thermoscientific

Determination of transition metals by ion chromatography

Keywords
Ion chromatography, IC, Dionex ICS-5000$^+$, Dionex IonPac CS5A

Introduction
Metal ions can exist in several different forms. The factors that determine the form of the metal ion are the extent of complexation and the oxidation state.

In many samples, metal ions are present in their hydrated forms. Hydrated metal ions are usually written without the water ligands included in the chemical formula. For example, chromic ion, Cr_3^+, is actually the hexaquo complex $Cr(H_2O)_6^{3+}$. Hydrated metal ions can also be complexed by weak ligands such as organic acids or amino acids. These ligands are generally displaced by the complexing agents used in IC eluents. Therefore, the IC methods described in this technical note will determine the total of both hydrated and weakly complexed metal ions.

More powerful complexing agents will not be displaced during chromatography. Since most complexing agents are anionic, the resulting metal complex will have a net negative charge. An example is the trivalent anion $Fe(CN)_6^{3-}$. Metals can also exist as oxyanions. These are actually metals with oxygen atoms as ligands. An example is the chromate ion, CrO_4^{2-}. The chromatography of these ions will be different from the hydrated and weakly complexed metal ions, so they must be determined using different IC methods. Metal oxyanions and other stable metal complexes are usually determined by anion exchange separation and suppressed conductivity detection.

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Separation

Hydrated and weakly complexed transition metals can be separated as cations on a cation exchange column. By adding a carboxylic acid chelating agent to the eluent, the net charge on the metal is reduced, since the carboxylic acids are anionic in solutions above their pKas. The selectivity of the separation is actually due to the different degrees of association between the metals and the chelating agents producing different net charges on the metal complexes.

If strong enough chelating agents are used in high enough concentration, the net charge of the metal complexes can be negative. These anionic metal complexes are separated by anion exchange. The Thermo Scientific™ Dionex™ IonPac™ CS5A column has both cation and anion exchange capacity, allowing metals to be separated as cations or anions on a single column. This is called a mixed mode separation.

Detection

Most hydrated and weakly complexed metals will precipitate in a suppressor and, therefore, cannot be detected by conductivity. Also, with a few exceptions, transition metals cannot be detected by direct UV absorbance. Therefore, the metal complexing agent 4-(2-pyridylazo)resorcinol (PAR) is added postcolumn to form a light-absorbing complex.

Experimental
Standards

Transition metal standards of 1,000 mg/L are available from chemical supply companies for use with atomic absorption spectrometry. These are always dissolved in dilute acid solutions and can also be used as IC standards.

Method A: transition metals using PDCA eluent
Analytes

Iron, both ferric (Fe_3^+) and ferrous (Fe_2^+), divalent cations of copper, nickel, zinc, cobalt, cadmium, and manganese.

Recommended equipment
- A Thermo Scientific™ Dionex™ DX 500* system consisting of:

  – GP40 Gradient Pump

  – AD20 Absorbance Detector

  – LC20 Chromatography Enclosure

  – PC10 Postcolumn Pneumatic Delivery Package

  – PC10 Automation Kit (optional)

* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system.

Solutions and reagents
- Eluent: 7.0 mM PDCA
                    66 mM Potassium hydroxide
                    74 mM Formic acid
                    5.6 mM Potassium sulfate

Dilute 200 mL of the Thermo Scientific™ Dionex™ MetPac™ PDCA Eluent Concentrate to 1.0 L with deionized water.

- Postcolumn Reagent: 0.5 mM PAR
                       1.0 M 2-Dimethylaminoethanol
                       0.50 M Ammonium hydroxide
                       0.30 M Sodium bicarbonate

Dissolve 0.12 g of PAR in 1.0 L of the Thermo Scientific™ Dionex™ MetPac™ Postcolumn Diluent. Ultrasonicate for 5 minutes, then stir until the solid is completely dissolved.

Conditions, Method A	
Columns:	Dionex IonPac™ CS5A Analytical and CG5A Guard
Eluent:	Dionex MetPac PDCA eluent
Flow Rate:	1.2 mL/min
Inj. Volume:	50 µL
Mixing Device:	375 µL knitted reaction coil
Postcolumn Reagent:	0.5 mM PAR, in Dionex MetPac PAR Postcolumn Diluent
Reagent Flow Rate:	0.7 mL/min
Detector Wavelength:	530 nm

Discussion of method

The analytical column used for this method is the Dionex IonPac CS5A column. Transition metals are separated as anionic complexes with the PDCA chelating agent added to the eluent. Note that both ferrous and ferric ions can be determined. Since the ferrous ion is easily oxidized to ferric, oxygen must be removed from the eluent by degassing. To remove oxygen from the analytical column, pump a solution of 0.1 M sodium sulfite (12.6 g/L Na_2SO_3) through the column for 2 hours.

The metals are detected by measuring the absorbance at 530 nm of the complex formed with the postcolumn PAR reagent. The prepared PAR reagent is also easily oxidized. Prepared reagents should be stored under an inert gas, such as nitrogen or helium, and used within two weeks of preparation. Trace-metal grade chemicals, such as the Dionex MetPac reagents, are recommended for the eluent and postcolumn reagents.

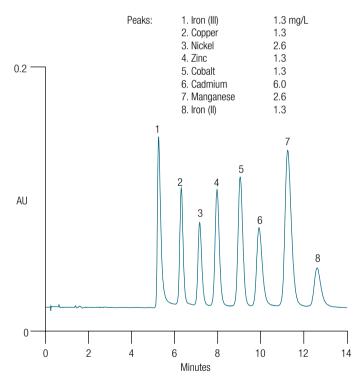| Peaks:		
1. Iron (III)	1.3 mg/L
2. Copper	1.3
3. Nickel	2.6
4. Zinc	1.3
5. Cobalt	1.3
6. Cadmium	6.0
7. Manganese	2.6
8. Iron (II)	1.3

Figure 1. Separation of transition metals using Dionex IonPac CS5A column with PDCA, method A conditions.

Method B: transition metals using oxalate buffer eluent

Analytes

Divalent cations of lead, copper, cobalt, zinc, and nickel.

Recommended equipment

- A Dionex DX 500 system* consisting of:

    – GP40 Gradient Pump

    – AD20 Absorbance Detector

    – LC20 Chromatography Enclosure

    – PC10 Postcolumn Pneumatic Delivery Package

    – PC10 Automation Kit (optional)

* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system.

Solutions and reagents

- Eluent: 8.0 mM Oxalic acid
                    50 mM Potassium hydroxide
                    100 mM Tetramethylammonium
                    hydroxide

Dilute 100 mL of the Thermo Scientific™ Dionex™ MetPac™ Oxalic Acid Eluent Concentrate to 1.0 L with deionized water.

- Postcolumn Reagent: 0.5 mM PAR
                    1.0 M 2-Dimethylaminoethanol
                    0.50 M Ammonium hydroxide
                    0.30 M Sodium bicarbonate

Dissolve 0.12 g of PAR in 1.0 L of the Dionex MetPac Postcolumn Diluent. Ultrasonicate for 5 minutes, then stir until the solid is completely dissolved.

Conditions, Method B

Columns:	Dionex IonPac CS5A Analytical and CG5A Guard
Eluent:	Dionex MetPac Oxalic Acid Eluent
Flow Rate:	1.2 mL/min
Inj. Volume:	50 µL
Mixing Device:	375 µL knitted reaction coil
Postcolumn Reagent:	0.5 mM PAR, in Dionex MetPac PAR Postcolumn Diluent
Reagent Flow Rate:	0.7 mL/min
Detector Wavelength:	530 nm

Discussion of method

As in the preceding method using PDCA eluent, the analytical column used for this method is the Dionex IonPac CS5A column. Transition metals are separated as both cationic and anionic complexes with the oxalate chelating agent added to the eluent. Using this method, cadmium and manganese coelute.

Oxalic acid eluents will not elute iron. Therefore, the column should be cleaned as needed to prevent excessive accumulation of iron from samples. Wash the column for 60 minutes with 1 M hydrochloric acid at the normal flow rate, then reequilibrate the column with the oxalic acid eluent.

The metals are detected by measuring the absorbance at 530 nm of the complex formed with the postcolumn PAR reagent. The prepared PAR reagent is also easily oxidized. Prepared reagents should be stored under an inert gas, such as nitrogen or helium, and used within two weeks of preparation. Trace-metal grade chemicals are recommended for both the eluent and postcolumn reagent.
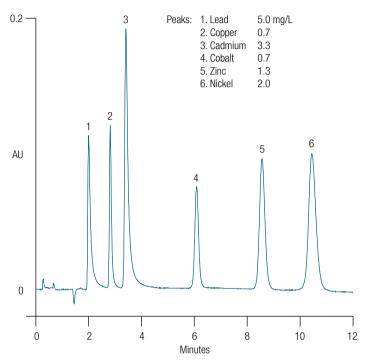

Figure 2. Separation of transition metals using oxalic acid with the Dionex IonPac CS5A column, method B conditions.

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