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QUANTITATION OF AMMONIA IN OIL SHALE PROCESS WASTEWATERS

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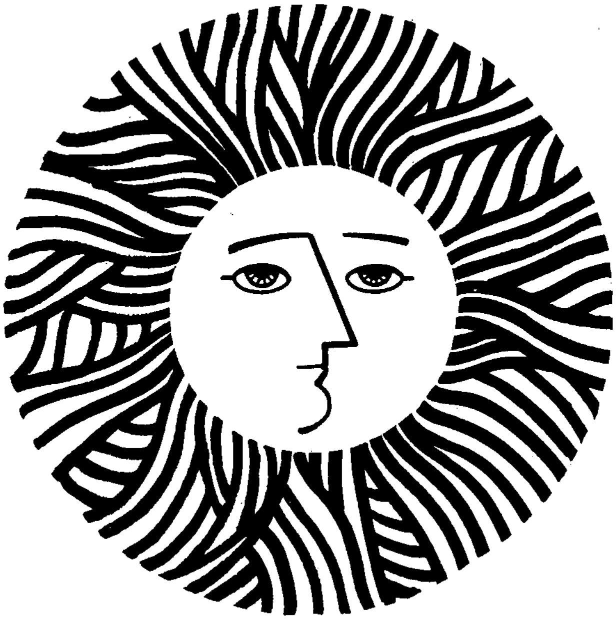

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DISCLAIMER

QUANTITATION OF AMMONIA IN OIL SHALE PROCESS WASTEWATERS

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Ammonia and its equilibrium ion, ammonium, are present in wastewaters from oil shale retorting at concentrations generally greater than several hundred parts per million. Methods for the quantitation of these species in synfuel wastewaters are necessary for research, treatment monitoring, and establishment of regulatory standards. The method of choice should be sufficiently simple to find applicability in the routine wet-chemistry laboratory. Published methods for determining ammonia in water may be applicable only to the particular sample matrix for which they were tested, and even conventional "standard methods" should not be used for oil shale wastewaters without validation and, often, modification.

Only three approaches are available to a routine wet-chemistry laboratory for quantitating the aqueous equilibrium pair as total ammonia: (1) colorimetry, (2) titration, and (3) direct ammonia-selective electrode. Methods that employ these approaches are numerous, and all of them give excellent results for particular sample matrices. The LBL-SEEHRL Oil Shale Program has extensively evaluated each of these approaches for several oil shale wastewaters. Methods for colorimetry and titration were validated, whereas gas-sensing electrodes from two manufacturers proved to be extremely unreliable even though they provided the fastest and easiest method. Ammonia-sensing electrodes generated unstable response curves in retort waters, probably because their membranes become easily fouled; their use should be limited to range finding.

Protocols for two oil shale wastewater ammonia methods, "Distillation Titration Ammonia Protocol" and "Colorimetric Ammonia Protocol" by J. Cantor, B.M. Jones, R.H. Sakaji, and C.G. Daughton, are appended. Ammonia quantitation by titration requires distillation of the ammonia from the water to eliminate the interferences of carbonate alkalinity and color. This is a straightforward method that relies on the pK_a of the ammonium-ammonia equilibrium. If a sample is maintained at a sufficiently high pH and temperature, the equilibrium pair can be stoichiometrically distilled as ammonia gas; if the adjusted pH is too high, digestion of organically bound nitrogen may occur and contribute a positive interference.

Ammonia quantitation by colorimetry involves the formation of an ammonia reaction product whose chromophore has a molar extinction coefficient sufficiently high to alleviate interferences by endogenous chromophores. Routine colorimetric methods include Nesslerization and various adaptations of the indophenol-blue procedure, which is also called the phenate or phenol-hypochlorite method.

The major advantage of the colorimetric phenate method is that of sample throughput. In our laboratory, an analyst can perform about 50 determinations per day versus 20 for the distillation method. The success of this method when applied to retort waters results from the dilution of the sample by the reagents, which effectively eliminates interference by endogenous chromophores. The disadvantage of the colorimetric method is that several range-finding dilutions may be required to bring the absorbance of an unknown sample within the standard curve range. Precision and accuracy are sacrificed when dilutions are performed, but more significantly, the large ratio of exposed surface to volume of samples contained in measuring devices exacerbates the loss of ammonia by degassing; this problem is magnified with the necessity of measuring small volumes. We have found that the most satisfactory solution to this problem is the use of glass capillaries for sampling and for accurate volume measurement. The titrimetric method also requires range finding; the appropriate normality of the titrant must be determined for each unknown. This problem can be alleviated by using an autotitrator capable of delivering microliter-volumes of titrant. Automation of the colorimetric method would be possible by segmented-flow or flow-injection analysis.

Representative results from distillation/titration and colorimetry for raw retort waters and for treated retort waters are presented in Table I; mean concentrations determined on different days for a sample type varied because subsamples were obtained from different lots and because of degassing during storage. In addition, with the use of either the colorimetric or distillation/titration method, recoveries of ammonia-N from either biologically-spent Oxy-6 retort water or from Oxy-6 gas condensate fortified with 100 to 50,000 ppm ammonia-N have been confined to the 93 to 110 per cent range. Slopes of the standard-additions curves were 1.00 (r^2=0.9999, n=11).

Table I

Evaluation of Methods for Determination of Ammonia in Oil Shale Process Waters

day of analysis	method	sample	$\bar{x}$[1]	s	%rsd	n[2]
a	phenate	rw[3]	1131	18.0	1.59	10
b	phenate	rw	1136	31.2	2.75	9
c	phenate	rw	1089	12.8	1.18	10
b	phenate	gc[4]	7339	102	1.39	10
d	phenate	gc	7214	215	2.98	10
e	phenate	gc	6757	177	2.62	20
f	phenate	gc	6759	95.4	1.41	10
g	dist/titr[5]	gc	6759	70.1	1.04	5
h	phenate	gc	149[6]	1.94	1.30	9
i	dist/titr	gc	134[6]	5.86	4.37	5
j	phenate	TV[7]	2279	31.5	1.38	10

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[1] mean concentration (mg/L NH_3-N)
[2] number of replicates
[3] Oxy-6 retort water
[4] Oxy-6 gas condensate
[5] distillation/titration
[6] stripped with hot air
[7] retort water from a near-commercial surface process

Glassware & Equipment (per sample)

500-mL Kjeldahl flask (discard any Kjeldahl flask with star-shaped cracks)
250-mL Erlenmeyer flask
magnetic stirring bar

Glassware Preparation

Soap wash. Rinse with deionized distilled water.

Reagents

All chemicals Analytical Reagent grade;
Deionized distilled water, ASTM Type I from Milli-Q system or equivalent.

Borate Buffer Solution:
Add 88 mL of 0.1 N NaOH to approximately 500 mL of 0.025 M sodium tetraborate solution (5.0 g $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per L) and dilute to 1 L with deionized distilled water (Standard Methods, p. 411).

Boric Acid Solution:
Dissolve 20 g of H_3BO_3 in deionized distilled water and dilute to 1 L (Standard Methods, p. 417; omit indicator).

Mixed Indicator Solution:
Dissolve 200 mg of methyl red indicator in 100 mL of 95% ethyl or isopropyl alcohol. Dissolve 100 mg of methylene blue in 50 mL of 95% ethyl or isopropyl alcohol. Combine the two solutions. Fresh indicator should be made every month (Standard Methods, p. 417).

0.1 N H_2SO_4:
Dilute one container of Hellige Standardized Concentrate R-1238C to 1 L with deionized distilled water, or prepare from concentrated H_2SO_4 and standardize as per Standard Methods, p. 279.

Phenolphthalein Indicator:
Dissolve 0.5 g phenolphthalein in 50 mL of 95% ethyl alcohol, add 50 mL deionized distilled water, and mix (Standard Methods, p. 662).

50% (20 N) Sodium Hydroxide Solution:
Use commercially prepared solution (e.g., J. T. Baker).

Procedure

1. Steam apparatus clean: Prior to each run, place 300 to 400 mL deionized distilled water and 1 or 2 boiling chips or glass beads in each Kjeldahl flask and attach to distillation apparatus. With cooling water off, distill approximately 150 mL; collect in any convenient container and discard.

2. **Receiving flasks:** Place 35 mL (measurement by graduated cylinder OK) boric acid solution in each 250-mL Erlenmeyer flask and place on rack in tilted position so that effluent tube-tips are completely submerged in acid solution.
3. **Samples:** Place boiling chips or glass beads and appropriate volume of sample in Kjeldahl flask. (Sample volume may be adjusted to optimize titrant volume based on expected sample concentration; a 5-mL sample containing 1000 ppm ammonia requires approximately 3.5 mL of 0.1 N H_2SO_4 to titrate.) Add deionized distilled water to bring the total volume to approximately 300 mL, add 2 drops phenolphthalein, and 10 mL borate buffer solution (automatic pipette recommended for convenience, but volume not crucial). Add 50% NaOH to Kjeldahl flask (0.5 mL or until pink) and **immediately** connect to distillation apparatus.
4. **Standard:** Use Hellige 1000 ppm-ammonia nitrogen standard R-2434 or equivalent and prepare the sample as in step 3.
5. **Blank:** Omit sample and prepare the flask contents as in step 3.
6. **Turn on cooling water** and set heat to maximum. After samples begin to boil, reduce heat as necessary to control boiling and foaming.
7. Collect approximately 100 mL of distillate.
8. Set collection flasks upright and rest effluent tubes on flask rims to prevent sample drawback during cooling. Turn off heat and collect distillate until distillation stops.
9. Add stirring bar and 4 drops of mixed indicator solution to each collection flask and titrate with 0.1 N H_2SO_4 to violet endpoint. Solution will turn from green to blue 1 or 2 drops before the endpoint is reached. Blank should require no more than 1 drop of titrant.
10. **Calculation:**

$$\text{mg/L ammonia nitrogen} = \frac{\left(\begin{array}{c}\text{sample}\\ \text{titrant}\\ \text{volume (mL)}\end{array} - \begin{array}{c}\text{blank}\\ \text{titrant}\\ \text{volume (mL)}\end{array}\right) \times \begin{array}{c}\text{normality}\\ \text{of acid}\\ \text{(meq/mL)}\end{array} \times \begin{array}{c}1000\\ \text{mL/L}\end{array} \times \begin{array}{c}14\\ \text{mg/meq}\end{array}}{\text{sample volume (mL)}}$$

Reference

Standard Methods For the Examination of Water and Wastewater, 14th ed.; American Public Health Association: Washington, D.C., 1976, 407-18.

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Glassware required (per sample)

One 20 X 50-mm test tube with Teflon-lined screw cap (recommended for convenience; Parafilm may be used instead). Acid wash all glassware. Rinse caps briefly several times with deionized distilled water (do not soak caps more than a few minutes, as the plastic deteriorates). Do not use tubes with chipped rims.

One 20-microliter Drummond Microcap.

Reagents

All chemicals Analytical Reagent grade.
Deionized distilled water, ASTM Type I from Milli-Q system or equivalent.

Phenol/Nitroprusside Solution:
Dissolve 5 g phenol and 25 mg sodium nitroferricyanide (nitroprusside) dihydrate [$Na_2Fe(CN)_5NO \cdot 2H_2O$] in deionized distilled water and dilute to 500 mL. Store in amber or foil-covered bottle at 4°C. Discard after one month (Weatherburn).

Alkaline Hypochlorite Solution:
Dissolve 2.5 g sodium hydroxide in deionized distilled water, add 4.2 mL of 5% sodium hypochlorite solution (J.T. Baker or equivalent) and dilute to 500 mL. Store in amber or foil-covered bottle at 4°C. Discard after one month, or when high blank values or change in slope of calibration curve are observed (Weatherburn).

1000-ppm Ammonia-Nitrogen Standard Stock Solution:
Dissolve 0.4717 g ammonium sulfate in deionized distilled water and dilute to 100 mL, or use Hellige standard R-2434 or equivalent.

Procedure

1. Dilute sample concentration to within a 10- to 100-ppm or 100- to 1000-ppm NH_3-N range.
2. Prepare standards from stock solution.
3. Place tubes for standards and samples in test tube rack. Samples and standards should be prepared and developed together.
4. Add 5 mL phenol/nitroprusside solution to each tube; include a tube for a reagent blank. An automatic air displacement pipettor is recommended for convenience.
5. Fill a Microcap with sample or standard and drop into tube containing phenol/nitroprusside solution without contacting rim of tube. Seal tube and shake vigorously about 10 times. (No more than 1/2 hour should be allowed to elapse before immersion of all samples in the warm water bath; the number of samples that can be prepared in this interval will depend on the operator's speed.) Repeat for all tubes. Breakage of the Microcap during shaking is inconsequential.
6. Immediately after adding 5 mL alkaline hypochlorite solution to each tube, replace cap and shake vigorously.
7. Immerse test tube rack in 37°C bath for 15 minutes.

8. Cool to approximately room temperature with cold tap water and promptly read absorbance vs. deionized distilled water (to allow detection of high blanks) at 635 nm (for 10- to 100-ppm NH_3-N range) or at 520 nm (for 100- to 1000-ppm range).

Calculations

Subtract absorbance of the blank from that of each standard or sample. Calculate regression equation for standards. Over the ranges of 10 to 100 ppm and 100 to 1000 ppm NH_3-N, response should be sufficiently linear to allow use of the regression equation for determining sample values (routinely $r^2 = 0.999+$). Between 1000 and 3000 ppm, the curve is usable, though non-linear, and graphic methods are recommended. Multiply result by appropriate dilution factor.

Notes on Procedure

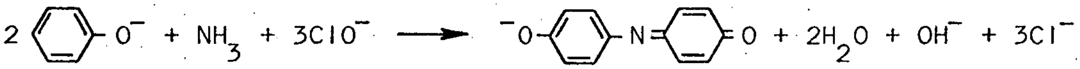
Hampson (1977) states that nitrogen from nitroprusside can enter the indophenol blue molecule and cause high blanks (see also: Interferences). High blanks have not been found to be a problem in the 10- to 1000-ppm NH_3-N range, but if blanks are found to be too high for determination of very low concentrations of ammonia, other catalysts (e.g., ferrocyanide) should be considered.

A spectrophotometer cell with a 1-cm light path has been used in our laboratory. A longer light path may be required for determination of lower ammonia concentrations.

A quick alternative to use of the dispenser supplied with the Microcaps follows. Prepare standard or sample in a small wide-mouthed container, such as a scintillation vial. Grasp the Microcap near the top with forceps and place in the container, leaning the Microcap against the rim. To fill Microcap, tilt container until Microcap is nearly horizontal. Adequate headspace must be left in the container to avoid spilling the sample. Remove Microcap from container with forceps, keeping Microcap horizontal. Remove excess liquid from outside of Microcap by gently scraping its entire length against rim of container. Do not tilt Microcap from horizontal until this step is completed. Relative standard deviations of less than 1.5% easily can be achieved using this method.

Theory

The indophenol blue (or "phenate", or "phenol/hypochlorite") method is based on the Berthelot color reaction catalyzed by nitroprusside (Scheiner):



Ammonia is converted to monochloramine between pH 9.7 and 11.5. Losses to dichloramine, nitrite, etc. occur above pH 11.5. Monochloramine reacts with phenol in the presence of chlorine to form indophenol blue via intermediates (Hampson).

Interferences

Weatherburn does not discuss interferences with the phenol/hypochlorite reaction, but other authors have investigated the subject. Hampson (1977) has reported that aliphatic amines and nitrite suppress color development significantly when present in excess of the quantity of ammonia in the sample. Zadarojny et al. described the effects of amino acids, urea, and 24 inorganic electrolytes on the analysis of a 0.2-ppm NH_3-N solution (expressed as per cent recovery). Apparent recoveries of 109 to 214% resulted from additions of 100 ppm of KCN, KSCN, Na_2S, NaF, $CuSO_4$, $CoCl_2$, and NiCl; recoveries of 38 to 93% were produced by additions of $NaNO_2$, $Na_2S_2O_2$, $HgCl_2$, and $AlCl_3$ at 100 ppm, and of L-cystine, L-methionine, and L-phenylalanine at 0.2 ppm amino acid-N. Interference by electrolytes was not evident below 5 ppm.

Gravitz and Gleye (1975) report the formation of an interfering substance having an absorbance maximum at 640 nm when the standards are exposed to sunlight. Standards so affected fail to follow Beer's law, and absorbance values for blanks are high. The interfering substance has been tentatively identified as indophenol, formed with nitrogen from the nitrosyl group of the nitroprusside molecule. In our laboratory, the test has been performed routinely under flourescent lighting, and these problems have not been encountered. If desired, light may be excluded from the reaction mixture by wrapping the test tubes in aluminum foil. This procedure is recommended for samples with low ammonia concentrations. Use of a vacuum-operated flow-through spectrophotometer cuvette minimizes light exposure during sample transfer.

Observations on one variation of the method may not be applicable to another. Presumably, certain interferences (including color) are minimized in Weatherburn's version by the 500-fold dilution of the sample in the reagents. In our laboratory, this method has yielded results for ammonia concentration in oil shale process waters comparable to those obtained by distillation and titration (Standard Methods), and no color interference has been observed.

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