Solution & Water Analysis Methods



AGRONOMIC SERVICES

Agronomic Services Division

North Carolina Department of Agriculture & Consumer Services

4300 Reedy Creek Rd. Raleigh, NC 27607

(919) 664-1600

Table of Contents

Introduction **3**

Sample Collection and Minimum Sample Volumes **3**

Sample Storage & Preparation **4**

Analytical Methods **4**

Inorganic Nitrogen: NO3-N and NH4-N 4

Chloride 5

Elemental Analysis 4

pH 5

Electrical conductivity 6

Carbonate and bicarbonate 6

References **7**

Introduction

The NCDA&CS Solution Analysis Lab performs the following analyses based on standard industry methods:

- Elements: Phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), sodium (Na), and aluminum (Al)
- Nitrate-nitrogen (NO_3-N)
- Ammonium-nitrogen (NH_4-N)
- Chloride (Cl)
- pH
- Soluble salts / Electrical conductivity
- Alkalinity

Method detection limits (MDL) are determined annually and when a new instrument or method is put into use.

Minimum Sample Volumes

No matter how precise and accurate an analytical method is, meaningful results are only as good as the sample itself. The most significant cause of poor statistical results in solution analysis is due to insufficient sample collection rather than analytical measurement.

To obtain a representative sample, NCDA&CS strongly recommends a sample volume of 8-16 oz (~500 mL). Where this is not possible, please note the minimum sample volume required to perform each analysis (Table 1).

Table 1. Solution methods summary with minimum volume that may be used.

Analyte	Minimum Volume	Analytical Method	Reference
NO_3-N, NH_4-N, and Cl^-	15 mL	Filtered; Flow injection analysis	EPA 350.1; EPA 353.2; EPA 325.2
P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, B, Na, Al, Mo, As, Cd, Cr, Ni, Pb, Se	15 mL	Filtered; ICP-OES	EPA 200.7
pH	50 mL	As-received; autotitrator	AOAC 973.41
EC/SS		As-received; autotitrator	EPA 120.1
Alkalinity (CO_3 and HCO_3)		Acid titration; autotitrator	AOAC 920.194

Sample Storage & Preparation

Samples are analyzed as-received for pH, EC and alkalinity. For elemental and ion analysis, they are first filtered through a pre-folded Advantec #2 filter paper. Prior to analysis, samples are homogenized by shaking. Except during analysis, samples are refrigerated at 4°C.

Analytical Methods

Inorganic Nitrogen: NO3-N and NH4-N

NO_3-N is determined by cadmium reduction, where nitrate is reduced to nitrite with copperized cadmium, under alkaline conditions. The NO_2-N concentration (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-Naphthyl) ethylenediamine dihydrochloride to form a magenta-colored azo dye which is measured at 520 and 600 nm (USEPA 1993a; FIA NO3-W-1-1).

NH_4-N is determined by the modified Berthelot reaction where hypochlorite and sodium salicylate react with ammonia in a two-step reaction, converting it to 5-aminosalicylate. The aminosalicylate is oxidized in the presence of sodium nitroferricyanide to form a blue-green colored complex, which is then measured at 660 nm (USEPA 1993b; FIA NO3-W-1-2).

Both NO_3-N and NH_4-N are quantified by flow injection analysis (FIAlyzer-1000, FIA Lab; Seattle, WA). Nitrate-nitrogen (NO_3-N) and nitrite-nitrogen (NO_2-N) are reported as NO_3-N and ammonium-nitrogen (NH_3-N + NH_4-N) is reported as NH_4-N. Results are expressed in mg L^{-1}.

Quality Controls

Samples are quantified using nine calibration standards. A method blank (DI water, filtered) is analyzed with each batch. A duplicate aliquot of a filtered solution sample is spiked and analyzed for analytical recovery with each batch. A calibration verification solution and calibration blank are analyzed at the beginning and end of each batch and after every 10 samples. Four independent calibration verification solutions are analyzed at the beginning and end of each run. Drift checks are analyzed at the beginning and end of each run and every 20 samples. Two nitrite checks (NO_2-N) are analyzed to verify the completeness of the nitrate reduction reaction at the beginning and end of each run.

Chloride

Cl^- is determined by the thiocyanate displacement method where thiocyanate is liberated from mercury(II) thiocyanate by the formation of soluble mercuric chloride. The liberated thiocyanate forms a red colored complex with ferric iron ions also present in solution (USEPA 1978a; FIA CL-W-1-1) This complex is quantified at 480 nm by flow injection analysis (FIAlyzer-1000, FIA Lab; Seattle, WA). Results are expressed in mg L^{-1}.

Elemental Analysis

Total elemental concentrations are determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Spectro Arcos EOP and Arcos II EOP, Spectro Analytical: A Division of Ametek; Mahwah, NJ) (USEPA 2001). Elements are measured at the wavelengths listed in Table 2. Results are expressed in mg L^{-1}.

Table 2. Wavelengths used to quantify total elemental concentrations in solutions.

Element	Wavelength (nm)
Aluminum (Al)	396.152
Arsenic (As)	189.042
Boron (B)	208.959
Cadmium (Cd)	214.438
Calcium (Ca)	183.801, 315.887, 318.128
Chromium (Cr)	267.716, 357.869
Copper (Cu)	324.754
Iron (Fe)	259.941
Lead (Pb)	220.353, 405.778
Magnesium (Mg)	279.079
Manganese (Mn)	257.611
Molybdenum (Mo)	202.095
Nickel (Ni)	341.476
Phosphorus (P)	178.287
Potassium (K)	404.721, 766.491
Selenium (Se)	196.090
Sodium (Na)	330.237, 589.592
Sulfur (S)	182.034
Zinc (Zn)	213.856

ICP-OES Quality Controls

A method blank (DI water, filtered) and calibration blank are analyzed with each batch. A calibration verification solution is run after the daily calibration, after every 10 samples, and at the end of each run. An independent calibration verification solution is analyzed at the beginning and end of each run.

pH

The pH of solution samples is determined directly on samples at room temperature using a Mettler Toledo T9 autotitrator and InMotion Max autosampler with a DGi115-SC pH electrode and DT1000 temperature probe (Mettler-Toledo, LLC; Columbus, OH) (APHA 2012; AOAC 1990c). pH is a measure of acidity or alkalinity on a scale of 1 to 14 and is reported on this scale (unitless).

pH Quality Control
A three-buffer calibration is performed daily with a slope maintained between 98% and 102%. The pH 7 buffer is read back at the beginning and end of each day and every 10 samples. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criterion of ±0.2 pH units.

Electrical Conductivity

Electrical conductivity (EC) is a measure of the ability of an aqueous solution to carry a current. The EC of an aqueous solution depends on the total concentration, mobility, and valence of ions and on the temperature of the sample. EC is measured directly on samples at room temperature using a Mettler Toledo T9 autotitrator and InMotion Max autosampler with a InLab 731-ISM conductivity sensor and DT1000 temperature probe (Mettler-Toledo, LLC; Columbus, OH) (AOAC 1990b; USEPA 1982). EC is also referred to as soluble salts (SS). EC is expressed in units of mS cm^{-1} and SS is expressed in units of 10^{-5} S cm^{-1}.

Electrical conductivity Quality Control
The calibration of the conductivity probe is checked daily with two EC checks. A 500 µS/cm check is analyzed at the beginning and end of each day. A 1413 µS/cm check is analyzed at the beginning and end of each day and every 10 samples. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criterion of < 2% relative standard deviation.

Carbonate and Bicarbonate

Alkalinity is a measure of water's ability to resist change in pH (aka pH buffering capacity) and is the sum of carbonate (CO_3) and bicarbonate (HCO_3) ions in solution. Carbonate (CO_3) and bicarbonate (HCO_3) concentrations are measured using a Mettler Toledo T9 autotitrator and InMotion Max autosampler with a DGi115-SC pH electrode and DT1000 temperature probe (Mettler-Toledo, LLC; Columbus, OH). The autotitrator conducts titration over the carbonate/bicarbonate pH range using a weak acid and determines the inflection point(s) of the titration curve. The amount of acid needed to lower the pH to the endpoint is inversely related to the alkalinity of the water. CO_3 and HCO_3 are reported in meq L^{-1}. Total alkalinity (TA) is reported in ppm of calcium carbonate ($CaCO_3$) and is calculated as follows:

$$TA = (CO3 + HCO3)\ x\ 50$$

Carbonate and Bicarbonate Quality Control
A three-buffer calibration is performed daily with a slope maintained between 98% and 102%. The pH 7 buffer is read back at the beginning and end of each day and every 10 samples. A 100 ppm $CaCO_3$ titration check is measured at the beginning and end of each analysis. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criterion of <3% relative standard deviation.

References

Association of Official Analytical Chemists. (1990a). AOAC official method 920.194: carbonate and bicarbonate in water—titrimetric method, final action. In: Official methods of analysis. 15th ed. Arlington (VA): AOAC International. P. 322.

Association of Official Analytical Chemists. (1990b). AOAC official method 973.40: Specific Conductance of Water. In: Official methods of analysis. 15th ed. Arlington (VA): AOAC International. p. 312.

American Public Health Association. (2012). Standard Methods for the Examination of Water and Wastewater. 22nd Edition. SM 4500 H^+: pH Value. Ch. 4-91. Rice EW, Baird RB, Eaton AD, Clesceri LS, editors. Washington (DC): Public Health Association, Water Environment Federation, and American Water Works Association.

FIA Lab. CL-W-1-1. Method for Chloride Determination by Ferric Thiocyanate, Version 7.

FIA Lab. NO3-W-1-1. Method for Nitrate Determination, Version 2.

FIA Lab. NH3-W-1-2. Method for Ammonia Determination by Salicylate Method, Version 1.

United States Environmental Protection Agency. (1993a). Method 353.2, Revision 2: Methods for Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry.

United States Environmental Protection Agency. (1993b). Method 350.1. Determination of Ammonia Nitrogen by Semi-Automated Colorimetry.

United States Environmental Protection Agency. (1978). Method 325.2: Methods for the Chemical Analysis of Water and Wastes. Chloride (Colorimetric, Automated Ferricyanide AAII .

United States Environmental Protection Agency. (1982). Method 120.1. Methods for the Chemical Analysis of Water and Wastes. Conductance (specific conductance, µmhos/cm at 25 °C).

United States Environmental Protection Agency. (2001). Method 200.7: Trace elements in water, solids, and biosolids by inductively coupled plasma–atomic spectrometry, revision 4.4.