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Laboratory Division
Texas Air Control Board

DETERMINATION OF AMMONIA

Phenol-Nitroprusside Method

A. GENERAL

Ammonia is collected in very dilute acid solution. The trapped ammonia reacts with phenol-nitroprusside and alkaline hypochlorite solutions to produce a blue complex that is measured colorimetrically. The intensity of the blue color is proportional to the amount of NH_3 absorbed.

B. APPLICABILITY

For ambient air sampling at a flow rate of 0.2 liters per minute, the lower limit for detection is 4.4 $\mu g/M^3$; increasing the flow rate to 0.6 liters per minute lowers the limit to 1.4 $\mu g/M^3$. The addition of the nitroprusside catalyst greatly increases the sensitivity of the method.

In addition to being highly dependent upon time and temperature for proper color development, this reaction is pH critical and hypochlorite ion concentration dependent. If the sample pH is less than 11, the color development will be drastically reduced. Also, if the NaOCl has deteriorated as a result of aging, the color will not develop properly.

It has been found that urea interferes positively as do monoalkylamines. Formaldehyde interferes negatively when present in amounts equal to 20% of the NH_3.

C. APPARATUS

Suitable sampling apparatus
2 - 1,000 ml volumetric flasks
2 - 500 ml volumetric flasks
8 - 100 ml volumetric flasks
8 - 10 ml volumetric pipets
3 - 5 ml volumetric pipets
1 - 3 ml volumetric pipet
1 - 2 ml volumetric pipet
1 - 1 ml volumetric pipet
1 - 0.5 ml volumetric pipet
- 5 ml graduated pipets
1 - 1 ml graduated pipet
ufficient storage bottles
ufficient 1" test tubes
10 mm cuvettes
pectrophotometer capable of operating at 626 nm
ater bath or oven capable of operation at 37° C.

D. REAGENTS

(1) Absorbing Solution

Add 1 ml formic acid (88%) to 2 liters deionized water.

(2) Phenol-Nitroprusside Solution

Dissolve 5 grams of phenol in 50 ml deionized water. Add 0.025 grams sodium nitroprusside (sodium nitroferricyanide). Transfer to a 500 ml volumetric flask and bring up to volume with deionized water.

NOTE: This solution may be kept up to one month if kept refrigerated in an amber bottle. However, if solution turns yellow, it should be discarded.

(3) Alkaline Hypochlorite

Transfer 4.0 mL commercially prepared NaOCl (such as "Clorox") and 6.25 ml of 10 N NaOH (or 2.5 grams NaOH pellets) to a 500 ml volumetric flask. Dilute with deionized water to the proper volume.

NOTE: This reagent may be stored up to one month if kept refrigerated in an amber bottle.

(4) Standard Stock Ammonia Solution

Dissolve 3.880 grams $(NH_4)_2SO_4$ in 1 liter deionized water. This solution contains 1000 µg NH_3/ml.

(5) Working Standard Ammonia Solution

(a) Dilute 10 ml of the Standard Stock Ammonia solution to 100 ml with absorbing solution. This solution has 100 µg/ml NH_3.

(b) Dilute 10 ml of the above solution (a) to 100 ml with absorbing solution. This solution has 10 µg/ml and will be used to prepare standards for the standard curve.

E. COLLECTION OF SAMPLE

The sample is collected using a known volume of dilute acid solution in a suitable impinger. When midget impingers are used for property line samples, air may be bubbled through at a rate of 1.5 - 2 liters per minute. Glass or plastic sampling lines are acceptable; galvanized, brass, or copper sampling lines should be avoided. Use 20 ml of absorber in a midget impinger. For ambient sampling use 50 ml of absorber in a NASN bubbler.

F. TEST PROCEDURE

(1) Preparation of Standard Curve

Using the second working standard (see Section D.(5)(b)), pipet 0.5, 1, 2, 3, 5, and 10 ml into a series of 100 ml volumetric flasks.

Make up to volume with absorbing solution. These solutions contain 0.05, 0.1, 0.2, 0.3, 0.5, and 1.0 µg/ml respectively.

Pipet 10 ml of each of the above standard solutions into test tubes. To each add 5 ml of the phenol-nitroprusside solution, mix, and then add 5 ml of the alkaline hypochlorite and mix well.

Prepare a blank using 10 ml absorbing solution and 5 ml of each developing reagent.

Heat standards and blank to 37°C for 30 minutes. Cool to room temperature. Measure the absorbance at 626 nm versus the blank. Plot the absorbance vs. µg NH_3/ml. The absorbance is stable for several hours.

(2) Sample Determination

Correct for any evaporation loss during sampling by bringing the sample back to the original volume with deionized water. Place a 10 ml aliquot of the sample into a test tube; add 5 ml of the phenol-nitroprusside and mix. Add 5 ml of the alkaline hypochlorite solution. Mix thoroughly after addition of each reagent. Heat the samples and the blank to 37° C for 30 minutes. Cool to room temperature and read absorbance at 626 nm versus blank. Calculate µg NH_3/ml from the least squares standard curve.

In some cases samples may yield final colors too intense for accurate reading. If the absorbance is over 0.8, take an aliquot of the sample and dilute with a part of the developed blank. Read the diluted sample versus the remaining blank. Calculate µg/ml for the diluted sample from the standard curve.

NOTE: The time and temperature of incubation are critical if reproducible results are to be obtained. It is considered good practice to prepare a new set of standards each time a set of samples is run. The standards, samples, and quality control samples are then all heated simultaneously; an oven with an internal fan to circulate air or a water bath may be used.

G. CALCULATION

$$\mu g\ NH_3/M^3 = \frac{(\mu g\ NH_3/ml) \times (\text{total ml absorber used})}{M^3 \text{ air sampled}} \times \frac{(20\ ml)^*}{(\text{ml developed sample taken for aliquot})}$$

*If no dilutions are required, the last factor is deleted.

H.ee QUALITY CONTROLeee

Duplicates should be run on 7% of the samples or ateleast onee duplicate per batch of 15 or less. Theseewill test thee precision of the procedure. The relative deviation should bee less than 5% ifethe absorbance reading is greater than 0.100.

$$\text{Relative Deviation (R.D.)} = \frac{\bar{d}}{\bar{v}} \quad \text{whereed} = e|v_1 - v_2|$$

$$\bar{v} = \frac{|v_1 + v_2|}{2}$$

v_1 andev$_2$ are the individual measurements.

Spiked samples shouldebe run to control theeaccuracy of the analysis. Spikedesamples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place 4 mleof the 1.0 µg/ml standardeinea test tube.eeAdd 6 ml of sample to the test tube. Adde5 ml of the phenol-nitroprusside solution, mix, then add 5 ml of the alkaline hypochlorite and mix well. Heat to 37° C for 30 minutes. Cool to room temperature. Measure the absorbance at 626 nm versus the blank.

$$\text{Percent recoveey} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100\text{eee}$$

For example,

A sample had a concentration of .300 µg NH_3/ml. The spike of the same sample had a measured concentration of 0.575 µg/ml. The spike was prepared as above. The calculated concentration of the spike was 0.400 µg/ml.

$$\text{Percent Recovery} = \frac{(0.575\ \mu g/ml) - (0.300\ \mu g/ml)\left(\frac{6\ ml}{10\ ml}\right)e}{0.400\ \mu g/ml} \times 100\text{eee}$$

$$=0.395/0.400\text{ex } 100 = e99\%$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analyses repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

Leithe, W., The Analysis of Air Pollutants, 1970, p. 172, 5.6.1.5. Special Topics, Nitrogen Containing Pollutants.

Weatherburn, M. W., "Phenol-Hypochlorite Reaction for the Determination of Ammonia", Anal. Chem. 39, 971 (1967).

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