Metrohm

Thermo. Titr. Application Note No. 71

Title:	**Determination of Ammonium Ion by Titration with Hypochlorite**

***Scope*:**	Determination of ammonium ion in ammonium salts and mixtures containing ammonium ion

***Principle*:**	Hypochlorite ions react with bromide ions to form hypobromite ions, which in turn rapidly oxidize ammonium ions to nitrogen. Hypobromite reacts more rapidly with ammonium than hypochlorite, and is formed *in situ* (Vogel, 1961). The titration is carried out with in a solution containing bromide and bicarbonate: $3OCl^- + 3Br^- \rightarrow 3OBr^- + 3Cl^-$ $2NH_3 + 3OBr^- \rightarrow N_2 + 3Br^- + 3H_2O$ $3OCl^- + 2NH_3 \rightarrow N_2 + 3Cl^- + 3H_2O$

Reagents:	*~0.25mol/L NaOCl solution.* Prepare from commercial concentrated sodium hypochlorite solution. Sodium hypochlorite solution from a swimming pool supply shop is satisfactory. Dilute 185-200mL of concentrated solution to 1000mL. Store in a brown glass bottle. *Bromide/bicarbonate solution.* Dissolve 200g KBr and 120g $KHCO_3$ in DI water and make to 1000mL with DI water. Store in a brown glass bottle. *1mol/L $Na_2S_2O_3$ solution.* Dissolve 248.2 A.R. $Na_2S_2O_3.5H_2O$ in DI water and make to 1000mL. Store in a brown glass bottle. *0.04mol/L KIO_3 solution*. Dry at least 10g A.R. KIO_3 at 120ºC for 2 hours. Cool in a dessicator, and weigh accurately approximately 8.56g. Make to 1000mL with DI water in a volumetric flask. *4mol/L KI solution.* Dissolve 166g A.R. KI in DI water, and make to 250mL with DI water. Store in a brown glass bottle. *Glacial acetic acid.* *Sulfuric acid, 25% w/v.*

Method:

Basic Experimental Parameters:

Titrant delivery rate (mL/min.)	4
Titration blank (mL)	0.050
Bromide/bicarbonate solution addition (mL):	10
No. of exothermic endpoints	1
Delay start of titration (secs.)	5
Data smoothing factor (DSF)	60
Stirring speed (802 stirrer)	8

Basic Method: The sample added to the titration vessel should ideally contain approximately 6 - 8mmole NH_4^+.

In the examples using reagent grade ammonium salts illustrated here, solutions were made to approximately 0.2mol/L with respect to NH_4^+, and added using a 800 Dosino. This was done to reduce errors in dispensing aliquots.

For the examples of commercial fertilizers illustrated here, weigh accurately approximately 1g of finely ground MAP, and transfer to a 250mL volumetric flask. Make to volume and mix well. Add a small magnetic spin bar, and stir contents for 10 minutes. Allow to stand for a few minutes to allow coarser solids to settle. The solution can be filtered if desired, but this is not necessary. Take a 25mL aliquot for analysis. This will contain the equivalent of approximately 0.1g of original material.

Standardization of NaOCl titrant.
It is necessary to trace the calibration of the NaOCl solution to a recognized primary standard. NaOCl solutions are conveniently calibrated against standard $Na_2S_2O_3$ solution, but $Na_2S_2O_3$ is not a recognized primary standard. However, $Na_2S_2O_3$ solutions may be standardized against solutions of KIO3, which is a primary standard.

*Standardization of $Na_2S_2O_3$ solution***.** Prepare a series of solutions in titration vessels as follows:

mL KIO_3 solution	mL DI water	mL 25% H_2SO_4
5	25	5
10	20	5
15	15	5
20	10	5
25	5	5

Prepare a titration program with a $Na_2S_2O_3$ titrant dose rate of 4mL/min. and a digital filtration value of 60. Immediately prior to the titration of each prepared solution, and while the solution is stirring, add 10mL 4mol/L KI solution. This can be added conveniently from a Dosino

Prepare a regression analysis, plotting mmol KIO_3 (x-axis) against mL $Na_2S_2O_3$ (y-axis), and calculate the gradient to the line of best fit. The molarity is calculated as 6/gradient. This is derived from:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$[I_2 + 2e \rightarrow 2I^-] \times 3$$

$$[2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e] \times 3$$

$$IO_3^- + 6S_2O_3^{2-} + 6H^+ \rightarrow 3S_4O_6^{2-} + 3H_2O + I^-$$

So that 1 mol IO_3^- ≡ 6 mol $S_2O_3^{2-}$

Standardization of NaOCl against $Na_2S_2O_3$. Because NaOCl solutions do not possess good long term stability, it is necessary to check the molarity of the NaOCl on a regular basis, say every few days. It is thus convenient to create a special standardization program in Titrotherm, where the NaOCl solution is dispensed as a pre-dose which is titrated with $Na_2S_2O_3$. Prepare solutions of 25mL DI water to which has been added 5mL 4mol/L KI and 5mL glacial acetic acid. In successive titrations, program the addition of 2, 4, 6, 8 and 10mL of NaOCl prior to the titration.

Prepare a regression analysis, plotting mmol $Na_2S_2O_3$ (from the volume of $Na_2S_2O_3$ titrated) on the

x-axis, and mL of NaOCl dispensed on the y-axis. The molarity is calculated as 0.5/gradient. This is derived from:

$$ClO^- + H_2O + 2e \rightarrow Cl^- + 2OH^-$$

$$2I^- \rightarrow I_2 + 2e$$

$$ClO^- + H_2O + 2I^- \rightarrow Cl^- + I_2 + 2OH^-$$

$$I_2 + 2e \rightarrow 2I^-$$

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$$

$$2S_2O_3^{2-} + ClO^- + H_2O \rightarrow S_4O_6^{2-} + Cl^- + 2OH^-$$

So that 2 mol $Na_2S_2O_3$ ≡ 1 mol NaOCl

Sample Preparation.

MAP Samples. Weigh accurately approximately 1g of finely ground MAP, and transfer to a 250mL volumetric flask. Make to volume and mix well. Add a small magnetic spin bar, and stir contents for 10 minutes. Allow to stand for a few minutes to allow coarser solids to settle. The solution can be filtered if desired, but this is not necessary.

A 25mL aliquot is taken for titration. This will contain the equivalent of approximately 0.1g of original material.

“Ammoniated” TSP sample. As for MAP samples, but weigh out accurately approximately 2g of material.

Titration. Set up a titration program with a NaOCl titration rate of 4mL/min, a digital filter value of 60, and a 10mL pre-dose of bromide/bicarbonate reagent

Examples:

Salts analyzed were reagent grade, but had been opened for some years (except for the $(NH_4)_2SO_4$, which was freshly opened)

Salt	*NH_4^+ content, %*	
	Theoretical	*Analyzed*
$(NH_4)_2SO_4$	27.32	27.26±0.007 (n=5)
$NH_4H_2PO_4$	15.68	15.71±0.005 (n=5)
$(NH_4)_2HPO_4$	27.31	27.22±0.010 (n=5)
$AlNH_4(SO_4)_4.12H_2O$	3.98	3.99±0.001 (n=5)

Fertilizers were supplied by a customer

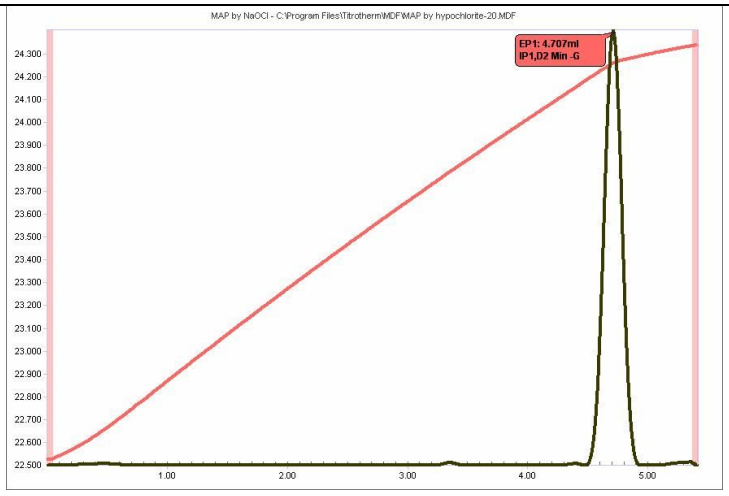
Sample	*Total Nitrogen*	
	As %N	*As % NH_4^+*
MAP #1	11.09±0.03 (n=9)	14.28±0.04
MAP #2	10.94±0.01 (n=8)	14.09±0.01
"ammoniated" TSP	3.08±0.01 (n=8)	3.97±0.01

Calculation:

$$\%NH_4^+ = \frac{((\text{Titre, mL} - \text{blank, mL}) \times \text{M NaOCl} \times 18.034 \times 100 \times 2)}{(\text{sample mass, g} \times 1000 \times 3)}$$

Titration Plot:

Legend:
Red = solution temperature curve
Black =second derivative curve (for endpoints)



Titrant calibration:

Gradient = 1.94674, molarity =0.5/gradient = 0.2568 mol/L