DETERMINATION OF NITRITE IN HARDENED CONCRETE
Chemical Procedure #C-20.0 (Revised 02/01/2005)
(Adapted from W. R. Grace Procedure by Ara A. Jeknavorian)
Type of Material Tested: Hardened Concrete Cores

** * This procedure does not purport to address all the safety concerns associated with its use. It's the responsibility of the user of this procedure to establish appropriate health and safety practices and dispose of hazardous materials in an approved manner.*

SIGNIFICANCE

This method is based on W. R. Grace Procedure #809 developed at the Washington Research Center in 1980. North Carolina specifications require a corrosion inhibitor (CI) in an amount determined by the mix design of the concrete. Since Corrosion Inhibitors normally contain 20.9% Nitrite, if, for example, 5.4 gallons of CI were added, the weight of only the nitrite portion per cubic yard would be 12.2 lbs.

$$(0.209)(5.4 \text{ gals CI})(1.3 \text{ Spgr.})(8.33 \text{ lbs water/gal}) = 12.2 \text{ lbs } NO_2^-$$

Due to the batch variation in concrete and variation in testing, North Carolina specifications permit the test results to be a minimum of 9.1 lbs/yd^3 in this case, however, CI requirements now are based on individual contracts.

SCOPE

A concrete sample is drilled, ground, and a representative portion is extracted with water, filtered, and the filtrate is diluted to a known volume. An aliquot is treated with sulfanilic acid which is diazotized by the nitrite. The diazotized sulfanilic acid is then coupled with N-(1-naphthyl) ethylenediamine to produce a purple color, which is measured by a spectrophotometer from 520 to 540 nm.

LIMITATIONS

Strong oxidizing, reducing, and complexing agents and colored substances may interfere. Furthermore, the amount of extractable nitrite vs. theoretical nitrite as a function of nitrite addition rate and cement content has not been evaluated. Analysis of concrete standards containing 658 pcy cement and 2% s/s calcium nitrite/cement indicate 85% recovery of the theoretical nitrite.

APPARATUS

1. Hammer Drill with 5/8" bit
2. Analytical balance, accurate to ± 0.1 mg.
3. Laboratory shaker (Burrell) with a 12 sample capacity
4. Erlenmeyer flasks, 500-mL. (Plastic or Nalgene© preferable)
5. Pipettes (Class A), 2.00 mL., 5.00 mL, 10.00 mL, 20.00 mL, and 50.00 mL
6. Volumetric flasks (Class A), 100 mL, 500 mL, and 1000 mL
7. Graduated cylinders, 50 mL, 200 mL
8. Funnels, 100 mm. (Belart #14646, Scienceware Urbanti High Speed)
9. Filter paper,.Whatman No. 44; 185 mm
10. Spectrophotometer with scanning capabilities
11. Glass cuvettes

REAGENTS

1. Sulfanilic Acid, ACS reagent grade.
2. Sulfanilic Acid, 0.6% Solution: Dissolve 0.60 g of sulfanilic acid in 70 mL of hot distilled water, cool the solution, add 20 mL of conc. HCl and dilute to 100 mL (volumetric flask) with distilled water and mix.

3. N-(1-Naphthyl) Ethylenediamine Dihydrochloride Solution (NED): Dissolve 0.60g of NED in 50 mL of distilled water acidified with 1mL of conc. HCl. Dilute to 100 mL (volumetric flask) and mix. Keep the solution refrigerated and prepare fresh weekly.
4. Sodium Nitrite, crystals, ACS reagent grade.
5. Sodium Nitrite – Primary Standard Solution: Dissolve 2.8g of sodium nitrite in distilled water and dilute to 1 liter in a volumetric flask.
6. Sodium Nitrite – Secondary Standard Solution: Dilute the primary standard solution 50/500 using a 50 mL volumetric pipette and a 500 mL volumetric flask.
7. Phenolphthalein indicator solution, 1% : Dissolve 1 gram of phenolphthalein in 95% ethyl alcohol.
8. Hydrochloric Acid, 1N: Dilute 8.6 mL of conc. HCl to 100 mL and mix.

PROCEDURE

This procedure is divided into three parts:
A. Preparation of Standard Calibration curve for nitrite ion.
B. Sample preparation extraction and nitrite determination.
C. Calculation.

Part A: Preparation of Standard Calibration Curve for Nitrite Ion

1. Using the appropriate volumetric pipettes and three 500 mL volumetric flasks, dilute the Secondary Sodium Nitrite Standard Solution 5mL/500, 10 mL/500, and 15mL/500.
2. Pipette 10 mL of each of the above solutions into separate 100 mL volumetric flasks containing approximately 50 mL of distilled water. Run a blank using only distilled water in a fourth flask.
3. To each 100-mL flask, add 2 mL of sulfanilic acid reagent, swirl, and allow to stand for 5 minutes.
4. Add 2 mL NED reagent, dilute to volume, and allow to stand for 10 minutes.
5. Zero the spectrophotometer at the proper wavelength (we use 540 nm), using the reagent blank in the sample cell.
6. Measure the absorbance of each Nitrite Standard at 540 nm.
7. Calculate the calibration curve from concentration in μg/mL nitrite vs. absorbance).

Part B: Typical Calibration Data for Standard Calibration Curve

The primary Sodium Nitrite Solution contains 2.800 g/L.

$$\frac{NO_2}{NaNO_2} = \frac{46}{69} = 0.6667$$

(2.8 g/L)(0.6667)(10^6 microgram /g)(50/500) = 186676 microgram /L NO_2^- = 186.7 microgram /mL NO_2^- in the Secondary Solution

Standards	Dilutions	Concentration in microgram /mL NO_2^-	Typical Absorbance*
1	186.7 microgram/mL (5mL/500)(10 mL/100)	0.187	0.182
2	186.7 microgram /mL (10 mL/500)(10 mL/100)	0.373	0.365
3	186.7 microgram /mL (15 mL/500)(10 mL/100)	0.560	0.550

*For example
Calculate the calibration curve by plotting concentration in microgram /mL vs. absorbance.

Part C: Sample Preparation, Extraction and Nitrite Determination

1. Drill two specimens from different locations on the side of a properly hardened concrete cylinder to make up the sample. The drillings should be 5/8" to 3/4" in diameter, approximately 2" deep, and on opposite sides of the cylinder. All relative wall fragments should be included with the sample.
2. Grind and pulverize the combined drillings to a uniform consistency.
3. Using an analytical balance, weigh out a representative 2.0 g sample.
4. Quantitatively transfer the sample to a 500-mL Erlenmeyer flask. Add 200 mL of distilled water using a graduated cylinder.
5. Place the stoppered Erlenmeyer flask into a laboratory shaker and agitate it for 30 minutes. Stop the shaker and allow the sample to settle.
6. Carefully decant the liquid through Whatman #44 filter paper into a 500-mL volumetric flask, leaving the residue in the Erlenmeyer flask.
7. Add a second 200 mL portion of distilled water to the flask containing the residue and agitate it in the shaker for 10 minutes. Stop the shaker and allow the sample to settle.
8. Repeat step 6, using the same 500-mL volumetric flask.
9. Repeat the extraction a third time, using 75 mL of distilled water.
10. After all the extractions are collected, dilute the volumetric flask to the line and mix.
11. From the 500 mL volumetric flask, transfer by pipette a 3 mL aliquot into a 100-mL volumetric flask containing 50 mL of distilled water. Add 2 drops of phenolphthalein indicator and neutralize the solution with 2 drops of 1N HCl. Add 2.00 mL of sulfanilic acid by pipette, swirl, and allow to stand for 5 minutes. A reagent blank should be run containing distilled water and the reagents.
12. Add 2.00 mL of N-(1-Naphthyl) ethylenediamine dihydrochloride reagent (NED), dilute the flask to volume, and allow the solution to stand for 10 minutes.
13. Zero the spectrophotometer with the reagent blank in the absorbance mode.
14. Pour a portion of the sample into a glass cuvette to the line, place it into the spectrophotometer and read the absorbance at 540 nm.

Part D: Calculations for Nitrite Determination

1. Read the micrograms/mL nitrite equivalent to the absorbance from the standard calibration curve. Calculate the % NO_2^- in the sample as follows:

$$\frac{(\text{micrograms/mL } NO_2^- \text{ in Sample from standard curve}) * (\text{Dilution/Aliquot}) * (500)}{(\text{Sample wt., grams})\ (10^6)} = \text{Fraction } NO_2^-$$

NOTE:

(a) The aliquots pipeted from the 500 mL extraction
(b) filtrate should be adjusted such that the absorbance is within the range of 0.10 to 0.80.
(b) The % NO_2^- as calculated above does not take into account the % recovery factor of the nitrite. For a particular set of lab concrete standards containing 658 pcy cement with 2% s/s Ca $(NO_2)_2$, 96% recovery of the theoretical nitrite was obtained on 200 sets of samples in 1989.

2. **Sample Calculation**

Assuming a concrete cylinder to be tested has a unit wt. of 137.9 lbs/ft^3. A 1.9463-gram sample was weighed, extracted, filtered and brought to a volume of 500 mL. From the 500 mL filtrate, a 3:100 dilution was made with the appropriate reagents added. The sample was read at 540 nm. on a spectrometer and an absorbency of 0.313 was obtained. The calibration curve was established to be $y = 0.99999x + 0.0127$ where y = abs. and x = conc. in microgram/mL

$0.313 = 0.99999x + 0.0127$ therefore, $x = \frac{0.313 - 0.0127}{0.99999}$, x(conc.) = 0.300 microgram/mL NO_2^-

Calculating, $\frac{(0.300 \text{ microgram/mL})(100/3)(500)}{(1.9463)(10^6)} = 0.00257$ (NO_2^- fraction)

Unit weight = 137.9 lbs/ft^3 x 27 = 3,723 lbs/yd^3

Therefore, $(0.00257)(3{,}723 \text{lbs/yd}^3) = 9.6$ lbs NO_2^-/yd^3 of the concrete

Calculations used in the Determination of Nitrite in Concrete

CI is normally a 30% solution of $Ca(NO_2)_2$. CI's theoretically contain 20.9% nitrite based on the following calculations:

$$\frac{2(NO_2)}{Ca(NO_2)_2} = \frac{92}{132} = 0.70 \quad \text{or} \quad 70\% \ NO_2 \text{ in } Ca(NO_2)_2$$

$$0.70 \times 30.00\% = 21\% \ NO_2^-$$

A 30% solution of $Ca(NO_2)_2$, therefore, contains approximately 21% NO_2. In practice, the actual figure used is 20.9%.

Example of units conversion to lbs/yd^3:

$(19.8 \text{ L/m}^3)(2.642 \times 10^{-1} \text{ gal/L}) = 5.23 \text{ gal/m}^3$

$\frac{5.23 \text{ gal/m}^3}{1.308 \text{ yd}^3/\text{m}^3} = 4.0$ gal/yd^3 Corrosion Inhibitor in Concrete

therefore, to determine NO_2^- content in Concrete:

$(0.209)\ (4.0 \text{ gal/yd}^3)(1.3)(8.33 \text{ lbs/gal}) = 9.1 \text{ lbs/yd}^3$ NO_2^- in concrete,

where, 0.209 = decimal percentage NO_2^- in a Corrosion Inhibitor on average
1.3 = specific gravity of CI
8.33 lbs/gal = weight of water per gallon
4.0 gal/yd^3 = CI in Concrete (for this example only)

As stated previously, North Carolina specifications requires a corrosion inhibitor in an amount determined by the mix design of the concrete. Since CI's normally contain 20.9% Nitrite if, for example, 5.4 gallons were added per cubic yard, the weight of only the nitrite portion per cubic yard would be 12.2 lbs.

$$(0.209)\ (5.4\ \text{gal/yd}^3)\ (1.3)\ (8.33\ \text{lbs/gal}) = 12.2\ \text{lbs}\ NO_2^-$$

Materials and Tests Chemical Lab uses the following procedure to determine the nitrite ion content of inorganic corrosion inhibitors:

1. Pipet 1 mL of the product to be tested into a 1000 mL volumetric flask and dilute to the line with distilled water.
2. Pipet 5 mL of the solution from #1 into a 50 mL volumetric flask and dilute to the line with distilled water.
3. Pipet 2 mL of the solution from #2 into a 100 mL volumetric flask containing 50 mL of distilled water, add 2 drops of phenolphthalein, 2 drops of 1N HCl, and 2 mL of sulfanilic acid reagent, mix, and allow to stand for 5 minutes.
4. Pipet 2 mL of N-(1-Naphthyl) ethylenediamine dichloride reagent (NED), and allow to stand 10 minutes to fully develop color.
5. Measure the absorbance of the standards along with the sample on the spectrometer at a wavelength of 540 nm.
6. Calculate nitrite content based on the standard calibration curve and report as percent nitrite.

End.

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