METHOD 42

REF: Regs:			
	8-3	8-19	8-32
	8-4	8-20	8-38
	8-11	8-23	8-43
	8-12	8-26	8-45
	8-13	8-29	8-51
	8-14	8-31	

DETERMINATION OF AMMONIA IN COATINGS, INKS AND RELATED MATERIALS

1) PRINCIPLE

1.1 Ammonia is an inorganic compound usually present in waterbased coatings, inks and related products. Its presence, if not subtracted from the total volatile content, will result in the overestimation of **the volatile organic compound (VOC)** content of a product.

1.2 This method is applicable to the determination of ammonia present in waterbased coatings, inks and related products.

1.3 A given weight of a sample is diluted with acid in a volumetric flask and allowed to stand undisturbed for 20 minutes to allow the solid to separate from the liquid.

1.4 An aliquot of the supernatant liquid is made basic with the addition of a pH adjusting solution (ISA) and the ammonia concentration is determined using the specific ion electrode.

1.5 The method is intended to provide a measure for ammonia in the range of 0.1 to 10 μg ammonia per 49 ml of the diluted sample. For ammonia concentration higher than 10 μg/49 ml, use less aliquot to bring the ammonia concentration to the working range of the standard curve.

1.6 Interferences

1.6.1 The presence of Monoethanolamine, Ethanolamine and Triethanolamine, with concentrations up to 10 % (W/W) of each does not interfere with the analysis of ammonia.

1.6.2 Some metal ions interfere by complexing with ammonia. The presence of EDTA in the pH adjusting ISA solution complexes these metals, freeing the ammonia for analysis.

2) APPARATUS

2.1 **Ionalyzer - Model 407A.** Orion Research Inc.

2.2 **Ammonia Selective Ion Electrode.** Orion Model 95-12.

2.3 **Red Devil Paint Action Shaker** for Gallon Size Cans.

2.4 **Analytical Balance.** Capable of Weighing to +/- 0.0001 gram.

2.5 **Stir Plate Model 58290.** Scientific Products.

2.6 **Teflon Magnetic Bars,** 1/2"x5/16".

2.7 **Beakers,** 100 ml, 1000 ml.

2.8 **Graduated Cylinders,** 50 ml.

2.9 **Volumetric Pipettes,** various sizes as needed.

2.10 **Beakers.** Tri-Pour Polypropylene Beakers, 100 ml. Lab Safety Supply Catalogue #TT7782.

2.11 **Ice Pick**

2.12 **Eberbach Shaker** for Quart Size and Pint Size Cans.

2.13 **Disposable Syringe,** 3 ml.

2.14 **Volumetric Flask,** 1000 ml.

2.15 **Hot Plate**

2.16 **Membranes/cap for probe** (Orion No. 951204 - box of 20 membranes or Cat. No. 951205 - bonded membrane cap - 3 per pak).

3) REAGENTS

3.1 **Hydrochloric Acid (0.01 N).** To a 1 liter volumetric flask containing approximately 800 ml of distilled water, pipette 0.84 ml of concentrated hydrochloric acid (37-38% assay) and dilute to the mark with distilled water. Cap the flask and invert several times to mix the solution.

3.2 **Ammonia pH adjusting ISA (Ionic Strength Adjustor).** Orion Research Inc. Cat. No. 951211.

3.3 Internal Filling Solution for the Electrode. Orion Research Inc. Cat. No. 95-12-02.

3.4 Ammonia Standard Solution as Nitrogen. 1000 ppm. Orion Research Inc. Cat. No. 951007.

3.5 Distilled Water

3.6 pH Indicator Strips

4) ANALYTICAL PROCEDURE

4.1 Sample Preparation

4.1.1 Mix the sample thoroughly for about 30 minutes at low speed in the Eberbach shaker. It is essential that the samples be well mixed to obtain valid results. Stirring with a spatula may also be required. **(NOTE 1)**

NOTE 1: Samples with high concentration of ammonia characterized by the bulging of the can should be handled with extreme caution. Release the pressure by punching a hole in the can using an ice pick. Transfer the contents of the can to a new container. Use a stirring rod or tongue depressor to mix the sample.

4.2 Screening the Sample for the Presence of Ammonia.

4.2.1 Transfer approximately 2 ml of the mixed sample to a test tube. Heat the test tube in the hot plate.

4.2.2 Using a pair of forceps, hold a moist litmus paper near the surface of the sample.

4.2.3 If the litmus paper turns blue, it indicates the presence of ammonia. Proceed to section 4.3.

4.3 Determination of the Ammonia Content of the Product by Specific Ion Electrode.

4.3.1 Prepare standard as described in Section 5.

4.3.2 Calibrate the ion meter as described in Section 6.

4.3.3 Fill a 3 ml disposable syringe with the freshly mixed sample **(4.1.1)**. Draw back the plunger a little, wipe off the excess paint and cap the syringe.

4.3.4 Place the capped syringe on the balance pan and tare to zero.

4.3.5 Remove the cap and transfer approximately 1 to 2 grams of the content of the syringe into a 1 liter volumetric flask containing approximately 500 ml of 0.01 N HCl, being careful not to get any sample on the neck or top of the flask. Pull the plunger back a little, cap the syringe and restopper the flask.

4.3.6 Place the capped syringe on the balance and record the weight to the nearest 0.0001 g.

4.3.7 Dilute the contents of the volumetric flask **(4.3.5)** to the mark with 0.01 N HCl. Cap the flask. Mix the solution by inverting the flask several times.

4.3.8 Pipette 49 ml of the supernatant liquid to a tri-pour polypropylene beaker. Place the beaker with the solution on the stir plate. Dip the electrode into the solution.

4.3.9 Add 1 ml ISA to **(4.3.8)**. The solution should be blue if it is in the expected pH range (pH 11-14). If the solution is not blue, check the pH with a litmus paper. Additional ISA may be added if the pH is not within the range **(NOTE 2)**.

4.3.10 Set the magnetic stirrer at low speed. Maintain a constant stirring rate and temperature at about 25°C throughout the analysis. Keep the electrode in solution until a stable reading is obtained. Record the meter reading (ppm). **(NOTES 3, 4, & 5)**

4.3.11 If the reading is beyond the working range of the meter, repeat Sections 4.3.8 through 4.3.10 using less aliquot of the supernatant liquid. Record the proper dilution factor (DF). **(Section 7.1)**

4.3.12 Analyze duplicate aliquot of the same sample. The meter readings should agree within $\pm$ 0.1 ppm of the mean.

NOTE 2: Record the volume of the additional ISA that has been added and make the necessary correction in the calculation.

NOTE 3: If electrode response is slow, check the membrane for any surface layer of contaminants. Refer to Orion Ammonia Electrode Instruction Manual for electrode preparation.

NOTE 4: If several samples are analyzed, verify calibration by running a 1 ppm and a 5 ppm Ammonia as Nitrogen standard for every five samples analyzed.

NOTE 5: After immersion in the solutions to be tested, check the membrane surface of the electrode for the presence of air bubbles. Remove the bubbles by shaking the electrode.

5) PREPARATION OF WORKING STANDARD

5.1 Working Standard. Dilute 5.0 ml of the 1000 ppm Ammonia as Nitrogen stock solution **(3.4)** to 100 ml with 0.01 N HCl in a volumetric flask to make a 50 µg/ml standard. **(NOTE 6)**

NOTE 6: Working standards are prepared fresh prior to analysis.

6) CALIBRATION

6.1 Calibration of the Instrument at 1 ppm (1 µg/ml) Ammonia as Nitrogen Standard

6.1.1 Pipette 1 ml of working standard to a tri-pour polypropylene beaker.

6.1.2 Add 48 ml of 0.01 N HCl to **(6.1.1)** and place on the stir plate.

6.1.3 Rinse the electrode with distilled water, blot dry and dip into the beaker containing the standard solution.

6.1.4 Add 1 ml of ISA and a stirring bar. Set the magnetic stirrer at low speed. Maintain a constant stirring rate and temperature

at about 25°C throughout the calibration. **(NOTES 7 & 8)**

6.1.5 Keep the electrode in solution until a stable reading is obtained.

6.1.6 Use the calibration knob to adjust the meter reading to 1 ppm.

NOTE 7: **Do not add the ISA solution before immersing the electrode because ammonia may be lost in a basic solution.**

NOTE 8: **Some magnetic stirrers generate enough heat to change the solution temperature. This effect can be minimized by placing a piece of insulating material such as a cork or styrofoam beneath the beaker.**

6.2 Calibration of the Instrument at 10 ppm (10 μg/ml) Ammonia as Nitrogen Standard.

6.2.1 Pipette 10.0 ml of working standard **(5.1)** to a tri-pour polypropylene beaker.

6.2.2 Add 39.0 ml of 0.01 N HCl to **(6.2.1)** and place on the stir plate.

6.2.3 Rinse the electrode with distilled water, blot dry and dip into the beaker containing the standard solution.

6.2.4 Add 1 ml of ISA and a stirring bar. Set the magnetic stirrer at low speed. Maintain a constant stirring rate and temperature at about 25°C throughout the calibration.

6.2.5 Keep the electrode in solution until a stable reading is obtained. **(NOTE 9)**

6.2.6 Use the % slope knob to adjust the meter reading to 10 ppm.

6.2.7 Recheck the 1 ppm Ammonia as N standard by repeating **(6.1.1)** to **(6.1.6)**.

NOTE 9: **Between measurements, rinse the electrode with distilled water, and blot dry with a tissue to prevent solution carry-over.**

7) CALCULATION

7.1 Total Ammonia (g) $= (4.3.10) \times 50/49 \times 10^{3} \times 10^{-6} \times 17/14 \times DF$

$= (4.3.10) \times 50/49 \times 10^{-3} \times 17/14 \times DF$

Where:

(4.3.10) = Meter reading (ppm)

ppm = µg/ml

50 = Total volume of solution

49 = Aliquot of sample

10^{3} = Total volume of sample in ml

10^{-6} = Factor for converting µg to g

17 = Molecular weight of Ammonia

14 = Atomic weight of Nitrogen

DF = Dilution factor. If no dilution factor is made then DF = 1

7.2 % Ammonia (W/W) $= \frac{(7.1) \times 100}{(4.3.6)}$

Where:

(4.3.6) = Weight of sample(g)

8) REFERENCES

8.1 Standard Methods for the Examination of Water and Wastewater, 18th Edition 1992. 4500-NH_3 F. Ammonia Selective Electrode Method.

8.2 Orion Ammonia Electrode Instruction Manual, Model 95-12.

TEST METHOD UPDATE FORM

Date: 4-16-96

Agency: Bay Area Air Quality Management District

Contact: Rudy Zerrudo

Test Method #: 42

Title: Determination of NH3 in coatings, Inks and Related Products

Principle: See Section 1) page 1 of Method 42 (enclosed)

Precision: The single operator, within laboratory precision of the method is ± 0.04%. (Pooled Standard Deviation) as shown on table 1.

Accuracy: The average relative % difference between the spiked coatings and Method 42 test result is 3.06%. The data is presented in Table II.

Range of Applicability: This method is applicable to the determination of waterbased coatings, inks and other related products.

Validation Tests: Not applicable.

Corresponding EPA Method: None

TABLE I

DATA ON SINGLE OPERATOR WITHIN LABORATORY PRECISION OF METHOD 42

	% NH3 (W/W)					
Sample Description	Run 1	Run 2	Run 3	Average	Theretical Value	Standard Deviation
Spiked Coating 1	0.5	0.5	0.52	0.51	0.50	0.0115
Spiked Coating 2	1.08	1.08	1.07	1.08	1.00	0.0058
Spiked Coating 3	2.02	1.98	2.09	2.03	2.00	0.0557
Spiked Coating 4	3.11	3.11	3.15	3.12	3.00	0.0231
Spiked Coating 5	3.96	4.07	4.01	4.01	4.00	0.0551
Spiked Coating 6	5.17	5.17	5.17	5.17	5.00	0.0000
Pooled Standard Deviation						0.0337

TABLE II

DATA ON ACCURACY OF METHOD 42

	% NH3 (W/W)						
Sample Description	Run 1	Run 2	Run 3	Average	Theoretical Value	Absolute % Difference	Relative % Difference
Spiked Coating 1	0.50	0.50	0.52	0.51	0.50	0.01	1.33
Spiked Coating 2	1.08	1.08	1.07	1.08	1.00	0.08	7.67
Spiked Coating 3	2.02	1.98	2.09	2.03	2.00	0.03	1.50
Spiked Coating 4	3.11	3.11	3.15	3.12	3.00	0.12	4.11
Spiked Coating 5	3.96	4.07	4.01	4.01	4.00	0.01	0.33
Spiked Coating 6	5.17	5.17	5.17	5.17	5.00	0.17	3.40
Average % Difference						0.07	3.06