

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 202.1

**DETERMINATION OF PARTICULATE AND GASEOUS CYANIDE
EMISSIONS FROM STATIONARY SOURCES**

**OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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METHOD 202.1

DETERMINATION OF PARTICULATE AND GASEOUS CYANIDE EMISSIONS FROM STATIONARY SOURCES

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1. Overview

1.1 Principle

Particulate and gaseous cyanide emissions are withdrawn isokinetically from the source by a wet impingement train containing 0.1N NaOH solution. The collected sample is analyzed for cyanide (CN^-) using the cyanide-specific ion electrode.

1.2 Applicability

This method is applicable for the determination of cyanides present in the exhaust gases from plating operations, and petroleum refinery operations. Application of this method for other stationary sources needs prior approval from the Executive Officer.

1.3 Range and Sensitivity

The range and sensitivity of this method have not yet been established. The recommended range is 0.2 to 100 mg/m³ of sampled gas.

1.4 Interferences

Sulfide ion irreversibly poisons the cyanide electrode and must be removed if present in the sample. Check for sulfide using lead acetate test paper. Other interfering substances may be present. Their effects are detected by using the standard addition procedure.

1.5 Precision and Accuracy

The precision and accuracy of this method have not been established.

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2. Field Procedures

2.1 Apparatus

A schematic of the sampling train is shown in Figure 202.1-1. It is similar to the Method 5.1 train. The train consists of the following components:

- a. Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Temperature Sensor, Metering System, and Gas Density Determination Equipment. Same as Method 5.1.
- b. Probe and Probe Liner

Stainless steel probe with probe liner made of borosilicate or quartz glass.

c. Impingers

Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first and second impingers are of the standard Greenburg-Smith design with the standard tip. The third and fourth impingers are modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cu (1/2 in.) from the bottom of the flask.

The first and second impingers contain 100 ml of 0.1N NaOH solution. The third impinger is kept empty. The fourth impinger contains a known weight of silica gel or equivalent desiccant. A thermometer capable of measuring temperature to within 1°C (2°F) is placed at the outlet of the fourth impinger to monitor outlet gas temperature.

Instead of using silica gel, the moisture leaving the third impinger can be measured by monitoring the temperature and pressure at the exit of the impinger train and using

Dalton's law of partial pressures. However, the use of silica gel (or equivalent) between impinger system and pump will prevent moisture condensation in the pump and metering device.

Acidic gases, such as SO₂ and CO₂, will expend the NaOH solution. Add extra impingers with NaOH solution, as needed.

d. Filter Holder (Optional)

Borosilicate glass with a rigid stainless steel wire screen filter support (do not use glass frit support) and a silicone rubber or Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter.

2.2 Reagents

Use ACS reagent grade chemicals or equivalent.

a. Water

Deionized, distilled water meeting ASTM specification D1193-77, Type 3. If high

concentrations of organic matter are not expected to be present, the KMnO_4 test may be omitted. Reference to water throughout this method implies deionized, distilled water.

b. Sodium Hydroxide, 0.1N

Dissolve 4.0 g NaOH in water and dilute to 1000 ml. Protect from exposure to air.

c. Silica Gel

Indicating-type; 6 to 16 mesh; fresh, or dried at 175°C (350°F) for 2 hours.

d. Filter (Optional)

Glass fiber filter, without organic binders, exhibiting at least 99.95 percent efficiency on 0.3 μm dioctyl phthalate smoke particles.

e. Crushed Ice or Dry Ice Pellets

2.3 Pretest Determination

Select the sampling site and the minimum number of sampling points according to Method 1.1.

Determine the stack pressure, temperature, and the range of velocity heads using Method 2.1. A leak check of the Pitot lines should be performed (see Method 2.1.)

With glass liners, install the selected nozzle using a Viton A, O-ring. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape to denote the proper distance into the stack for each sample point.

Assemble the train as shown in Figure 202.1-1 using a light coat of stopcock grease on ground glass joints, greasing only the outer portion to avoid possibility of contamination by the grease.

Place crushed ice or dry ice pellets around the impingers.

Determine the moisture content of the stack gas using Method 4.1 or its alternative to make

sampling rate settings. Determine the stack gas dry molecular weight as outlined in Method 3.1.

Select a nozzle size for the range of velocity heads encountered, so that it is not necessary to change the nozzle to maintain isokinetic sampling rates. Do not change the nozzle during the run. Choose the differential pressure gauge for the range of velocity heads encountered.

Select a probe length suitable for sampling all traverse points. For large stacks, consider sampling from opposite sides of the stack (four sampling port holes) to reduce the length of the probe.

Collect sample over a minimum of 2 hours (minimum sample volume of 60 ft³). The sampling time must be an integer plus one-half minute and the same at each point.

2.4 Gas Volume Meter Checks

See Method 5.1, Section 2.4.

2.5 Leak Checks

Follow the procedure described in Method 5.1, Section 2.6.

2.6 Sampling Train Operation

Follow the procedure described in Method 5.1, Section 2.7.

2.7 Calculation of Percent Isokinetic

Calculate percent isokinetic using the equation in Figure 202.1-2 to determine whether the run was valid or another test should be made.

2.8 Sample Handling

Follow the procedure as described in Method 5.1, Section 2.9.

2.9 Calibration

See Chapter III.

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3. Laboratory Procedures

3.1 Apparatus

3.1.1 Sample Collection

A schematic of the sampling train is shown in Figure 202.1-1. For nozzle, probe, probe liner, impinger train, filter holder and filter see Sections 2.1 and 2.2.

3.1.2 Sample Recovery

a. Rinse Bottles

b. Sample Containers

500 ml polyethylene bottles (1000
ml, if necessary).

c. Balance

Capable of weighing to ± 0.5 g.

d. Graduated Cylinder

500 ml (1000 ml, if necessary), with stopper.

e. Nylon Brush

Properly shaped and sized to brush out the probe and nozzle.

3.1.3 Sample Analysis

a. Cyanide Ion Selective Electrode

Orion 94-06, or equivalent.

b. Single Junction Reference Electrode

Orion 90-01, or equivalent.

c. Millivolt/pH Meter

Expanded scale, digital readout.

d. Beakers

150 ml, plastic.

e. Magnetic Stirrer and Stirring Bars

f. Volumetric Pipets

Class A: 1, 2, 3, 4, 5, 10, 20 and
100 ml.

3.2 Reagents

3.2.1 Sample Collection and Recovery

Water, sodium hydroxide 0.1N, silica gel.
See Section 2.2.

3.2.2 Sample Analysis

a. Potassium Cyanide Standards

CAUTION: Do not get on skin or breath
vapors.

Dissolve 0.188 g NaCN or 0.025 g KCN in 0.1N NaOH and dilute to 100 ml with additional 0.1N NaOH for 1000 ppm CN^- (1000 $\mu\text{g/ml}$). This solution should be made on a weekly basis.

All other dilutions should be made fresh daily.

Dilute 10 ml of 1000 ppm CN^- to 100 ml with 0.1N NaOH for 100 ppm CN^- .

Dilute 10 ml of 100 ppm CN^- to 100 ml with 0.1N NaOH for 10 ppm CN^- .

Dilute 10 ml of 10 ppm CN^- to 100 ml with 0.1N NaOH for 1 ppm CN^- .

b. Lead Acetate Paper

c. Cadmium Carbonate

3.3 Preparation of Sampling Train

Place 100 ml of 0.1N NaOH in the first and the second impinger. Leave the third impinger empty.

Place approximately 200 to 300 g of silica gel in the fourth impinger.

If moisture content is to be determined gravimetrically, weigh each impinger plus contents to the nearest 0.5 g and record the weights.

3.4 Sample Recovery

Upon receipt inspect the train for general condition. Note if the silica gel is expended. Note any unusual conditions that may affect results. Recover the sample as follows:

3.4.1 Container No. 1 (Nozzle, Probe Liner, and Impingers)

In a clean area, wipe down the outside of the equipment to prevent contamination of the sample. Weigh each impinger to the nearest 0.5 g and record these weights. This information is used to calculate the moisture content of the effluent gas. The moisture content also may be determined by measuring the increase in impinger solution volume using a graduated

cylinder. Place the impinger contents into a 500 ml graduated cylinder.

Using 0.1N NaOH, rinse each impinger plus all connecting glassware into the cylinder at least three times. Brush rinse the nozzle and probe liner using a Nylon brush and 0.1N NaOH into the same cylinder. Dilute the sample to 500 ml with 0.1N NaOH and mix well. Transfer the sample to a container and seal it well. Mark the level of the liquid and label the container.

Limit the amount of rinse water to the minimum required for quantitative recovery. Check the pH of the solution and add 10N NaOH dropwise to bring the pH to 10-11, if necessary.

3.4.2 Container No. 2 (Impinger Solution as Blank)

Dilute 200 ml of reagent blank to 500 ml with 0.1N NaOH as above. Transfer the blank to container; seal, mark, and label.

3.4.3 Container No. 3 (Silica Gel)

Note the color of the indicating silica gel to determine whether it has been completely expended, and make a notation of the condition. Transfer the silica gel from its impinger to its original container and seal. As aids, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. Weigh the spent silica gel to the nearest 0.5 g and record this weight. Alternatively, weigh silica gel with the impinger.

3.4.4 Container No. 4 (Filter)

If a filter was used, carefully remove it from the filter holder, place it in a 100 ml glass sample bottle and add 20 to 40 ml

0.1N NaOH. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon brush and a sharp-edged blade. Seal the container. Label the container to identify its contents.

3.4.5 Container No. 5 (Filter Blank)

If a filter was used, treat an unused filter from the same lot used for sampling in the same manner as Container No. 4.

3.5 Sample Preparation

Check level of the liquid in each container to ensure that no liquid was lost.

3.5.1 Containers No. 4 and 5

If a filter was used, filter the contents of containers No. 4 and 5 separately through Whatman No. 40 filter paper. Wash these filters three times with 0.1N NaOH

and add to the filtrate. Add the filtrate of Container No. 4 to Container No. 1. Add the filtrate of Container No. 5 to Container No. 2.

3.6 Sample Analysis

Sulfide ion irreversibly poisons the cyanide ion selective electrode and must be removed if present in the sample. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by discoloration of the paper.

Sulfide is removed by the addition of a small amount of powdered cadmium carbonate to the sample. Swirl to disperse the solid, and re-check the liquid with a drop on a piece of lead acetate paper. If sulfide ion is not removed completely, add more cadmium carbonate.

When a drop of liquid no longer discolors a strip of lead acetate paper, remove the solid by filtering through a plug of wool and proceed with the analysis.

3.6.1 Calibration Curve

Check the cyanide electrode response by constructing a calibration curve before proceeding with the analysis. Place the electrode in the 1 ppm standard solution while stirring gently with a magnetic stirrer. Record the stable mv reading. Rinse the electrodes, blot them dry, and continue with the 10 ppm and 100 ppm standards in the same manner. The slope of $\log(\text{conc.})$ vs. mv should be -57 ± 3 mv. If it is not, troubleshoot the system following the manufacturers instructions to correct the problem.

NOTE: Cyanide slowly erodes the membrane of the cyanide electrode. Do not leave the electrode in cyanide solutions longer than necessary to make a reading. Measurements of concentrations greater than 20 ppm should be made only occasionally.

3.6.2 Sample Measurements

Rinse the electrode and blot it dry.

Place it in 100.0 ml of the sample to be measured, while stirring gently. Record the stable mv reading and estimate the cyanide concentration from the calibration curve (see Section 3.6.1). Unless there are specific reasons to think otherwise, assume that the sample contains interfering substances, and proceed with standard addition.

Using the estimate concentration of the sample, double the concentration by adding 10.0 ml of a standard that is approximately ten times as concentrated as the sample. Other concentrations and volumes that provide an equivalent amount of cyanide may be used. Record the exact volume and concentration of the standard added. Allow the solutions to mix thoroughly; record the stable mv reading.

Samples and standards must be at the same temperature.

Measurements of very low cyanide concentrations may be made using one more serial dilution of the standard with plasticware for both the standard and sample. Measure the reagent blank using the same procedure as above.

3.7 Calculations

Calculate the slope of log (conc.) vs. mv. Slope must be -57 ± 3 mv or the analysis is void.

Calculate the concentration of cyanide in the sample from standard additions as follows:

$$C_{sp} = \frac{(V_s/V_{sp}) C_s}{(1 + V_s/V_{sp}(10 E/S)) - 1}$$

where:

C_{sp} = Concentration of the sample, ppm
($\mu\text{g/ml}$)

V_s = Volume of standard added

V_{sp} = Volume of sample (usually 100.0 ml)

E = Change in mv produced by standard addition

S = Electrode slope

C_S = Concentration of the standard added,
ppm (µg/ml)

V = Total recovered volume of the
sample, ml

Calculate the total cyanide as:

$$M_t = \frac{(C_{sp})(V)}{1000}$$

where:

V = Total recovered volume of the sample,
ml

M_t = Total cyanides in sample, mg

Report as CN⁻ to the nearest 0.1 mg.

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4. Engineering Calculations

Use a calculation sheet as shown in Figure 202.1-2.

To calculate cyanide concentration in the stack gas use the following equation:

$$C_S = K \times M_t / V_m (\text{std})$$

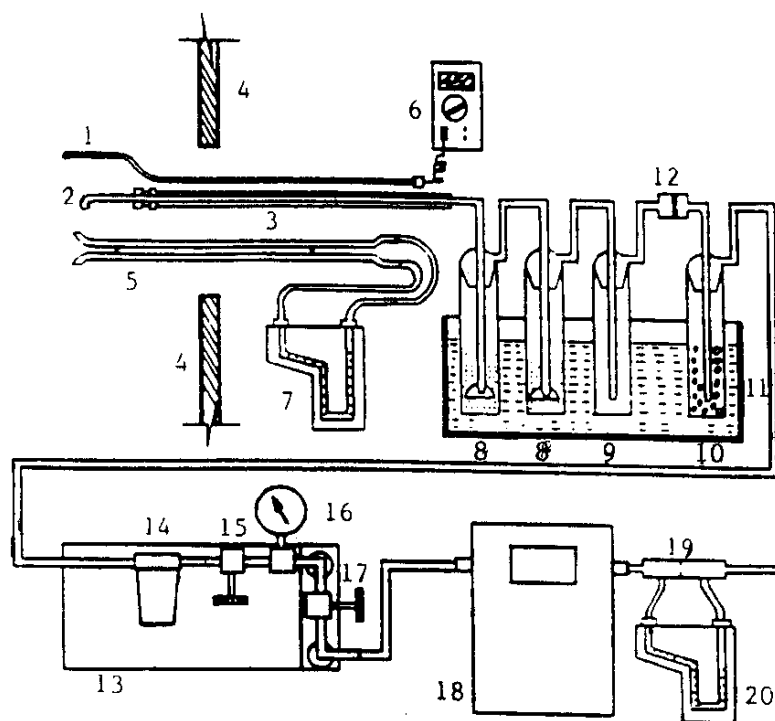
where:

$$C_S = \text{Concentration of cyanide, mg/dscm}$$

$$K = 1.00 \text{ m}^3/\text{m}^3, \text{ if } V_m (\text{std}) \text{ is} \\ \text{expressed in Metric Units}$$
$$= 35.31 \text{ ft}^3/\text{m}^3, \text{ if } V_m (\text{std}) \text{ is} \\ \text{expressed in English Units}$$

M_t = Total cyanides in sample, mg

V_m (std) = Total sample volume, dscm (dscf)



- | | |
|--------------------------------------|---|
| 1. Temperature Sensor | 11. Ice Bath |
| 2. Nozzle | 12. Filter |
| 3. Glass Lined Stainless Steel Probe | 13. Sealed Pump (Leak Free) |
| 4. S-type Pitot Tube | 14. Filter for Pump |
| 5. Stack Wall | 15. Metering Valve |
| 6. Temperature Sensor Meter | 16. Vacuum Gauge |
| 7. Pitot Tube Inclined Manometer | 17. By-pass Valve |
| 8. Impinger with 100 ml 0.1N NaOH | 18. Temperature Compensated Dry Gas Meter |
| 9. Empty Bubbler | 19. Orifice |
| 10. Bubbler with Silica Gel | 20. Orifice Inclined Manometer |

Figure 202.1-1
Cyanide Sampling Train Setup-Wet Impingement Method

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Test No. _____ Sampling Train _____ Date _____
 Calculated By _____ Checked By _____

SOURCE TEST CALCULATIONS

SUMMARY

A. Average Traverse Velocity (Pre-Test) fps
 B. Average Reference Point Velocity (Pre-Test) fps
 C. Average Traverse Velocity (During Test) fps
 D. Gas Meter Temperature (Use 60°F, for Temp. Comp. Meters) °F
 E. Gas Meter Correction Factor
 F. Average Stack Temp. °F
 G. Stack Cross-Sect. Area ft²
 H. Barometric Pressure "HgA
 I. Gas Meter Pressure "HgA
 J. Total Stack Pressure .. "HgA
 K. Pitot Correction Factor
 L. Sampling Time min
 M. Nozzle Cross-Sect. Area ft²
 N. Net Sample Collection .. mg
 O. Net Solid Collection .. mg
 P. Water Vapor Condensed .. ml
 Q. Gas Volume Metered dcf
 R. Corrected Gas Volume Metered $\left[(Q \times 1/29.92) \times \frac{520}{(460 + D)} \times E \right]$ dscf

PERCENT MOISTURE / GAS DENSITY

S. Percent Water Vapor in Gas Sample $\left[\frac{4.64 \times P}{(0.0464 \times P) + R} \right]$ %
 T. Average Molecular Weight (Wet):

(Component)	(Volume % / 100) x (1 - S/100) x (Molec. Wt.) = (Wt./Mole)	
Water	1.00	18.0
Carbon Dioxide	Dry Basis	44.0
Carbon Monoxide	Dry Basis	28.0
Oxygen	Dry Basis	32.0
Nitrogen/Inerts	Dry Basis	28.2
(Sum)		

FLOW RATE

U. Gas Density Correction Factor ($\sqrt{28.95/T}$)
 V. Flue Correction Factor (A/B)
 W. Velocity Pressure Correction Factor ($\sqrt{29.92/J}$)
 X. Corrected Velocity (C x K x U x V x W) fps
 Y. Flow Rate (X x G x 60) cfm
 Z. Flow Rate $\left[Y \times \frac{J}{29.92} \times \frac{520}{(460 + F)} \right]$ scfm
 AA. Flow Rate $\left[Z \times (1 - S/100) \right]$ dscfm

SAMPLE CONCENTRATION/EMISSION RATE

BB. Sample Concentration ($0.01543 \times N/R$) gr/dscf
 CC. Sample Concentration ($54,143 \times BB / \text{Molec. Wt.}$) ppm (dry)
 DD. Sample Emission Rate ($0.00057 \times AA \times BB$) lb/hr
 EE. Solid Emission Rate ($\frac{0.0001322 \times Q \times AA}{R}$) lb/hr
 FF. Isokinetic Sampling Rate $\left(\frac{G \times R \times V \times 100}{L \times M \times AA} \right)$ %

Figure 202.1-2
 Source Test Calculation Sheet