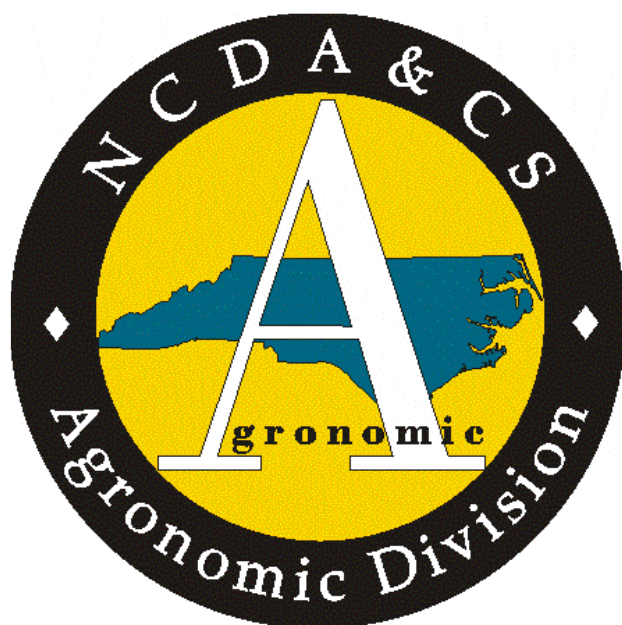


NCDA&CS Methods for Solution Analysis



Plant/Waste/Solution/Media Laboratory

Agronomic Division

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<http://www.ncagr.gov/agronomi/uysoln.htm>

Solution Analysis

Solution analysis is used to test the inorganic minerals and other parameters of surface water, well water and nutrient solutions for varied agricultural purposes such as irrigation, fertilization (nutrient solutions), livestock and poultry production, pesticide preparation, pond management and aquaculture. The NCDA&CS Agronomic Division does not perform any testing for microbial agents (e.g. pathogens, algae) or organic contaminants (e.g. pesticides, herbicides, petroleum products) nor does the Division provide recommendations for human drinking water.

The standard solution analysis includes measurement of nitrate-nitrogen (NO₃-N), ammonium-nitrogen (NH₄-N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), sodium (Na), aluminum (Al), and chloride (Cl) concentrations. Measurements of pH, soluble salts (SS or EC), and total alkalinity as well as values of hardness and sodium adsorption ratio (SAR) are reported. For irrigation water, most source waters and nutrient solutions, the amount of sulfuric acid needed to adjust alkalinity (Acid Requirement) is also reported.

Standard solution analysis for N.C. residents	\$5.00
Standard solution analysis for non-N.C. residents	\$25.00
‡Standard solution analysis for N.C. researchers	\$12.00
‡Standard solution analysis for non-N.C. researchers	\$25.00

‡ A completed NCDA&CS Research Project Agreement is **required prior to submission** of research samples. *Please contact Dr. Kristin Hicks at Kristin.Hicks@ncagr.gov to set up a Research Project Agreement. The NCDA&CS Cooperative Research Agreement can be found here: http://www.ncagr.gov/agronomi/documents/Research_Project_Agreement_PWSM.pdf*

In addition to the standard analysis, certain tests are available by request for an additional fee per sample.

Additional tests available by request:

- Molybdenum (Mo) + \$2
- ‡ Heavy Metals: cadmium, nickel, lead, arsenic, chromium, selenium + \$20

(‡ **Note: heavy metals analysis is available only for research purposes with a valid research agreement from a university, government agency or private scientific research institute. NO EXCEPTIONS.**)

Sampling instructions can be found here:

http://www.ncagr.gov/agronomi/pdf/Solution_sampling_Quick_Guide.pdf

The Sample Submission form for growers can be found here:

http://www.ncagr.gov/agronomi/pdf/Solution_Sample_Submission_Form_Fillable.pdf

The Sample Submission form for researchers can be found here:

http://www.ncagr.gov/agronomi/pdf/Solution_Sample_Submission_Form_Researcher.pdf

Minimum Sample Volumes

In order 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.

Solution Samples Method Summary			
Sample Test	Minimum Volume	Analytical Method	Reference
NO ₃ -N, NH ₄ -N, Cl ⁻	15 mL	Filtered; Continuous Flow Analysis	EPA 350.1; EPA 353.1; 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	10 mL	As-received; pH meter	AOAC 973.41
EC/SS		As-received; EC meter	EPA 120.1
Alkalinity (CO ₃ and HCO ₃ ⁻)	25 mL	Acid titration for total alkalinity determination	AOAC 920.194

Analytical Methods

Sample Processing & Storage

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

Inorganic Nitrogen: NO₃-N and NH₄-N

Nitrate-nitrogen (NO₃-N) and ammonium-nitrogen (NH₄-N) are determined on a 15 mL sample which is shaken and then filtered through a pre-folded Whatman #2 filter paper (Texas Scientific Products, Argyle, TX).

NO₃-N is determined on the filtrate by the hydrazine reduction method, where nitrate is reduced to nitrite with hydrazinium sulfate catalyzed by Cu²⁺, under alkaline conditions and at elevated temperature (Kempers and Luft 1988). The NO₂-N concentration (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with α-naphthyl-ethylenediamine dihydrochloride to form a highly-colored azo dye which is

measured at 540 nm (modified Griess reaction) (USEPA 1978b; Kempers and Luft 1988; Skalar Analytical 2018c). $\text{NH}_4\text{-N}$ is based on the modified Berthelot reaction where, after oxidation and oxidative coupling, a green-colored complex is formed, which is then measured at 660 nm (Krom 1980; Skalar Analytical 2018a; USEPA 1993).

Both $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ are quantified by continuous flow analysis using an auto-flow spectrophotometric analyzer (San⁺⁺ Segmented Flow Auto-Analyzer, Skalar Instruments; Breda, The Netherlands). Nitrate-nitrogen ($\text{NO}_3\text{-N}$) and nitrite-nitrogen ($\text{NO}_2\text{-N}$) are reported as $\text{NO}_3\text{-N}$ on the Solution Analysis Report. Ammonium-nitrogen ($\text{NH}_3\text{-N} + \text{NH}_4\text{-N}$) is reported as $\text{NH}_4\text{-N}$ on the Solution Analysis Report. Results are expressed in parts per million (ppm) [equivalent to mg L^{-1}].

Inorganic Nitrogen Quality Controls

Method detection limits (MDL) are determined when a new instrument or method is put into use and verified annually. **The MDLs for NH_4 and NO_3 are 0.87 ppm and 0.45 ppm, respectively.**

Samples are quantified using nine calibration standards. A method blank and duplicate spike sample are analyzed 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 ($\text{NO}_2\text{-N}$) are analyzed to verify the completeness of the nitrate reduction reaction at the beginning and end of each run.

Chloride (Cl^-)

Chloride concentration is determined on a 15 mL sample which is shaken and then filtered through a pre-folded Whatman #2 filter paper (Texas Scientific Products, Argyle, TX).

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; Zall et al. 1956; Skalar 2018b). This complex is measured at 470 nm on a segmented flow analyzer (San⁺⁺ Segmented Flow Auto-Analyzer, Skalar Instruments; Breda, The Netherlands). Results are expressed in parts per million (ppm) [equivalent to mg L^{-1}].

Cl Quality Control

Method detection limits (MDL) are determined when a new instrument or method is put into use and verified annually. **The MDL for Cl is 1.27 ppm.**

Phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), sodium (Na), aluminum (Al), molybdenum (Mo), cadmium (Cd), nickel (Ni), lead (Pb), arsenic (As), chromium (Cr), and selenium (Se)

Total elemental concentrations are determined on a 15 mL sample, which is first shaken and then filtered through a pre-folded Whatman #2 filter (Texas Scientific Products, Argyle, TX), using 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.

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

Results are expressed in parts per million (ppm) [equivalent to mg L⁻¹].

ICP-OES Quality Controls

Elements are measured using a curve with at least five calibration points for most analytes. A five-point calibration is used for Mo and a seven-point curve for heavy metals (As, Cd, Cr, Ni, Pb, Se).

A method blank, calibration blank and reference material are analyzed with each batch. A calibration verification solution is run after the daily calibration, after every 10th sample and at

the end of each run. An independent calibration verification solution is analyzed at the beginning and end of each run. The method detection limits (MDLs) for each analyte are listed in Table 3.

Table 3. MDLs of total elemental concentrations in solutions by ICP-OES.

Element	MDL (ppm)
Aluminum (Al)	0.025
Arsenic (As)	0.003
Boron (B)	0.025
Cadmium (Cd)	0.002
Calcium (Ca)	2.362
Chromium (Cr)	0.004
Copper (Cu)	0.006
Iron (Fe)	0.047
Lead (Pb)	0.006
Magnesium (Mg)	1.059
Manganese (Mn)	0.003
Molybdenum (Mo)	0.001
Nickel (Ni)	0.004
Phosphorus (P)	0.022
Potassium (K)	0.193
Selenium (Se)	0.004
Sodium (Na)	0.657
Sulfur (S)	0.048
Zinc (Zn)	0.010

pH

The pH of water and solution samples is determined directly on samples at 25 °C using a Thermo Scientific Orion Versa Star Pro pH meter with a green epoxy non-fillable pH electrode with BNC connection (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%. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criteria of ± 0.2 pH units.

Electrical conductivity (EC)

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 25 °C. EC is measured using a conductivity meter and probe (SevenMulti; 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 $10^{-5} \text{ S cm}^{-1}$.

Electrical conductivity Quality Control

The EC meter is calibrated daily with a $1000 \mu\text{S}$ conductivity standard. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criteria of $< 2\%$ relative standard deviation.

Carbonate (CO_3) and bicarbonate (HCO_3), i.e. Total Alkalinity

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 by titrating a weak acid into water until the water reaches a colorimetric endpoint, using phenolphthalein and methyl orange as endpoint indicators (AOAC 1990a). The amount of acid needed to lower the pH to the colorimetric 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:

$$TA = (\text{CO}_3 + \text{HCO}_3) \times 50$$

Carbonate and Bicarbonate Quality Control

A three-buffer calibration is performed daily with a slope maintained between 98% and 102%. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criteria of $< 3\%$ relative standard deviation.

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