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EMISSION MEASUREMENT TECHNICAL INFORMATION CENTER
NSPS TEST METHOD
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Method 7 - Determination of Nitrogen Oxide Emissions from Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 milligrams $N0_x$ (as $N0_2$) per dry standard cubic meter, without having to dilute the sample.

1.2 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

2. APPARATUS

2.1 Sampling (see Figure 7-1). Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator, U.S. Environmental Protection Agency. The following equipment is used in sampling:

2.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon (Note: Mention of trade names or specific products does not constitute endorsement by U.S. EPA) tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

2.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

2.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

2.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1°C (2°F) intervals from -5 to 50°C (25 to 125°F).

2.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with "T" connection and T-bore stopcock.

2.1.6 Vacuum Gauge. U-tube manometer, 1-meter (36-in.), with 1-mm (0.1-in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

2.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

2.1.8 Squeeze Bulb. One-way.

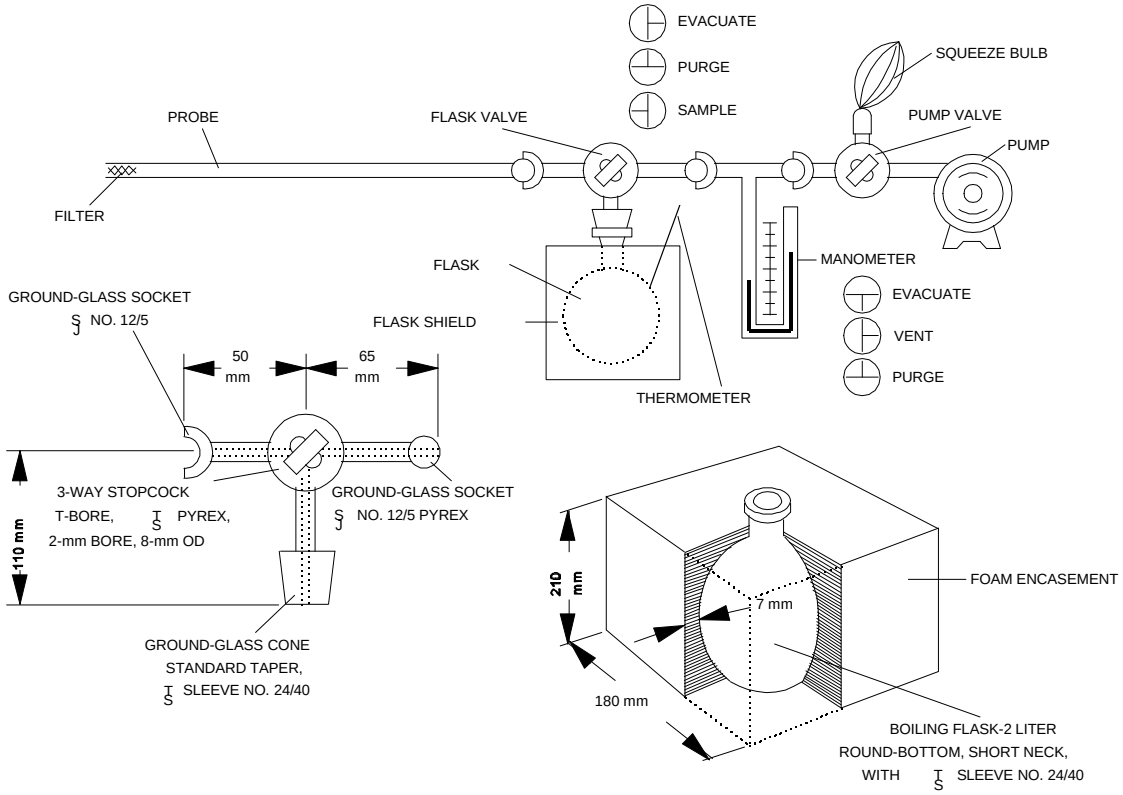

Figure 7-1. Sampling Train, Flask Valve, and Flask

2.1.9 Volumetric Pipette. 25-ml.

2.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-5S has been found to be effective.

2.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See Note in Method 5, Section 2.1.9.

2.2 Sample Recovery. The following equipment is required for sample recovery:

2.2.1 Graduated Cylinder. 50-ml with 1-ml divisions.

2.2.2 Storage Containers. Leak-free polyethylene bottles.

2.2.3 Wash Bottle. Polyethylene or glass.

2.2.4 Glass Stirring Rod.

2.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3 Analysis. For the analysis, the following equipment is needed:

2.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10—ml, and one 25-ml for each sample and standard.

2.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallow-form, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration (see Section 4.3).

2.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70°C (160°F) are acceptable alternatives.

2.3.4 Dropping Pipette or Dropper. Three required.

2.3.5 Polyethylene Policeman. One for each sample and each standard.

2.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

2.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working standard $KN0_3$ solution), and 1000-ml (one).

2.3.8 Spectrophotometer. To measure at 410 nm.

2.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

2.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3.11 Analytical Balance. To measure to within 0.1 mg.

3. REAGENTS

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise,

use the best available grade.

3.1 Sampling. Two reagents are required:

3.1.1 Water. Deionized distilled to conform to ASTM specification D 1193—77, Type 3. At the option of the analyst, the $KMn0_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated H_2S0_4 to 1 liter of water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample Recovery. Two reagents are required for sample recovery:

3.2.1 Water. Same as in 3.1.1.

3.2.2 Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in water, and dilute to 1 liter.

3.3 Analysis. For the analysis, the following reagents are required:

3.3.1 Water. Same as in 3.1.1.

3.3.2 Sulfuric Acid. Concentrated, 95 percent minimum assay. HANDLE WITH CAUTION.

3.3.3 Potassium Nitrate ($KN0_3$). Dried at 105 to 110°C (220 to 230°F) for a minimum of 2 hours just prior to preparation of standard solution.

3.3.4 Standard $KN0_3$ Solution. Dissolve exactly 2.198 g of dried $KN0_3$ in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

3.3.5 Working Standard $KN0_3$ Solution. Dilute 10 ml of the standard solution to 100 ml with water. One milliliter of the working standard solution is equivalent to 100 µg nitrogen dioxide ($N0_2$).

3.3.6 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 25 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide - HANDLE WITH CAUTION), and heat at 100°C (212°F) for 2 hours. Store in a dark, stoppered bottle.

3.3.7 Concentrated Ammonium Hydroxide. Reagent grade.

3.3.8 Quality Assurance Audit Samples. Nitrate samples in glass vials prepared by EPA's Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park, North Carolina 27711. Each set will consist of two vials having solutions of unknown concentrations. Only when making compliance determinations, obtain an audit sample set from the quality assurance management office at each EPA regional office or the responsible enforcement agency. (Note: The tester should notify the quality assurance office or the responsible enforcement agency at least 30 days prior to the test date to allow sufficient time for sample delivery.)

4. PROCEDURES

4.1 Sampling.

4.1.1 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1, and place the probe at the sampling point. Make sure 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. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm (3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its "vent position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position, and do the same with pump valve. 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. Next, turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position, and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position, and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion of N0 to $N0_2$ (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of N0 in N_2), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (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.

4.2 Sample Recovery. Let the flask set for a minimum of 16 hours, and then shake the contents for 2 minutes. Connect the flask to a mercury filled U—tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding sodium hydroxide (1 N), 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. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

4.3 Analysis.

4.3.1 Note the level of the liquid in the container, and confirm whether any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods,

subject to the approval of the Administrator, to correct the final results.

4.3.2 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 water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator), as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of water; filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

4.3.3 Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 5.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds A_4, the absorbance of the 400-µg $N0_2$ standard (see Section 5.2.2).

4.4 Audit Sample Analysis.

4.4.1 Concurrently analyze the two audit samples and a set of compliance samples (Section 4.3) in the same manner to evaluate the technique of the analyst and the standards preparation. (Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to optimize the system accuracy and precision. One source of these samples is the Source Branch listed in Section 3.3.9.) The same analysts, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

4.4.2 Calculate the concentrations in mg/dsm^3 using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dsm^3 and compliance results in total µg NO_2/sample by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30—day period.

4.4.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual audit concentrations. If the 10—percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report (see Note in the first paragraph of this section).

4.4.4 Failure to meet the 10-percent specification may require retests until the

audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

5. CALIBRATION

5.1 Flask Volume. The volume of the collection flask-flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

5.2 Spectrophotometer Calibration.

5.2.1 Optimum Wavelength Determination.

5.2.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

5.2.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 µg $N0_2$ standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0.0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the $KN0_3$ working standard solution (1 ml = 100 µg $N0_2$) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution, 10 ml water, and sodium hydroxide (1 N) dropwise until the pH is between 9 and 12 (about 25 to 35 drops each). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of Section 4.3 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{Eq. 7-1}$$

where:

K_c = Calibration factor.

A_1 = Absorbance of the 100-µg $N0_2$ standard.

A_2 = Absorbance of the 200-µg $N0_2$ standard.

A_3 = Absorbance of the 300-µg $N0_2$ standard.

A_4 = Absorbance of the 400-µg $N0_2$ standard.

5.2.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. These calculated concentration values should not differ from the actual concentrations (i.e., 100, 200, 300, and 400 µg NO_2) by more than 7 percent for three of the four standards.

5.3 Barometer. Calibrate against a mercury barometer.

5.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

5.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in 2.1.6.

5.6 Analytical Balance. Calibrate against standard weights.

6. CALCULATIONS

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

6.1 Nomenclature.

A = Absorbance of sample.

C = Concentration of $N0_x$ as N_20, dry basis, corrected to standard conditions, mg/dsm^3 (lb/dscf).

F = Dilution factor (i.e., 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of the calibration).

K_c = Spectrophotometer calibration factor.

m = Mass of $N0_x$ as $N0_2$ in gas sample, µg.

P_f = Final absolute pressure of flask, mm Hg (in. Hg).

P_i = Initial absolute pressure of flask, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_f = Final absolute temperature of flask, °K (°R).

T_i = Initial absolute temperature of flask, °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{sc} = Sample volume at standard conditions (dry basis), ml.

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

2 = 50/25, the aliquot factor. (If other than a 25-ml aliquot was used for analysis, the corresponding factor must be substituted.)

6.2 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = (V_f - V_a) \frac{T_{std}^f}{P_{std}^f} \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right]$$

$$^{ff} = K_1^{ffff} (V_f - 25) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \qquad \text{Eq. 7-2}$$

where:

K_1 = 0.3858 °K/mm Hg for metric units,

= 17.64 °R/in. Hg for English units.

6.3 Total µg $N0_2$ per sample.

$$m = 2 K_c A F \qquad \text{Eq. 7-3}$$

Note: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

6.4 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2 (m/V_{sc}) \qquad \text{Eq. 7-4}$$

where:

K_2 = 10^3 $(mg/m^3)/(\mu g/ml)$ for metric units,

= 6.242×10^{-5} (lb/scf)/(µg/ml) for English units.

6.5 Relative Error (RE) for QA Audit Samples, Percent.

$$RE = 100 (C_d - C_a)/C_a \qquad \text{Eq. 7-5}$$

where:

C_d = Determined audit sample concentration, mg/dsm^3.

C_a = Actual audit sample concentration, mg/dsm^3.

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