



# THE DOW CHEMICAL COMPANY

MIDLAND, MICHIGAN

## ANALYTICAL METHOD

EFFECTIVE: July 7, 1986  
SUPERCEDES: (NEW)

DOWM 100077

### Trace Copper, Manganese and Nickel in Sodium Hydroxide

#### 1. Scope

This method is applicable to the determination of nickel, manganese, and copper in sodium hydroxide (caustic soda) products by inductively coupled plasma atomic emission spectroscopy (ICP-AES). This method is applicable over the concentration range listed below on a 100% sodium hydroxide basis.

<u>Metal</u>	<u>Concentration Range, ppm</u>
Nickel	.09 - 18
Manganese	.09 - 18
Copper	.09 - 18

#### 2. Safety Precautions

2.1 Each analyst should be acquainted with potential hazards of the reagents, products, and solvents before commencing laboratory work. SOURCES OF INFORMATION INCLUDE: MATERIAL SAFETY DATA SHEETS, LITERATURE, AND OTHER RELATED DATA. Safety information on non-Dow products should be requested from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.

2.2 Sodium hydroxide is a serious skin and eye hazard. Chemical goggles and rubber gloves should be worn for protection. If eye contact occurs, wash the eyes continuously with water for a minimum of fifteen minutes and secure immediate medical attention. In the event of skin contact, wash the affected area with copious amounts of water.

2.3 Concentrated hydrochloric acid is used to acidify samples and constitutes a skin and eye hazard. Acidify sodium hydroxide samples in a fume hood. Chemical goggles and rubber gloves should be worn for protection.

2.4 Intense heat and ultraviolet radiation are emitted from the inductively coupled plasma source. Take care to prevent thermal burns due to direct contact with the source housing. View the source through the cobalt glass viewport to prevent eye injury. Consult the instrument manual for the ICP in use for appropriate safety precautions.

#### 3. Principle

The sodium hydroxide sample is dissolved in water, neutralized and acidified with hydrochloric acid, and diluted to a known volume with redistilled deionized water. The resulting solution along with an acid blank is then analyzed by ICP-AES for nickel, manganese, and copper.

#### 4. Apparatus

4.1 The Inductively Coupled Plasma-Scanning Atomic Emission Spectrometer, 35000 ICP, available from Applied Research Laboratories, 9545 Wentworth St., Sunland, CA 91040 equipped as given in Table II.

4.2 Ordinary laboratory equipment, including polypropylene volumetric flasks, an analytical balance, a hot plate, volumetric glassware, and a top-loader balance suitable for weighing to 0.01 grams.

#### 5. Reagents

5.1 Concentrated hydrochloric acid, available from Mallinckrodt Inc., Paris, KY 40361. Analytical reagent grade or equivalent.

5.2 Water, deionized and redistilled. The Corning Mega-Pure water still has been found to be satisfactory, available from Corning Glass Works, Houghton Pk., Corning, NY 14830.

5.3 Standard solutions of the required metals as needed. Prepare primary standards with reagent grade acids, metals, or metal salts. These are available from most chemical supply companies. Prepare dilute standards by volumetric dilution of the primary standard.

5.3.1 Nickel, copper; 1% primary standard. Place appropriate amount of pure metal or metal salt in 100 mL of concentrated nitric acid. Heat gently on hot plate to dissolve. Dilute to volume in a 500 mL volumetric flask with distilled, deionized water.

5.3.2 Manganese, 1% primary standard. Repeat step 5.3.1 substituting hydrochloric acid for nitric acid.

#### 6. Calibration

6.1 Prepare, by appropriate dilution, a 1.0  $\mu\text{g/mL}$  and a 0.2  $\mu\text{g/mL}$  standard of each metal from the primary standards.

6.2 Ignite the ICP, observing the conditions described in Table III and the instrument manual for the ICP in use.

6.3 Program sequential monitoring of the three analytical wavelengths.

6.4 Introduce the 1.0  $\mu\text{g/mL}$  standard into the ICP by means of the nebulizer tube and actuate the program. Integration time should be consistent with detection limit requirements. When intensities for each metal are obtained, input the 1.0  $\mu\text{g/mL}$  concentration for each into the data system.

6.5 Repeat the above step with the 0.2  $\mu\text{g/mL}$  standard of each metal along with redistilled deionized water. When intensities for each metal are obtained, input the concentration for each into the data system.

6.6 Now store generated calibration data in the instrument. Run 1.0 and 0.2  $\mu\text{g/mL}$  standards again. Compare results obtained with known concentrations to test validity of data. Recalibrate if necessary.

#### 7. Instrument Conditions

The operating conditions of the ICP-AES are given in Table III. Analytical wavelengths are given in Table I.

## 8. Procedure

8.1 Weigh a known amount of sample (to the nearest 0.01 g) into a 50-mL polypropylene volumetric flask. Since sodium hydroxide samples can have various concentrations of NaOH choose sample weight to equal 3% Na in 50-mL volume.

8.2 Dilute the sample to approximately 25 mL with redistilled deionized water.

8.3 Slowly introduce 7.5 mL of concentrated hydrochloric acid to acidify the sample.

8.4 Dilute to volume with redistilled deionized water.

8.5 Analyze the sample by ICP-AES as described in the Calibration Section, using the operating conditions as described in Table III.

8.6 Repeat steps 8.1 through 8.3 with the addition of a known amount of dilute standard metal solution to the flask and dilute to volume with redistilled deionized water. Choose the dilute standard metal solution from those prepared in Section 6.1.

8.7 Repeat step 8.5. Determine recovery for each metal spiked.

## 9. Calculations

9.1 The ICP-AES 35000 has a direct readout concentration mode from which  $\mu\text{g/mL}$  are taken as compared to the standard. Compare the sample concentration of metal in sodium hydroxide products by the following formula:

$$M = \frac{A \times B \times 10,000}{C \times D \times E}$$

where: A =  $\mu\text{g/mL}$  metal in diluted sample (blank corrected)  
 B = total dilution volume of sample (mL)  
 C = weight of sample (g)  
 D = % NaOH  
 E = % recovery of metal (9.2)  
 M = concentration of metal in sample (ppm on 100% sodium hydroxide basis)

### 9.2 Calculations for % recovery of added metal standard

$$D = \frac{x - z}{y} \times 100$$

where: x =  $\mu\text{g/mL}$  metal (sample + added metal)  
 y =  $\mu\text{g/mL}$  metal added  
 z =  $\mu\text{g/mL}$  metal (sample only)  
 D = % recovery of metal

## 10. Precision and Recovery

10.1 Data obtained from this procedure indicate a relative standard deviation and relative precision at the 95% confidence level as follows:

<u>Metal</u>	<u>Ni</u>	<u>Mn</u>	<u>Cu</u>
Relative Standard Deviation (%)	2.3	2.4	5.2
Relative Precision at the 95% Confidence Level (+%)	4.6	4.8	10

These results were obtained by multiple analyses of a sample containing 0.1  $\mu\text{g}$  of each of the three metals for detection limits equivalent to 1.85 ppm on a 100% caustic basis.

10.2 Recoveries of each metal are summarized below. (See 12.1)

<u>Metal</u>	<u>Ni</u>	<u>Mn</u>	<u>Cu</u>
Average Recovery (%)	83.6	78.4	86.2
Range (%)	80 - 87	76 - 81	75 - 91

## 11. Limit of Detection

11.1 The detection limits (defined as three times the relative standard deviation of the background noise) for each metal are given below.

<u>Metal</u>	<u>Ni</u>	<u>Mn</u>	<u>Cu</u>
Limit of Detection (100% Sodium Hydroxide Basis)	0.05	0.003	0.02

## 12. Notes

12.1 The low recoveries of a 0.1  $\mu\text{g}$  spike (equivalent to 1.85 ppm on a 100% sodium hydroxide basis) are due to viscosity differences between the standard solutions and the sodium hydroxide sample solutions. The uptake of a sodium hydroxide sample solution, by the nebulizer, is considerably slower than that of standard solutions. Use of a peristaltic pump may eliminate the low recoveries.

12.2 The use of background correction is necessary due to the large background shifts observed when the sodium hydroxide samples (3% Na) are being analyzed.

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Table I

## ICP Wavelength for Trace Metals

<u>Metal</u>	<u>Wavelength (A)</u>
Copper	3273.96
Manganese	2576.1
Nickel	2316.04

Table II

## Standard Equipment

Power Amplifier	2500 Watts
Source	ICP
Nebulizer	TR-30-A3 Concentric (Meinhardt Assoc.)
Grating	1200 grooves/mm
Photomultiplier	R-106 (Hamamatsu, Inc.)

Table III

## Standard Operating Conditions

Incident Power	1200 Watts
Reflected Power	<5 Watts
Plasma Flow	1.0 L/min (argon)
Coolant Flow	11.5 L/min (argon)
Nebulizer Flow	1.0 L/min (argon)
Sample Uptake	1.5 mL/min (free-flow)