3. Helium. Ultra-high purity for GC carrier gas and detector makeup gas.

3.3.4. Hydrogen. Ultra-high purity for nitrogen-phosphorous detector (NPD).

3.3.5. Air. For NPD, filtered.

4. PROCEDURE

4.1. Sampling.

4.1.1. Preparation of Sampling Apparatus. Position sampling probe within effluent stream near the center of the stack. Secure probe to prevent movement. Fill impinger with 25 mL of clean methanol; place in Dewar flask and surround with ice. Allow sufficient time before sampling for solvent to reach approximately 0 °C. Score both ends of each charcoal tube and break the tips. Attach one end to the impinger tubing and the other end to the pump tubing. Connect impinger inlet line to the sampling probe by means of a reducing union and Swagelok fittings

(see Section 2.1.3.). Securely tighten all joints to eliminate any possibility of leakage and inspect during sampling to ensure good leak-free connections.

4.1.2. Sample Collection. Record the ambient temperature in the vicinity of the pumps, the atmospheric pressure, initial count on the pump meter, and the temperature of the stack gas. Connect the probes to the impingers, turn on each pump, and begin timing. Record the temperature and pressure after 30 min and at the end of the run. After 1 hour of sampling, turn pumps off and record final count on the pump meter.

4.1.3. Sample Recovery. Disconnect the impingers from the probes. Remove charcoal tubes, cap the ends tightly, and label. Pour the contents of the impingers into individual sample storage bottles. Rinse each impinger three to four times with clean methanol, and add the washings to the sample storage bottles. Seal tightly and label each. Place charcoal tubes and sample bottles in an insulated chest with ice.

4.2. Sample Preparation.

4.2.1. Impingers. Remove from cold storage only the samples to be analyzed that day. Spike exactly 5μL of pure, undiluted valeronitrile directly into each sample solution and invert container several times to mix thoroughly.

4.2.2. Sorbent Tubes. Remove from cold storage only the charcoal tubes to be extracted that day. Score glass and break open tube discarding the foam and glass wool. Transfer the front section charcoal (800 mg) and the backup charcoal (200 mg) to 10 mL and 5 mL vials, respectively. Add precisely 8 mL of methanol containing 2% formic acid to the front section charcoal and 2 mL to the backup charcoal. Desorb for about 1 hour with occasional agitation.

4.3. Sample Analysis.

4.3.1. Impingers. Inject duplicate 1 μL aliquots of each impinger solution into a calibrated gas chromatograph. Bracket each set of duplicate injections with a standard injection at a concentration comparable to that found in the samples. Repeat

this pattern for all samples to be analyzed. Plot the chromatograms and collect the integration data for later analysis.

4.3.2. Sorbent Tubes. Transfer 490 μL aliquots of the charcoal tube extracts to small vials (1.7-2.0 mL capacity). Add to each sample vial precisely 10 μL of internal standard diluted 1:100 according to Section 4.4.3, and mix thoroughly. Make replicate injections in the manner as described above (Section 4.3.1.). Plot chromatograms and collect the data.

4.4. Calibration.

4.4.1. Pump. Set pumps to a sampling rate of 50 mL/min. Attach a complete sample train (sample probe, impinger containing methanol solvent placed in Dewar with ice, and charcoal tube) to each pump. Calibration is made using a soap-film flowmeter or other appropriate device. This is accomplished by determining the number of pump strokes needed to pull the soap film through an accurately known volume (100 mL is convenient). Calculate a pump factor, mL/count, for each individual pump. The calibration of pumps should be conducted within a few days prior to their intended use with fully charged batteries. Only pumps that are known to be reliable should be used in field sample collection.

4.4.2. Gas Chromatograph. A multilevel calibration of the GC is performed using the internal standard method and a series of solutions of AN at known concentrations. The internal standard, valeronitrile, is spiked into the standard solutions to give a concentration of 159 ng/μL. The AN standards are prepared volumetrically at concentrations of 316 ng/μL, 29.3 ng/μL, and 2.99 ng/μL.

4.4.3. Preparation of Standards. All three standards shall have a total volume of 1000 μL each. This or a similar recipe should be followed each time a fresh series of calibration standards is prepared. Care must be taken to ensure accuracy and consistency of technique when measuring and adding liquid volumes. When using the pure liquids, they should be at about the same temperature (20 °C) on each occasion to ensure consistent density

from one use to another. Prepare stock solutions of AN and valeronitrile. Valeronitrile (1:100 dilution): To a 1 mL class A volumetric microflask (± 0.01 mL), add 10 μL of undiluted valeronitrile and dilute with methanol to 1 mL (7950 ng/μL final conc.). AN (1:2500 dilution): To a 5 mL class A volumetric microflask (± 0.02 mL), add 2 μL of undiluted AN and dilute with methanol to 5 mL (322.4 ng/μL final conc.). Prepare three levels of calibration standards. High level: Add 980 μL of AN stock solution to a small vial (1.7-2.0 mL). Add 20 μL of the internal standard stock solution to give a final concentration of 316 ng/μL. Mid-level: To another small vial add 100 μL of AN stock solution and 980 μL of methanol. Transfer 100 μL of this mixture to a third small vial to be used for the low-level calibration standard. Add 20 μL of internal standard stock solution to give a final concentration of 29.3 ng/μL. Low-level: Complete the low-level calibration standard by adding 880 μL of methanol and 20 μL of internal standard stock solution. Final concentration is 2.99 ng/μL.

5. CALCULATIONS

5.1. Field Data. Calculate the number of moles of air sampled:

$$n_1 = \frac{P_A V}{P_S T_A R} \qquad \text{Eq. 1}$$

Where:
- n_1 = Number of moles of air sampled.
- V = Volume of air sampled, liters.
- P_S = Standard pressure, 760 mm Hg.
- P_A = Average ambient pressure during sample collection, mm Hg.
- T_A = Average ambient temperature during sample collection, °K.
- R = Gas constant, 0.08206 L atm/°K mol.

5.2. Laboratory Data. Calculate the number of moles of AN collected

$$n_2 = \frac{C_1 V_1 + C_2 V_2}{M.W.} \times (10^{-9}) \qquad \text{Eq. 2}$$

Where:
- n_2 = Number of moles of AN collected.
- V_1 = 25,000 μL (impinger samples).

V_2 = 8,000 μL (charcoal tube samples).
C_1 = Impinger sample concentration, ng/μL.
= R_i C_i
C_i = Measured concentration in impinger sample, average of the replicate determinations.
R_i = (Prepared conc. of calibration standard)/(measured conc. of calibration standard); the measured concentration of calibration standard is taken to be the average of two determinations that bracket C_i.
C_2 = Charcoal tube, concentration in desorbing solution, ng/μL.
= $R_{ii}C_{ii}$
C_{ii} = Measured concentration of desorbing solution.
R_{ii} = (Prepared conc. of calibration standard)/(measured conc. of calibration standard); the measured concentration of calibration standard is taken to be the average of two determinations that bracket C_{ii}.
M.W. = Gram molecular weight of AN, 53.06 g/mole.

Notes :

The individual calibration factors are necessary due to daily variation (usually minor) in the response of the instrument to AN in relation to its response to the internal standard, valeronitrile.

The internal standard method of calibration and analysis permits precise measurements to be made by internally compensating for variation in the injected volume of sample aliquots and for subtle changes in the split ratio (but not changes in relative response as mentioned above). In addition, this method eliminates the need to know the precise liquid volume of the samples, provided that they are properly spiked with internal standard solution.

The values for V_1 and V_2 are derived from the manner in which the sample is prepared for analysis and the way in which the instrument calibration is performed. For example, the system is calibrated by analyzing a prepared mixture containing valeronitrile at 159 ng/μL and AN at some nominal level. (A calibration curve for AN is generated internally by the integrator based on the response of the detector to AN at the prepared concentration.) The impinger samples are assumed to contain exactly 25 mL of liquid. The actual volume may differ

from this. A sufficient amount of valeronitrile is then added to this assumed volume to give an apparent concentration of 159 ng/μL (i.e., 5 μL of undiluted valeronitrile, density 0.795 g/mL). The integrator assumes that all samples will be spiked with internal standard to that concentration. When a sample is analyzed, a comparison is made between the response to the internal standard in the sample and the response for the internal standard when the calibration was performed. If there is any difference between the sample and the standard, a factor is applied to the internal standard in the sample to make it agree with the calibration standard. This factor is applied likewise to the response obtained for the AN in the sample. Thus, even though the reported concentration is not necessarily the true concentration, it is the concentration that would be present if the sample volume was at exactly 25,000 μL. Therefore, the volume in Equation 2 is 25,000 μL for V_1. The same reasoning can be applied to the 490 μL aliquots of the charcoal tube extracts, and the volume in Equation 2 is 500 μL for V_2.

5.3. Source Concentration. Calculate the AN source concentration:

$$C_s = (n_2/n_1)\ 10^6 \qquad \text{Eq. 3}$$

Where: C_s = AN source concentration, ppm.

5.4. Statistical Treatment. The data for each sample set is used to determine the precision of the samples by calculating the relative standard deviation of the measurements within that particular sample set:

$$\%\ RSD = (s/x)\ 100 \qquad \text{Eq. 4}$$

Where: RSD = Relative standard deviation of sample set results.
s = Standard deviation of sample set data.
x = Average concentration of sample set.