# Free Ammonia Analysis in the Presence of Monochloramine Using CHEMetrics® Instrumental Ammonia (HBA) Vacu-vials Test Kit, Cat. No. K-1413

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## Overview

Chloramination, the disinfection of water with chloramines, is routinely used as the secondary disinfection process to maintain long-lived residuals in water distribution pipelines. Monochloramine is formed by the reaction of free ammonia ($NH_3$ and $NH_4^+$) with free chlorine. Without free ammonia residual, di- and tri-chloramines are formed by the reaction of excess free chlorine with monochloramine. To prevent formation of these less desirable chloramines, chloramination processes are optimized for monochloramine production in drinking water distribution systems by maintaining a free ammonia residual. Additionally, insufficient free ammonia and excess free chlorine can lead to formation of hazardous trihalomethanes in distribution systems. Conversely, excess free ammonia increases the potential for undesirable nitrification. A sudden drop in free ammonia in the system suggests that it is being converted to nitrite.

Monitoring free ammonia concentrations in addition to the monochloramine and free chlorine levels can help operators optimize their chloramination processes.

## Sequential Monochloramine and Free Ammonia Analysis

The most expeditious way to measure free ammonia in the presence of monochloramine using CHEMetrics instrumental kits is to use Ammonia Vacu-vials® Test Kit, Cat. No. K-1413.

The hydroxybenzyl alcohol (HBA) chemistry employed with the K-1413 Ammonia Test Kit measures the sum of free ammonia and monochloramine (referred to as “Total Ammonia”). Free ammonia first reacts with hypochlorite to form monochloramine, and monochloramine then reacts with HBA in the presence of sodium nitroferricyanide to form a green-colored complex.

To determine free ammonia only, two K-1413 Vacu-vials ampoules are required. The first ampoule is used to measure only monochloramine by excluding addition of hypochlorite to the sample. The second ampoule is used to determine “total ammonia.” To determine the free ammonia concentration, the monochloramine result is subtracted from the total ammonia result. This subtraction step is accomplished easily with CHEMetrics photometers so that the free ammonia test result is displayed directly on the instrument. Procedures for measuring free ammonia with CHEMetrics multianalyte photometers as well as spectrophotometers are described below.

## V-3000 Test Procedure Using Program # 117

*Instrument Set-up*

1. Select Program 117 under the Photometry menu. Perform the zero adjustment procedure using the sealed ZERO ampoule supplied in the K-1413 Vacu-vials kit.
2. Press the FORM key so that **NH2Cl-N** is displayed in the right-hand corner of the display. The measurement range will be 0.00 – 1.60 ppm.

*Free Ammonia Test Procedure*

3. To measure monochloramine only, complete steps 1 – 3 and 5 – 8 according to the 0 – 3 ppm Test Procedure in the K-1413 kit instructions. Do NOT perform step 4.
4. Insert the clean, dry ampoule as prompted and press START/ENTER.
5. If desired, the monochloramine concentration can be obtained at this point. For results expressed in ppm monochloramine as chlorine (ppm $NH_2Cl$-N), press the FORM key to toggle from NH2Cl-N to NH2Cl-Cl2. Record the result.
   *IMPORTANT NOTE: Press the FORM key again to toggle back to NH2Cl-N before continuing with the free ammonia test.*
6. Leave the monochloramine ampoule in the V-3000. Press the CAL\ZERO key. Select Measure blank value.
7. Confirm Start measurement by pressing the START/ENTER key.
8. The blank absorbance value will be displayed, and a message will confirm the blank measurement was successful. Press the START/ENTER key to accept the value. Remove the monochloramine test ampoule from the V-3000.
9. Use a new ampoule to measure “total ammonia” (free ammonia + monochloramine) by completing steps 1 – 8 of the 0 - 3 ppm Test Procedure in the K-1413 kit instructions.
10. Insert the clean, dry ampoule as prompted and press START/ENTER.
11. Record the free ammonia test result, expressed in ppm ammonia-nitrogen.

## V-2000 Test Procedure Using Program # 12

*Instrument Set-up*

*Refer to Section 3-2 in the V-2000 Operator’s Manual, Procedure A – Zeroing, Program Selection and Measuring.*

1. Zero the V-2000 using the sealed ZERO ampoule supplied in the K-1413 Vacu-vials kit by pressing the **zero** key.
2. Press the **prgm** key and enter Program 12. Press the **yes** key.

*Free Ammonia Test Procedure*

3. To measure monochloramine only, complete steps 1 – 3 and 5 – 8 according to the 0 – 3 ppm Test Procedure in the K-1413 kit instructions. Do NOT perform step 4.
4. Insert the clean, dry ampoule and press the **meas** key.
5. If desired, record the monochloramine test result, expressed as ppm monochloramine as nitrogen (N), obtained in Step 4. To convert this result to ppm monochloramine as chlorine ($NH_2Cl$-$Cl_2$), multiply by 5.
6. Leave the monochloramine ampoule in the V-2000. Press the **setup** key and use the ▲ or ▼ keys until “BLANK” is displayed, then press the yes key.
7. “SET BLNK?” will be displayed, press the **yes** key.
8. “SAMPLE?” will be displayed.
9. Cover the ampoule with the light shield, then press the **yes** key. The instrument will read the ampoule, display an absorbance value momentarily, and then move to the next setup function.
10. Press the **meas** key to exit the setup menu. The instrument display will return to the Program 12 screen. The “blank” icon will be displayed in the upper center of the LCD display. Remove the monochloramine test ampoule from the V-2000.
11. Use a new ampoule to measure “total ammonia” (free ammonia + monochloramine) by completing steps 1 – 8 of the 0 - 3 ppm Test Procedure in the K-1413 kit instructions.
12. Insert the clean, dry ampoule and press the **meas** key.
13. Record the free ammonia test result in ppm ammonia-nitrogen ($NH_3$-N).

**Generalized Test Procedure for Spectrophotometers**

*Instrument Set-up*

1. Set the wavelength to 690 nm and set the instrument to absorbance mode. Use the sealed ZERO ampoule supplied in the K-1413 kit to zero the instrument.

*Free Ammonia Test Procedure*

2. To measure monochloramine only, complete steps 1 – 3 and 5 – 8 according to the 0 – 3 ppm test procedure in the K-1413 kit instructions. Do NOT perform step 4.
3. Insert the clean, dry ampoule into the instrument.
4. If desired, the monochloramine concentration can be determined at this point. Record the displayed absorbance value, then use the equation below to convert absorbance to ppm monochloramine as chlorine.
   ppm $NH_2Cl$-$Cl_2$ = 4.42(abs) + 0.05
5. Leave the monochloramine ampoule in the instrument. Re-zero the instrument. Remove the monochloramine test ampoule from the instrument.
6. Use a new ampoule to measure “Total Ammonia” (free ammonia + monochloramine). Complete steps 1 – 8 of the 0-3 ppm Test Procedure in the K-1413 kit instructions.
7. Insert the clean, dry ampoule into the instrument.
8. Record the absorbance value. Use the equations below to convert absorbance to the free ammonia test result expressed as ppm ammonia-nitrogen ($NH_3$-N).
   Eq 1 Result = 4.42(abs) + 0.05
   ppm $NH_3$-N = Eq 1 Result ÷ 5