Manganese, atomic absorption spectrometric, chelation-extraction

Parameter and Code:
Manganese, dissolved, I-1456-85 (µg/L as Mn): 01056

1. Application

This method may be used to analyze water and brines containing from 1 to 100 µg/L of manganese. Brines containing more than 100 µg/L need either to be diluted or to be read on a less expanded scale. Samples containing more than 100 µg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method, providing that the interference limits discussed in that method are not exceeded.

2. Summary of method

Manganese is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with chloroform. The extract is evaporated to dryness, treated with hot nitric acid to destroy organic matter, dissolved in hydrochloric acid, and diluted to a specified volume with demineralized water. The resulting solution is aspirated into the air-acetylene flame of the spectrometer.

3. Interferences

Concentrations of iron to 4 X 10^6 µg/L do not interfere; higher concentrations were not tested.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

Grating ---------- Ultraviolet
Wavelength ---------- 279.5 nm
Source (hollow-cathode lamp) ---------- Manganese
Oxidant ---------- Air
Fuel ---------- Acetylene
Type of flame ---------- Oxidizing

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution,* 4 g/100 mL: Dissolve 4 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromocresol green indicator solution,* 0.1 g/100 mL: Dissolve 0.1 g bromocresol green in 100 mL 20-percent ethanol.

5.3 *Chloroform.*

5.4 *Hydrochloric acid, 4M:* Mix 333 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.5 *Manganese standard solution I,* 1.00 mL = 100 µg Mn: Dissolve 0.1000 g manganese flakes in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.6 *Manganese standard solution II,* 1.00 mL = 1.00 µg Mn: Immediately before use, dilute 10.0 mL manganese standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.7 *Sodium hydroxide,* 0.25*M*: Dissolve 10 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample containing less than 5 µg Mn (50 mL max) into a 125-mL separatory funnel. Adjust the volume to approx. 50 mL.

6.3 Prepare a blank and at least six standards, and adjust the volume of each to approx. 50 mL with demineralized water.

6.4 Add 2 drops bromocresol green indicator solution and adjust the pH of each sample, standard, and blank to 4.0 (light olive-green color) with the addition of 0.25*M* NaOH.

6.5 Add 5.0 mL APDC solution and mix.

6.6 Add 10 mL chloroform and shake for 2 min.

6.7 Allow the phases to separate and drain the chloroform phase into a 100-mL beaker.

6.8 Repeat the extraction with an additional 10 mL chloroform and drain the chloroform phase into the same beaker.

6.9 Place the beaker on a steam bath and evaporate just to dryness.

6.10 Hold the beaker at a 45° angle, and slowly add 2 mL concentrated HNO_3 (sp gr 1.41), rotating the beaker to effect thorough contact of the acid with the residue (**CAUTION**-NOTE 1).

NOTE 1. If acid is added to the beaker in a vertical position, a violent reaction may occur accompanied by high heat and spattering.

6.11 Place the beaker on a hotplate at low heat and evaporate just to dryness.

6.12 Add 2 mL 4*M* HCl and heat, while swirling, for 1 min.

6.13 Cool and transfer the solution to a 10-mL volumetric flask and dilute to volume with demineralized water.

6.14 While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration control to set the digital display to read concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

Determine the micrograms per liter of dissolved manganese in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of manganese that exceed the working range of the method. Repeat those analyses and multiply by the proper dilution factors.

8. Report

Report manganese, dissolved (01056), concentrations as follows: less than 10 µg/L, nearest microgram per liter; 10 µg/L and above, two significant figures.

9. Precision

Precision for dissolved manganese for three samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
6	22.2	16
6	121	7
6	291	5