

## Thermo. Titr. Application Note No. H-048

**Title:** Standardization of disodium dimethylglyoximate for the determination of nickel

**Scope:** Standardization of disodium dimethylglyoximate by thermometric titration with standard Ni(II) solution.

**Principle:** Standardization of disodium dimethylglyoximate ( $\text{Na}_2\text{DMG}$ ) solution by titration with standard Ni solution to an exothermic endpoint in buffered ammonia solution. Two moles of DMG react with one mole of Ni(II). Acidic Ni solutions possibly containing Al(III) and Fe(III) should be complexed with tartrate prior to basification.

**Reagents:**

Titration: 0.5 mol/L disodium dimethylglyoximate. Dissolve 153.6 g disodium dimethylglyoximate (99% pure, FW = 304.21) in deionized water and make to 1000mL in a volumetric flask.

$\text{NH}_3/\text{NH}_4\text{Cl}$  buffer: Dissolve 17.5 g A.R.  $\text{NH}_4\text{Cl}$  in 172 mL A.R. conc.  $\text{NH}_3$  soln. Make to 250 mL with deionized water.

Kna tartrate solution, 450g/L.

Standard Ni solution, 0.1 mol/L. In the exercise described here, a reference sample of nickel oxide was kindly supplied by a nickel refinery. The stated purity was  $78.4 \pm 0.24\%$  Ni, determined by gravimetric analysis by the dimethylglyoxime method. Sufficient NiO to make 500mL of 0.1 mol/L solution was weighed into a 150mL beaker provided with a magnetic stirrer. 20mL concentrated  $\text{HNO}_3$  and 60mL  $\text{HClO}_4$  was added and heated with stirring until near boiling, continuing the heating until all the oxide was dissolved (a little colloidal silica remained). The solution was cooled and made to 500mL with DI water in a volumetric flask.

**Method:**

## Basic Experimental Parameters:

Titrant delivery rate (mL/min.)	2
No. of exothermic endpoints	1
Data smoothing factor	60
Stirrer speed	12*

Procedure: The sodium dimethylglyoximate was dispensed from a 10mL Dosino. The standard Ni solution was also dispensed from a Dosino, as was the  $\text{NH}_3/\text{NH}_4\text{Cl}$  buffer solution using the pre-dose function of the Titrotherm software.

If a Dosino is used to dispense the standard Ni solution, it is only necessary to add 30mL of DI water and 5mL KNa tartrate solution to the titration vessel prior to the determination. The tartrate solution is used to prevent interference from Al(III) and Fe(III) impurities in samples containing Ni, and is added in the case of high purity Ni solution to “matrix match”. The aim is to have a solution volume of 40-45mL prior to the titration. This higher than normal volume together with the high stirrer speed\* reduces the detrimental effect that the highly viscous nickel dimethylglyoximate precipitate has on the endpoint.

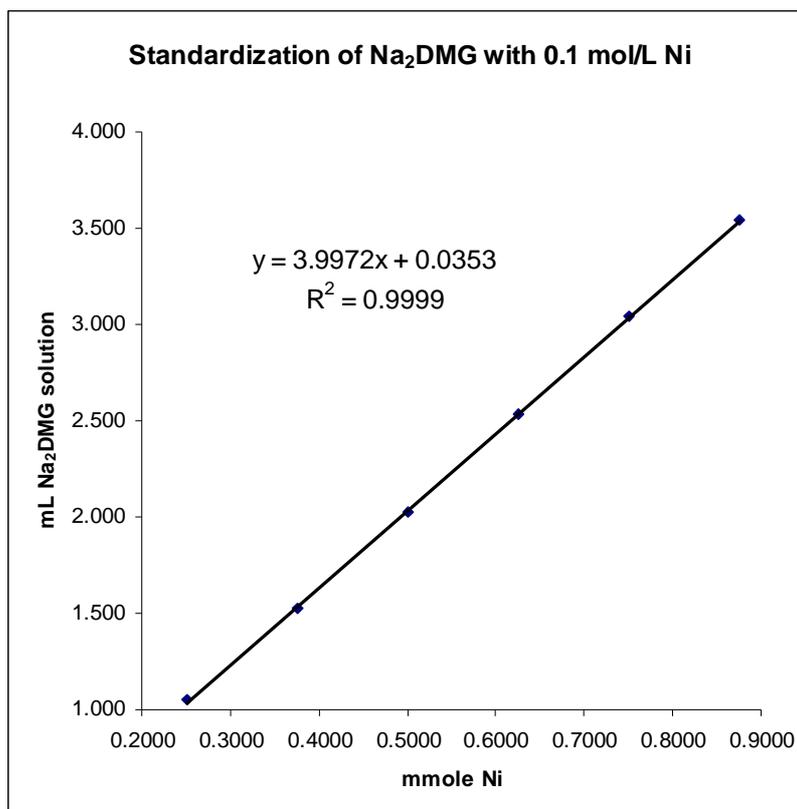
Equipment stained by the Ni dimethylglyoximate precipitate may be cleaned by soaking in a solution of a strong mineral acid; eg, 1 mol/L HCl. During the standardization exercise, the titration assembly was cleaned between each titration, and rinsed thoroughly with DI water.

<b>Results:</b>	Titration of aliquots of standard 0.10036 mol/L Ni(II) solution, dispensed by Dosino		
	mL Ni(II) soln.	mmole Ni	mL Na <sub>2</sub> DMG soln.
	2.50	0.2503	1.050
	3.75	0.3755	1.526
	5.00	0.5007	2.028
	6.25	0.6259	2.533
	7.50	0.7510	3.043
	8.75	0.8762	3.541

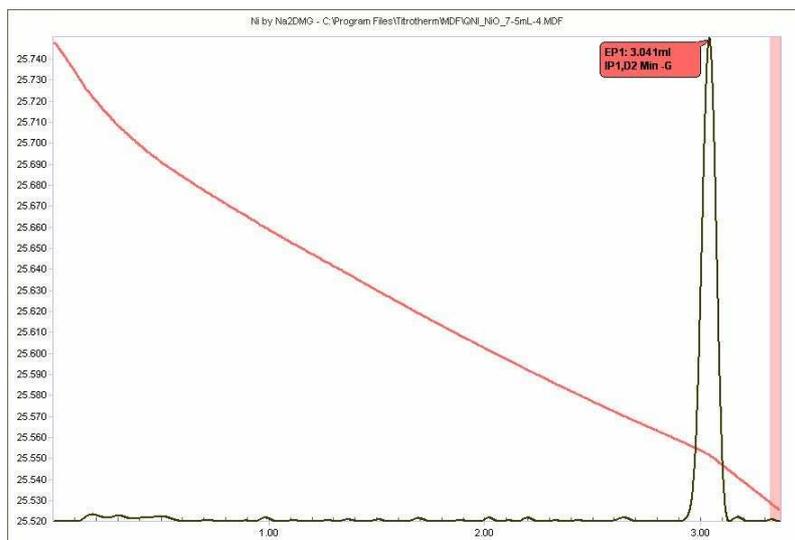
**Molarity Determination:**

Molarity Na<sub>2</sub>DMG =  
 2/gradient (since 1 mole Ni ≡ 2 mole DMG)  
 = 2/3.9972  
 = 0.5004 mol/L

Method blank =  
 y-intercept = 0.0353 mL



### Thermometric Titration Plot:



#### Legend:

Red = solution temperature curve

Black = second derivative curve

*Note that the solution temperature falls during the determination. Prior to the titration, an exothermic reaction (neutralization) occurs between the  $\text{NH}_3$  in the  $\text{NH}_3/\text{NH}_4\text{Cl}$  buffer and the mineral acids in the standard Ni solution. The exothermic formation of nickel dimethylglyoximate occurs against a background of falling solution temperature as a result of cooling.*