

**SUMMARY SHEET 7**  
**Nitrogen Oxides**

		Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 7			
Job No.		FDS 7			
Sampling Location		FDS 7			
Run ID#		FDS 7			
Test Date		FDS 7			
Run Start Time		FDS 7			
Run Finish Time		FDS 7			
Traverse Points (if applicable)		FDS 7			
Initial Temperature, °F	$t_i$	FDS 7			
Initial Absolute Temperature, R	$T_i$	SS 7			
Final Temperature, °F	$t_f$	FDS 7			
Final Absolute Temperature, R	$T_f$	SS 7			
Initial Barometric Pressure, in. Hg	$P_{bi}$	FDS 7			
Initial Vacuum, in. Hg	$P_{gi}$	FDS 7			
Initial Absolute Pressure, in. Hg	$P_i$	SS 7			
Final Barometric Pressure, in. Hg	$P_{bf}$	FDS 7			
Final Vacuum, in. Hg	$P_{gf}$	FDS 7			
Final Absolute Pressure, in. Hg	$P_f$	SS 7			
Flask Volume, mL	$V_f$	CDS 7			
Volume Absorbing Reagent, mL	$V_a$	FDS 7			
Gas Sample Volume, mL	$V_{sc}$	SS 7			
Spectrophotometer Calibration Factor	$K_c$	LDS 7			
Sample Solution Volume, mL		LDS 7			
Average NO <sub>2</sub> Per Sample, µg	$m_{avg}$	LDS 7			
Sample Concentration, lb/dscf	$C$	SS 7			
Audit Relative Error, %	RE	QA1			
Post-test Calibration Checks					
Temperature, Barometer, and Vacuum Gauges		CDS 2d			

*Note: Consider  $P_{gi}$  and  $P_{gf}$  to be positive.*

$$V_{sc} = 17.64 (V_f - V_a) \left[ \frac{(P_{bf} - P_{gf})}{(460 + t_f)} - \frac{(P_{bi} - P_{gi})}{(460 + t_i)} \right]$$

$$C = 6.242 \times 10^{-5} \frac{m_{avg}}{V_{sc}}$$

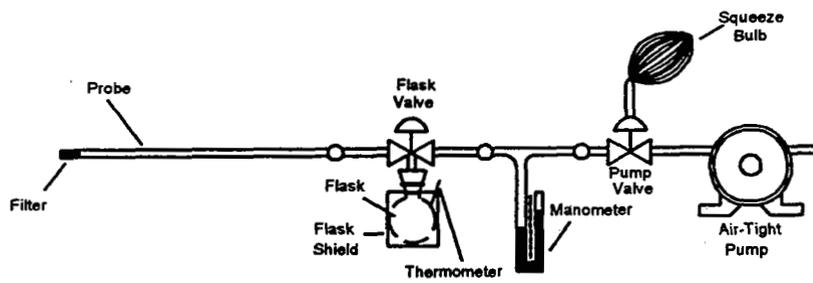


Figure F7-1. Sampling Train, Flask Valve, and Flask.

**FIELD PROCEDURE 7**  
**Nitrogen Oxides (Evacuated Flask)**

*Note: Except for some minor variations, this procedure is also used for Method 7A or 7B.*

**A. Pre-test Preparation**

1. Pipette 25 mL of absorbing solution into a sample flask.
2. Retain enough absorbing solution to prepare the calibration standards.

**B. Sampling**

1. Assemble the sampling train as shown in Figure F7-1, and place the probe at the sampling point.
2. Ensure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high-temperature chlorofluorocarbon-based stopcock grease.
3. Evacuate the flask to  $\pm 3$  in. Hg absolute pressure, preferably to the vapor pressure of water at existing temperature.
4. Check for leakage by observing the manometer for any pressure fluctuation (must not vary  $> 0.4$  in. Hg in 1 min).
5. Record the data as shown in FDS 7.
6. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears.
7. Take flask pressure readings.
8. Extract sample slowly until pressures in the flask and sample line (i.e., duct, stack) are equal (usually 15 sec); a longer period indicates a "plug" in the probe.
9. After collecting the sample, close the flask valve, and disconnect the flask from the sampling train.
10. Shake the flask for at least 5 min and let the flask set for  $\geq 16$  hr.

**C. Sample Recovery**

1. Shake the contents for 2 min.
2. Connect the flask to a mercury filled U-tube manometer.
3. Open the valve from the flask to the manometer, and record the flask temperature, the barometric pressure, and the flask vacuum.
4. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-mL portions of deionized distilled water, and add the rinse water to the bottle.

5. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step.
6. Seal and label the container. Mark the height of the liquid level.

**D. Post-test Calibrations**

Calibrate thermometers, barometer, and vacuum gauges (if other than mercury manometer). See CP 2d, 2e, and 2f.

**E. Method 7A**

1. FP 7A is the same as that for FP 7, except omit step C5 (adjusting the pH). Use FDS 7.
2. FP 7A may be subject to a low bias when  $SO_2 > 2000$  ppm.

**F. Method 7B**

1. Apply this procedure to emissions from nitric acid plants only.
2. Follow the procedure in FP 7 up and including step C2. Use FDS 7. Do not increase  $H_2O_2$  concentration.
3. Transfer the contents of the flask to a 100-mL volumetric flask.
4. Rinse the flask three times with 10-mL portions of deionized distilled water, and add to the volumetric flask.
5. Dilute to 100 mL with deionized distilled water. Mix thoroughly. Analyze the sample (see LP 7B).

**G. Sampling Gas Stream with Insufficient Oxygen**

Introduce oxygen into flask by one of the following three methods:

1. Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to  $\pm 3$  in. Hg absolute pressure.
2. Inject oxygen into the flask after sampling.
3. Terminate sampling with a minimum of 2 in. Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

**FIELD DATA SHEET 7**  
**Evacuated Flask Sample**

Method (Circle) 7 7A 7B

Client/Plant Name \_\_\_\_\_ Job # \_\_\_\_\_

City/State \_\_\_\_\_ Date/Time \_\_\_\_\_

Test Location/Run # \_\_\_\_\_ Personnel \_\_\_\_\_

Clock Time	Steps	Sample #	Sample #	Sample #	Sample #
	Initial Vacuum ( $\leq 3$ in. abs ?) (in. Hg)				
	Leak Check ( $\leq 0.4$ in. Hg/min ?) (in. Hg)				
	Flask ID/Valve #				
	Flask/Valve Volume (cc)				
	Initial Temperature, $t_i$ (°F)				
	Initial Barometric Pressure, $P_{bi}$ (in. Hg)				
	Purge (no condensation?) (✓)				
	Initial Vacuum (Leg A + Leg B), $P_{gi}$ (in. Hg)				
	Initial Pressure, $P_i$ (in. Hg)				
	Shake for 5 minutes ? (✓)				
	Flask stand for $\geq 16$ hr ? (✓)				
	Shake for 2 minutes ? (✓)				
	Final Flask Temperature, $t_f$ (°F)				
	Final Barometric Pressure, $P_{bf}$ (in. Hg)				
	Final Vacuum (Leg A + Leg B), $P_{gf}$ (in. Hg)				
	Final Pressure, $P_f$ (in. Hg)				
	Adjust pH (9-12), M7 only? (✓)				
	Seal and mark liquid level? (✓)				
	Label container ? (✓)				
	Sample Volume, $V_{sc}$ (mL)				

$$V_{sc} = 17.64 (V_f - V_a) \left[ \frac{P_f}{T_f} - \frac{P_i}{T_i} \right]$$
 Add 460 to  $t_f$  and  $t_i$  to obtain  $T_f$  and  $T_i$ , respectively.

**Post-test Calibrations**

Attach FDS 2d for pressure, barometric pressure, and temperature post-test checks (temperature  $\leq \pm 2^\circ\text{F}$ ).

**QA/QC Check**

Completeness \_\_\_\_\_ Legibility \_\_\_\_\_ Accuracy \_\_\_\_\_ Specifications \_\_\_\_\_ Reasonableness \_\_\_\_\_

Checked by: \_\_\_\_\_ Personnel (Signature/Date) \_\_\_\_\_ Team Leader (Signature/Date) \_\_\_\_\_

**LABORATORY PROCEDURE 7**  
**Nitrogen Oxides**

**A. Reagent Preparation**

1. Hydrogen Peroxide, 3%. Dilute 30% H<sub>2</sub>O<sub>2</sub> 1:9 with deionized distilled water. Prepare fresh daily.
2. Absorbing Solution. Cautiously add 2.8 mL conc. H<sub>2</sub>SO<sub>4</sub> to 1 L of deionized distilled water. Mix well, and add 6 mL 3% H<sub>2</sub>O<sub>2</sub>. Use within 1 week of preparation. Do not expose to extreme heat or direct sunlight.
3. Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in deionized distilled water, and dilute to 1 L.
4. Potassium Nitrate Standard. Dry KNO<sub>3</sub> at 105 to 110°C for at least 2 hr just before preparation. Dissolve exactly 2.198 g dried KNO<sub>3</sub> in deionized distilled water, and dilute to 1 L with deionized distilled water in a 1000-mL volumetric flask.
5. Working Standard KNO<sub>3</sub> Solution, 100 µg NO<sub>2</sub>/mL. Dilute 10 mL standard solution to 100 mL with deionized distilled water.
6. Phenoldisulfonic Acid Solution. Dissolve 25 g pure white phenol solid in 150 mL conc. H<sub>2</sub>SO<sub>4</sub> on a steam bath. Cool, add 25 mL fuming H<sub>2</sub>SO<sub>4</sub> (15 to 18% by weight free sulfur trioxide - HANDLE WITH CAUTION), and heat at 100°C for 2 hr. Store in a dark, stoppered bottle.
7. QA Audit Samples. Obtain from EPA (see QA 1).

**B. Spectrophotometer Calibration Factor K<sub>c</sub>**

1. Calibrate the wavelength scale of the spectrophotometer, if not done within the past six months. (See CP 7a).
2. Add 0.0 mL, 2.0 mL, 4.0 mL, 6.0 mL, and 8.0 mL of the KNO<sub>3</sub> working standard solution (1 mL = 100 µg NO<sub>2</sub>) to a series of five 50-mL volumetric flasks.
3. To each flask, add 25 mL of absorbing solution, 10 mL deionized distilled water, and 1 N NaOH dropwise until the pH is between 9 and 12 (about 25 to 35 drops each).
4. Dilute to the mark with deionized distilled water, and mix thoroughly.
5. Pipette a 25-mL aliquot of each solution into a separate porcelain evaporating dish.
6. Follow steps D6 through D13.
7. Measure the absorbance of each solution, at 410 nm or the wavelength determined in CP 7a.
8. Repeat this calibration procedure on each day that samples are analyzed.

9. Calculate the spectrophotometer calibration factor K<sub>c</sub>.

**C. Spectrophotometer Calibration Quality Control**

1. Multiply the absorbance value obtained for each standard by the K<sub>c</sub> factor (least squares slope) to determine the distance each calibration point lies from the theoretical calibration line.
2. These calculated concentration values should not differ from the actual concentrations (i.e., 100, 200, 300, and 400 µg NO<sub>2</sub>) > 7% for three of the four standards.

**D. Analysis**

1. Note the level of the liquid in the sample containers, and determine loss; note this loss, if any, on the analytical data sheet.
2. Immediately prior to analysis, transfer the contents of the shipping container to a 50-mL volumetric flask, and rinse the container twice with 5-mL portions of deionized distilled water.
3. Add the rinse water to the flask, and dilute to mark with deionized distilled water; mix thoroughly.
4. Pipette a 25-mL aliquot into the porcelain evaporating dish.
5. Return any unused portion of the sample to the polyethylene storage bottle.
6. Evaporate the 25-mL aliquot to dryness on a steam bath, and allow to cool.
7. Add 2 mL phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Ensure the solution contacts all the residue.
8. Add 1 mL deionized distilled water and 4 drops of conc. sulfuric acid. Heat the solution on a steam bath for 3 min with occasional stirring. Allow the solution to cool.
9. Add 20 mL deionized distilled water, mix well by stirring. Add conc. ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper).
10. If the sample contains solids, filter as follows (centrifuging may also be used):
  - a. Filter through Whatman No. 41 filter paper into a 100-mL volumetric flask.
  - b. Rinse the evaporating dish with three 5-mL portions of deionized distilled water.
  - c. Filter these three rinses.

- d. Wash the filter with at least three 15-mL portions of deionized distilled water.
  - e. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with deionized distilled water.
  - f. If solids are absent, transfer the solution directly to the 100-mL volumetric flask and dilute to the mark with deionized distilled water.
11. Mix the contents of the flask thoroughly, and measure the absorbance at the wavelength used for the standards, using the blank solution as a zero reference.
  12. Dilute the sample and the blank with equal volumes of deionized distilled water if the absorbance exceeds  $A_4$ , the absorbance of the 400- $\mu\text{g}$   $\text{NO}_2$  standard.
  13. Concurrently analyze the two audit samples and a set of compliance samples, if applicable, in the same manner as the samples.



**CALIBRATION PROCEDURE 7**  
**Evacuated Flask**

1. Assemble the flask and flask valve, and fill with deionized distilled water to the stopcock. A hypodermic syringe may be helpful.
2. Measure the volume of water to  $\pm 10$  mL, using a 500-mL glass (Class A) graduated cylinder.
3. Make duplicate runs and average the volumes.
4. Record this average volume on the flask.
5. If flask valves are not switched, this calibration is required once.



**CALIBRATION PROCEDURE 7a**  
**Spectrophotometer Calibration**

*Note: Recalibrate the wavelength scale of the spectrophotometer every 6 months as follows:*

**A. Calibration Check**

1. Use an energy source with an intense line emission such as a mercury lamp, or use a series of glass filters spanning the measuring range of the spectrophotometer, to check the calibration of the spectrophotometer. Follow the manufacturer's recommended procedures.
2. The wavelength scale of the spectrophotometer must agree to within  $\pm 5$  nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Use 410 nm for all measurements of the standards and samples.

**B. Alternative Calibration Check**

1. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200  $\mu\text{g}$   $\text{NO}_2$  standard solution in the sample cell and a blank solution in the reference cell. If no peak occurs, the spectrophotometer is probably malfunctioning; repair it. When a peak is within the 400 to 415 nm range, use the wavelength at which this peak occurs for the measurement of absorbance of both the standards and the samples.
2. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. For the measurements of samples, use the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

**CALIBRATION DATA SHEET 7b**  
**Spectrophotometer**  
**(Alternative Procedure)**

Spectrophotometer ID# \_\_\_\_\_

Date \_\_\_\_\_

Personnel \_\_\_\_\_

Date of Prev. Cal. \_\_\_\_\_  
 (≤ 6 months between calibrations?)

*This data sheet is designed for a single-beam spectrophotometer. For a double-beam spectrophotometer, fill in the second column only.*

Spectrophotometer setting (nm)	Absorbance of 200 $\mu\text{g}$ $\text{NO}_2$ Standard (OD)	Absorbance of blank (OD)	Actual Absorbance of Standard (OD)
399			
400			
401			
402			
403			
404			
405			
406			
407			
408			
409			
410			
411			
412			
413			
414			
415			
416			

\_\_\_ Circle the wavelength at which the maximum peak absorbance (last column for single-beam and second column for double-beam) occurs.

\_\_\_ If there is no peak absorbance, repair or recalibrate the spectrophotometer.

**QA/QC Check**

Completeness \_\_\_ Legibility \_\_\_ Accuracy \_\_\_ Specifications \_\_\_ Reasonableness \_\_\_

Checked by: \_\_\_\_\_

Personnel (Signature/Date)

\_\_\_\_\_

Team Leader (Signature/Date)

**SUMMARY SHEET 7A**  
**Nitrogen Oxides**

		Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 7			
Job No.		FDS 7			
Sampling Location		FDS 7			
Run ID#		FDS 7			
Test Date		FDS 7			
Run Start Time		FDS 7			
Run Finish Time		FDS 7			
Traverse Points (if applicable)		FDS 7			
Initial Temperature, °F	$t_i$	FDS 7			
Initial Absolute Temperature, R	$T_i$	SS 7			
Final Temperature, °F	$t_f$	FDS 7			
Final Absolute Temperature, R	$T_f$	SS 7			
Initial Barometric Pressure, in. Hg	$P_{bi}$	FDS 7			
Initial Vacuum, in. Hg	$P_{gi}$	FDS 7			
Initial Absolute Pressure, in. Hg	$P_i$	SS 7			
Final Barometric Pressure, in. Hg	$P_{bf}$	FDS 7			
Final Vacuum, in. Hg	$P_{gf}$	FDS 7			
Final Absolute Pressure, in. Hg	$P_f$	SS 7			
Flask Volume, mL	$V_f$	CDS 7			
Volume Absorbing Reagent, mL	$V_a$	FDS 7			
Gas Sample Volume, mL	$V_{sc}$	SS 7			
Chromatographic Calibration Factor	S	LDS 7A			
Sample Solution Volume, mL		LDS 7A			
Average NO <sub>2</sub> Per Sample, µg	m	LDS 7A			
Sample Concentration, lb/dscf	C	SS 7A			
Audit Relative Error, %	RE	QA1			
Post-test Calibration Checks					
Temperature, Barometer, Vacuum Gauge		CDS 2d			

$$C = 6.242 \times 10^{-5} \frac{m}{V_{sc}}$$

**LABORATORY PROCEDURE 7A**  
**Nitrogen Oxides (Ion Chromatographic Method)**

**A. Reagent Preparation**

1. Stock Standard Solution, 1 mg NO<sub>2</sub>/mL. Dry NaNO<sub>3</sub> at 105 to 110°C for ≥2 hr just before preparing the standard solution. Dissolve exactly 1.847 g dried NaNO<sub>3</sub> in deionized distilled water, and dilute to 1 L in a volumetric flask. Mix well. Date this solution. Do not use after 1 month.
2. Working Standard Solution, 25 µg/mL. Dilute 5 mL of the standard solution to 200 mL with deionized distilled water in a volumetric flask, and mix well.
3. Eluent Solution, 0.0024 M Na<sub>2</sub>CO<sub>3</sub>/0.003 M NaHCO<sub>3</sub>. Weigh 1.018 g Na<sub>2</sub>CO<sub>3</sub> and 1.008 g NaHCO<sub>3</sub>, and dissolve in 4 L deionized distilled water. Other eluents appropriate to the column type may be used.
4. Quality Assurance Audit Samples. Obtain from EPA (see QA 1).

**B. Sample, Standards, and Chromatograph Preparations**

1. Analyze samples within 4 days after collection.
2. Note the level of the liquid in the container, and determine loss; note this loss, if any, on the laboratory data sheet.
3. Immediately before analysis, transfer the contents of the shipping container to a 50-mL volumetric flask, and rinse the container twice with 5-mL portions of deionized distilled water. Add the rinse water to the flask, and dilute to the mark with deionized distilled water. Mix thoroughly.
4. Pipet a 5-mL aliquot of the sample into a 50-mL volumetric flask, and dilute to the mark with deionized distilled water. Mix thoroughly. For each set of determinations, prepare a reagent blank by diluting 5 mL of absorbing solution to 50 mL with deionized distilled water. (Alternatively, eluent solution may be used in all sample, standard, and blank dilutions.)
5. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 mL of working standard solution (25 µg/mL) to a series of five 50-mL volumetric flasks. (Masses are 25, 50, 100, 150, and 250 µg.) Dilute each flask to volume with deionized distilled water, and mix well.
6. Calibrate the conductivity detector according to manufacturer's specifications prior to initial use.

**C. Analysis**

1. Inject the calibration standards.
2. Inject samples and a blank, using same injection volumes as that of the standards.
3. Inject another set of calibration standards.
4. Repeat step C2 with a duplicate set of samples and blank.
5. Inject a final set of calibration standards.
6. Analyze the audit samples, if applicable.
7. Determine peak heights (if symmetrical) or, in all other cases, peak areas. Determine the averages.
8. Prepare or calculate a linear regression plot of the standards in µg (x-axis) versus their peak heights or areas. Determine the slope, and its reciprocal. If any point deviates from the line by more than 7% of the concentration, remake and reanalyze. (See LDS 7A).
9. Perform all analyses on the same day. Dilute any sample and the blank with equal volumes of deionized distilled water if the concentration exceeds that of the highest standard.
10. Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed. (See LDS 7A).



**SUMMARY SHEET 7B**  
**Nitrogen Oxides**

			Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 7				
Job No.		FDS 7				
Sampling Location		FDS 7				
Run ID#		FDS 7				
Test Date		FDS 7				
Run Start Time		FDS 7				
Run Finish Time		FDS 7				
Traverse Points (if applicable)		FDS 7				
Initial Temperature, °F	t <sub>i</sub>	FDS 7				
Initial Absolute Temperature, R	T <sub>i</sub>	SS 7				
Final Temperature, °F	t <sub>f</sub>	FDS 7				
Final Absolute Temperature, R	T <sub>f</sub>	SS 7				
Initial Barometric Pressure, in. Hg	P <sub>bi</sub>	FDS 7				
Initial Vacuum, in. Hg	P <sub>gi</sub>	FDS 7				
Initial Absolute Pressure, in. Hg	P <sub>i</sub>	SS 7				
Final Barometric Pressure, in. Hg	P <sub>bf</sub>	FDS 7				
Final Vacuum, in. Hg	P <sub>gf</sub>	FDS 7				
Final Absolute Pressure, in. Hg	P <sub>f</sub>	SS 7				
Flask Volume, mL	V <sub>f</sub>	CDS 7				
Volume Absorbing Reagent, mL	V <sub>a</sub>	FDS 7				
Gas Sample Volume, mL	V <sub>sc</sub>	SS 7				
Spectrophotometer Calibration Factor	K <sub>c</sub>	LDS 7B				
Sample Solution Volume, mL		LDS 7B				
Average NO <sub>2</sub> Per Sample, µg	m	LDS 7B				
Sample Concentration, lb/dscf	C	SS 7B				
Audit Relative Error, %	RE	QA1				
Post-test Calibration Checks						
Temperature, Barometer, Vacuum Gauge		CDS 2d				

$$C = 6.242 \times 10^{-5} \frac{m}{V_{sc}}$$

**LABORATORY PROCEDURE 7B**  
**Nitrogen Oxides**  
**(Ultraviolet Spectrophotometry)**

*Note: This procedure is similar to that of Method 7, except for the following:*

**A. Reagent Preparation**

1. Working Standard  $\text{KNO}_3$  Solution, 10  $\mu\text{g NO}_2/\text{mL}$ . Dilute 10 mL of the standard solution to 1000 mL with deionized distilled water.
2. Quality Assurance Audit Samples. Obtain from EPA (see QA 1).

**B. Determination of Spectrophotometer Standard Curve**

1. Add 0.0 mL, 5 mL, 10 mL, 15 mL, and 20 mL  $\text{KNO}_3$  working standard solution to a series of five 100-mL volumetric flasks.
2. To each flask, add 5 mL absorbing solution. Dilute to the mark with deionized distilled water. The resulting solutions contain 0.0, 50, 100, 150, and 200  $\mu\text{g NO}_2$ , respectively.
3. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference.

4. Plot absorbance vs.  $\mu\text{g NO}_2$ . Calculate the spectrophotometer calibration factor. (See LDS 7B).

**C. Analysis**

1. Pipette a 20-mL aliquot of sample into a 100-mL volumetric flask. If other than 20-mL is used, adjust standards and blank solutions accordingly.
2. Dilute to 100 mL with deionized distilled water.
3. Analyze the sample on the ultraviolet spectrophotometry at 210 nm, using the blank as zero reference.
4. With each set of compliance samples or once per analysis day, or once per week when averaging continuous samples, analyze each performance audit in the same manner as the sample to evaluate the analyst's technique and standard preparation. (See QA 1).



**SUMMARY SHEET 7C**  
**Nitrogen Oxides**

		Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 6/7C			
Job No.		FDS 6/7C			
Sampling Location		FDS 6/7C			
Run ID#		FDS 6/7C			
Test Date		FDS 6/7C			
Run Start Time		FDS 6/7C			
Run Finish Time		FDS 1			
Traverse Points (if applicable)					
Net Run Time, min	$\theta$	FDS 6/7C			
Dry Gas Meter Calibration Factor	Y	FDS 6/7C			
Barometric Pressure, in. Hg	$P_b$	FDS 6/7C			
Average DGM Temperature, °F	$t_m$	FDS 6/7C			
Absolute Average DGM Temperature, R	$T_m$	FDS 6/7C			
Average CO <sub>2</sub> , %	%CO <sub>2</sub>	FDS 7C			
Correction Factor for CO <sub>2</sub>	X	SS 7C			
Volume of Metered Gas Sample, dcf	$V_m$	FDS 6/7C			
Volume of Metered Gas Sample, dscf	$V_{m(std)}$	SS 6			
Spectrophotometer Calibration Factor	$K_c$	LDS 7C			
Average NO <sub>2</sub> Per Sample, µg	m	LDS 7C			
Sample Concentration, lb/dscf	C	SS 7C			
Audit Relative Error, %	RE	QA1			
Post-test Calibration Checks					
Temperature and Barometer		CDS 2d			
Metering System		CDS 6			

$$X = \frac{100}{(100 - \%CO_2)}$$

$$V_{m(std)} = 17.64 V_m X Y \frac{P_b}{T_m}$$

$$C = 6.242 \times 10^{-5} \frac{m}{V_{m(std)}}$$

**FIELD PROCEDURE 7C**  
**Nitrogen Oxides (Alkaline-Permanganate)**

**A. Pre-test Preparation**

1. Prepare the collection train as follows:
  - a. Add 200 mL  $\text{KMnO}_4/\text{NaOH}$  solution to each of three impingers.
  - b. Assemble the train as shown in Figure F7C-1.
  - c. Adjust probe heater to a temperature sufficient to prevent water condensation.
2. Determine the sampling point or points.
3. *Optional:* Leak-check the sampling train (see FP 3c, sections C and D).
4. *Optional:* Check of rotameter calibration accuracy as follows:
  - a. Disconnect the probe from the first impinger, and connect the filter.
  - b. Start the pump, and adjust the rotameter to read between 400 and 500 cc/min.
  - c. After the flow rate has stabilized, measure the volume sampled from the DGM and the sampling time. Collect enough volume to measure accurately the flow rate, and calculate the flow rate (must be <500 cc/min for the sample to be valid).

**B. Sampling**

1. Record the initial DGM reading and barometric pressure. Use FDS 6 and attach FDS 7C.
2. Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to between 400 and 500 cc/min.
3. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 min.
4. Record the DGM temperature, and check the flow rate at least every 5 min.

5. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings.
6. Divide the sample volume by the sampling time to determine the average flow rate (must be <500 cc/min).
7. *Mandatory:* Leak-check the sampling train (see FP 3c, sections C and D).
8. During sampling, use Method 3 (Orsat or Fyrite) to measure  $\text{CO}_2$  of the stack gas near the sampling point. If single-point grab sampling procedure is used, conduct measurements at least three times (near the start, midway, and before the end of a run), and the average  $\text{CO}_2$  concentration.

**C. Sample Recovery**

1. Disconnect the impingers. Pour the contents of the impingers into a 1 L polyethylene bottle using a funnel and a stirring rod (or other means) to prevent spillage.
2. Rinse the impingers and connecting tubes with deionized distilled water until the rinsings are clear to light pink, and add the rinsings to the bottle.
3. Mix the sample, and mark the solution level. Seal and identify the sample container.

**D. Post-test Calibrations**

Conduct post-test calibrations of metering system and temperature gauges. (See FP 2d and CP 6).

**E. Special Considerations**

1. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hr, sampling 20 min at each traverse point.
2. For RA tests with  $\text{SO}_2 \geq 1200$  ppm, sample for 30 min (10 min at each point).

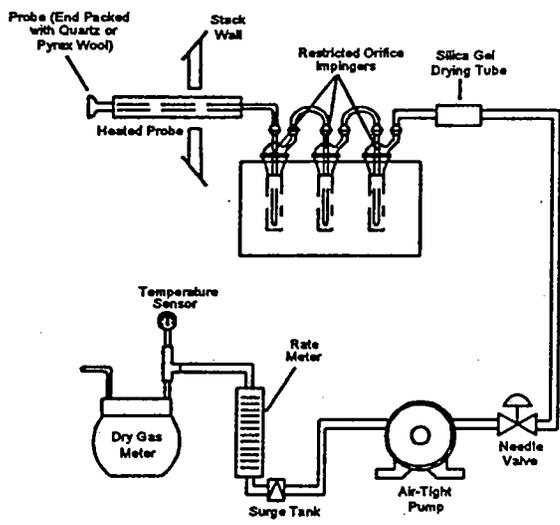


Figure F7C-1. NO<sub>x</sub> Sampling Train.

**FIELD DATA SHEET 7C**  
**Nitrogen Oxides (Alkaline Permanganate)**

Client/Plant Name \_\_\_\_\_ Job # \_\_\_\_\_

Test Location/Run # \_\_\_\_\_ Personnel \_\_\_\_\_

Use FDS 6 and attach this data sheet. For CO<sub>2</sub> (integrated sample), use FDS 3 and attach to FDS 6.

Continuation sheet of FDS 6 for FDS 7C

Trav. Pt.	Samplg time (min)	DGM Rdg (cf)	Rotameter Rdg (cc/min)	Temperature (°F)		Flow Rate Deviation	
				DGM	Imp. Exit	$\Delta V_m$	$\Delta V_m / \Delta \bar{V}_m$
	Total Time, $\theta_s$	Volume, $V_m$	Avg	Avg, $t_m$	Max $\leq 68^\circ\text{F}$ ?	Avg	0.90 - 1.10?

For Fyrite, single point analysis, fill in information in table.

Fyrite, Single Point Grab Sampling			
Run #	Clock Time		%CO <sub>2</sub>
1	Beginning		
2	Midway		
3	Ending		
Average:			

\_\_\_\_\_ Flow Rate  $\leq 500$  cc/min?

*If Relative Accuracy test of CEMS:*

\_\_\_\_\_ Sampling time of 1 hr, 20 min/point?

\_\_\_\_\_ SO<sub>2</sub>  $\geq 1200$  ppm? Run for 30 min, 10 min/point.

**QA/QC Check**

Completeness \_\_\_\_\_ Legibility \_\_\_\_\_ Accuracy \_\_\_\_\_ Specifications \_\_\_\_\_ Reasonableness \_\_\_\_\_

Checked by: \_\_\_\_\_ Personnel (Signature/Date) \_\_\_\_\_ Team Leader (Signature/Date) \_\_\_\_\_

**LABORATORY PROCEDURE 7C**  
**Nitrogen Oxides**

**A. Reagent Preparation**

1. Potassium Permanganate, 4.0%, Sodium Hydroxide, 2.0%. Dissolve 40.0 g  $\text{KMnO}_4$  and 20.0 g NaOH in 940 mL water.
2. Oxalic Acid Solution. Dissolve 48 g  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  in water, and dilute to 500 mL. Do not heat.
3. Sodium Hydroxide, 0.5 N. Dissolve 20 g NaOH in water, and dilute to 1 L.
4. Sodium Hydroxide, 10 N. Dissolve 40 g NaOH in water, and dilute to 100 mL.
5. Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5%. Dissolve (using a magnetic stirrer) 6.5 g EDTA (disodium salt) in water, and dilute to 100 mL.
6. Column Rinse Solution. Add 20 mL 6.5% EDTA solution to 960 mL water, and adjust the pH to 11.7 to 12.0 with 0.5 N NaOH.
7. Hydrochloric Acid (HCl), 2 N. Add 86 mL conc. HCl to a 500-mL volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.
8. Sulfanilamide Solution. Add 20 g sulfanilamide (melting point 165 to 167°C) to 700 mL water. Add, with mixing, 50 mL conc. phosphoric acid (85%), and dilute to 1 L. Refrigerate. Do not use after 1 month.
9. N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g NEDA in 500 mL water. Use only if this aqueous solution has an absorption peak at 320 nm over the range of 260 to 400 nm. Protect from sunlight and refrigerate. Do not use after 1 month.
10. Cadmium. See Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalogue No. 2001. Prepare (in an exhaust hood away from flame as  $\text{H}_2$  is liberated) by rinsing in 2 N HCl for 5 min until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper.
11.  $\text{NaNO}_2$  Standard Solution, Nominal Concentration, 1000  $\mu\text{g NO}_2^-/\text{mL}$ . Desiccate  $\text{NaNO}_2$  overnight. Accurately weigh 1.4 to 1.6 g  $\text{NaNO}_2$  (assay of 97%  $\text{NaNO}_2$  or greater), dissolve in water, and dilute to 1 L. Calculate the exact  $\text{NO}_2^-$  concentration. Do not use after 6 months.
12.  $\text{KNO}_3$  Standard Solution. Dry  $\text{KNO}_3$  at 110°C for 2 hr, and cool in a desiccator. Accurately weigh 9 to 10 g  $\text{KNO}_3$  to within

0.1 mg, dissolve in water, and dilute to 1 L. Calculate the exact  $\text{NO}_3^-$  concentration. Do not use after 2 months.

13. Spiking Solution. Pipette 7 mL  $\text{KNO}_3$  standard into a 100-mL volumetric flask, and dilute to volume.
14. Blank Solution. Dissolve 2.4 g  $\text{KMnO}_4$  and 1.2 g NaOH in 96 mL water. Alternatively, dilute 60 mL  $\text{KMnO}_4/\text{NaOH}$  solution to 100 mL.
15. Quality Assurance Audit Samples. Obtain from EPA (see QA 1).

**B. Calibration Curve for Spectrophotometer**

1. Dilute 5.0 mL  $\text{NaNO}_2$  standard solution to 200 mL with water to obtain nominally 25  $\mu\text{g NO}_2^-/\text{mL}$ . Using pipettes, prepare at least three calibration standards each for the linear and slightly nonlinear curve to cover the range of 0.25 to 3.00  $\mu\text{g NO}_2^-/\text{mL}$ .
2. Analyze the standards and a water blank.
3. Plot the net absorbance vs.  $\mu\text{g NO}_2^-/\text{mL}$ . Draw a smooth curve through the points and the origin. The curve should be linear from zero up to an absorbance of about 1.2 with a slope of about 0.53 absorbance units/ $\mu\text{g NO}_2^-/\text{mL}$ . The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

**C. Sample Preparation**

1. Prepare a cadmium reduction column as follows:
  - a. Fill the burette with water. Add freshly prepared cadmium slowly with tapping until no further settling occurs. Final height of the cadmium column should be 39 cm. Do not use cadmium (e.g., regenerated) that causes a band of cadmium fines.
  - b. When not in use, store the column under rinse solution (A6).
2. Note the level of liquid in the sample container, and determine loss; note this loss, if any, on the laboratory data sheet.
3. Quantitatively transfer the contents to a 1 L volumetric flask, and dilute to volume.
4. Take a 100-mL aliquot of the sample and blank (unexposed  $\text{KMnO}_4/\text{NaOH}$ ) solutions, and transfer to 400-mL beakers containing magnetic stirring bars.
5. Using a pH meter, add conc.  $\text{H}_2\text{SO}_4$  with stirring until a pH of 0.7 is obtained.

6. Allow the solutions to stand for 15 min.
7. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50°C. Keep <60°C.
8. Dissolve 4.8 g oxalic acid in a minimum (about 50 mL) volume of water at room temperature. Do not heat the solution.
9. Slowly add oxalic acid solution to the  $\text{KMnO}_4$  until it becomes colorless. If the color is not completely removed, prepare more of the oxalic acid solution, and add until a colorless solution is obtained.
10. Add an excess of oxalic acid by dissolving 1.6 g oxalic acid in 50 mL water, and add 6 mL to the colorless solution.
11. If suspended matter is present, add conc.  $\text{H}_2\text{SO}_4$  until a clear solution is obtained.
12. Allow samples to cool to room temperature, and ensure samples remain clear.
13. Adjust the pH to 11.7 to 12.0 with 10 N NaOH.
14. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. Filter the mixture into a 500-mL filtering flask. Wash the solid material four times with water.
15. When filtration is complete, wash the Teflon tubing, transfer the filtrate to a 500-mL volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction.
16. Pipette a 50-mL aliquot of the sample into a 150-mL beaker, and add a magnetic stirring bar.
17. Pipette in 1.0 mL 6.5% EDTA solution, and mix.
18. Set stopcock to establish a flow rate of 7 to 9 mL/min of column rinse solution through the cadmium reduction column. Use a 50-mL graduated cylinder to collect and measure the solution volume.
19. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, add sample, and collect it in a 250-mL graduated cylinder.
20. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 mL column rinse solution, and collect the rinse solution until the solution just disappears from the funnel.
21. Quantitatively transfer the sample to a 200-mL volumetric flask (250-mL may be required), and dilute to volume. The samples and blank are now ready for  $\text{NO}_2^-$  analysis.
22. Run two spiked samples with every group of samples passed through the column.
  - a. Prepare spiked samples by taking 50-mL aliquots of the sample suspected to have the highest  $\text{NO}_2^-$  concentration, and adding 1 mL spiking solution.
  - b. Calculate spike recovery and column efficiency. If either is <95%, prepare a new column, and repeat the cadmium reduction.

#### D. Analysis

1. Pipette 10 mL sample into a culture tube. Do not use test tubes, unless it has a low blank  $\text{NO}_2^-$  value.
2. Pipette in 10 mL sulfanilamide solution and 1.4 mL NEDA solution.
3. Cover the culture tube with parafilm, and mix the solution.
4. Prepare a blank in the same manner using the sample from treatment of the unexposed  $\text{KMnO}_4/\text{NaOH}$  solution (A1).
5. Prepare a calibration standard to check the slope of the calibration curve.
6. After a 10-min color development interval, measure the absorbance at 540 nm against water.
7. Read  $\mu\text{g NO}_2^-/\text{mL}$  from the calibration curve. If the absorbance is greater than that of the highest calibration standard, pipette less than 10 mL, and repeat the analysis.
8. Determine the  $\text{NO}_2^-$  concentration using the calibration curve obtained in B3.
9. Analyze the audit samples, if applicable.



**SUMMARY SHEET 7D**  
**Nitrogen Oxides**

		Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 6/7C			
Job No.		FDS 6/7C			
Sampling Location		FDS 6/7C			
Run ID#		FDS 6/7C			
Test Date		FDS 6/7C			
Run Start Time		FDS 6/7C			
Run Finish Time		FDS 1			
Traverse Points (if applicable)					
Net Run Time, min	$\theta$	FDS 6/7C			
Dry Gas Meter Calibration Factor	Y	FDS 6/7C			
Barometric Pressure, in. Hg	$P_b$	FDS 6/7C			
Average DGM Temperature, °F	$t_m$	FDS 6/7C			
Absolute Average DGM Temperature, R	$T_m$	FDS 6/7C			
Average CO <sub>2</sub> , %	%CO <sub>2</sub>	FDS 7C			
Correction Factor for CO <sub>2</sub>	X	SS 7C			
Volume of Metered Gas Sample, dcf	$V_m$	FDS 6/7C			
Volume of Metered Gas Sample, dscf	$V_{m(std)}$	SS 7C			
Average NO <sub>2</sub> Per Sample, µg	m	LDS 7D			
Sample Concentration, lb/dscf	C	SS 7D			
Audit Relative Error, %	RE	QA1			
Post-test Calibration Checks					
Temperature and Barometer		CDS 2d			
Metering System		CDS 6			

$$C = 6.242 \times 10^{-5} \frac{m}{V_{m(std)}}$$

**LABORATORY PROCEDURE 7D**  
**Nitrogen Oxide**

**A. Reagent Preparation**

1. The following are the same as that in LP 7C:
  - a. Potassium Permanganate, 4.0%, Sodium Hydroxide, 2.0% (A1).
  - b. Standard Potassium Nitrate (A12).
  - c. Blank Solution (A14).
2. Hydrogen Peroxide, 5%. Dilute 30% H<sub>2</sub>O<sub>2</sub> 1:5 (v/v) with water.
3. Eluent, 0.003 M NaHCO<sub>3</sub>/0.0024 M Na<sub>2</sub>CO<sub>3</sub>. Dissolve 1.008 g NaHCO<sub>3</sub> and 1.018 g Na<sub>2</sub>CO<sub>3</sub> in water, and dilute to 4 L. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.
4. Quality Assurance Audit Samples. Obtain from EPA (see QA 1).

**B. Calibration Curve for Ion Chromatograph.**

1. Dilute a given volume (1.0 mL or greater) of the KNO<sub>3</sub> standard solution to a known volume with water.
2. With the KNO<sub>3</sub> solution prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions.
3. Prepare the chromatograph and set the conditions to operate properly.
4. Analyze standards according to section D.
5. Determine peak height or area, and plot the individual values versus concentration in μg NO<sub>3</sub><sup>-</sup>/mL. Do not force the curve through zero. Draw a smooth curve through the points. Use linear regression to determine the calibration equation.

**C. Sample Preparation**

1. Note the level of liquid in the sample container, and determine loss; note this loss, if any, on the laboratory data sheet.
2. Quantitatively transfer the contents to a 1 L volumetric flask, and dilute to volume.
3. Prepare samples 36 hr after collection to ensure that all NO<sub>2</sub><sup>-</sup> is converted to NO<sub>3</sub><sup>-</sup>.

4. Take a 50-mL aliquot of the sample and blank, and transfer to 250-mL Erlenmeyer flasks. Add a magnetic stirring bar. Stir as fast as possible without loss of solution.
5. Using a 5-mL pipette, add 5% H<sub>2</sub>O<sub>2</sub>.
6. When the KMnO<sub>4</sub> color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the KMnO<sub>4</sub> color persists, add more H<sub>2</sub>O<sub>2</sub>, with stirring, until the supernatant liquid is clear. The faster the stirring rate, the less volume of H<sub>2</sub>O<sub>2</sub> required to remove the KMnO<sub>4</sub>.
7. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter. Filter the mixture into a 500 mL filtering flask. Wash the solid material four times with water.
8. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-mL volumetric flask, and dilute to volume. Analyze the samples and blank.

**D. Analysis**

1. Establish a stable baseline.
2. Inject a sample of water, and determine whether any NO<sub>3</sub><sup>-</sup> appears in the chromatogram.
3. If NO<sub>3</sub><sup>-</sup> is present, repeat the water load/injection procedure approximately five times; then re-inject a water sample, and observe the chromatogram.
4. When no NO<sub>3</sub><sup>-</sup> is present, the instrument is ready for use.
5. Inject calibration standards.
6. Inject samples and a blank.
7. Repeat the calibration standards injection (to compensate for any drift in response of the instrument).
8. Measure the NO<sub>3</sub><sup>-</sup> peak height or peak area, and determine the sample concentration from the calibration curve.
9. Analyze the audit samples, if applicable.



**FIELD PROCEDURE 7E**  
**Nitrogen Oxides**  
**(Instrumental Analyzer Procedure)**

**Note:** The procedure for FP 7E is essentially the same as that for FP 6C, except for the obvious differences due to the gases being analyzed and the detection device. The analyzer must be based on the principles of chemiluminescence. Follow FP 6C, except for the following:

1. Obtain calibration gases (NO in N<sub>2</sub>). Ambient air may be used for the zero gas.
2. For non-Protocol 1 calibration gases, Method 7 is the reference method and the acceptance criterion is  $\pm 10\%$  or 10 ppm, whichever is greater. See CDS 6Ca.
3. Initially and whenever changes are made in the instrumentation that could alter the interference response (e.g., changes in the gas detector), conduct the interference response test according to FP 20, step B3.
4. If the NO<sub>2</sub> concentration within the sample stream is  $> 5\%$  of the NO<sub>x</sub> concentration, conduct an NO<sub>2</sub> to NO conversion efficiency test according to FP 20, step B5.
5. Select a measurement site and sampling points using the same criteria that are applicable to tests performed using Method 7.
6. Run for the same sampling duration per run as that used for Method 7 plus twice the stable response time for the instrument.

**LABORATORY DATA SHEET 7E**  
Interference Response

Date \_\_\_\_\_ Personnel \_\_\_\_\_

Analyzer Type \_\_\_\_\_ Analyzer ID# \_\_\_\_\_

Test Gas	Nominal Concentration	Actual Concentration	Analyzer Response	% of Span
<b>Method 20</b>		<b>Span Value:</b>		
CO	500 ± 50 ppm			
SO <sub>2</sub>	200 ± 20 ppm			
CO <sub>2</sub>	10 ± 1 %			
O <sub>2</sub>	20.9 ± 1%			
<b>Method:</b>		<b>Span Value:</b>		

$$\% \text{ of Span} = \frac{\text{Analyzer Response}}{\text{Instrument Span}} \times 100$$

\_\_\_\_\_ Sum of the interference responses to the test gas for either the NO<sub>x</sub> or diluent analyzer <2% of span value?

**NO<sub>2</sub>-NO Converter Efficiency**

Peak response recorded during test \_\_\_\_\_

Response recorded at end of 30 minutes \_\_\_\_\_ (Attach strip chart or recorder readout)

% Decrease from peak response \_\_\_\_\_ (≤2%?)

**QA/QC Check**

Completeness \_\_\_\_\_ Legibility \_\_\_\_\_ Accuracy \_\_\_\_\_ Specifications \_\_\_\_\_ Reasonableness \_\_\_\_\_

Checked by: \_\_\_\_\_  
Personnel (Signature/Date)
Team Leader (Signature/Date)

