

Environmental Water Testing: Surface Water, Groundwater, Hard Water, Wastewater, & Seawater

Matrix-specific sample preparation and testing methods for environmental waters

Problem Statement

1. ANDalyze metal test kits are designed for use out of the box with drinking water; however they can be used for environmental water analysis with some minor protocol modifications.
2. Below are instructions for testing samples obtained from sources such as:
 - Surface Water (rivers, lakes, ponds)
 - Ground Water (wells, aquifers)
 - Hard or Very Hard Water (multiple sources)
 - Treated Wastewater – Finished or treated and diluted tenfold
 - Seawater (from the surface, not the sediment/water column interface)

Materials

Each matrix type may require one or more of the following pre-treatment kits. Read guidelines for each matrix. Kits may be purchased from ANDalyze wherever indicated or individual components for pre-treatment may be purchased through a scientific supply company.

ANDalyze Dilution Kit

- 50 mL Self-standing sample tube
- 5 mL Fixed Volume Pipette & Tips
- Reagent grade water

ANDalyze pH Adjustment Kit

- Sodium Hydroxide Neutralization Solution, 1% (w/v) sodium hydroxide in a dropper bottle
- Nitric Acid Neutralization Solution, 1.5% (w/v) nitric acid in a dropper bottle
- pH paper

ANDalyze Iron Interference Kit

- Sodium Hydroxide Neutralization Solution, 1% (w/v) sodium hydroxide in a dropper bottle
- Hydrogen Peroxide Solution, 30% (w/v) hydrogen peroxide in a dropper bottle

ANDalyze Filtration Kit **(Available now from ANDalyze)**

- 0.45 μ m Nylon filter, 25 mm diameter (Nalgene)
- 20 mL Syringe
- 50 mL Self-standing sample tube

Solution Statement

ANDalyze kits may be used to test many different environmental waters. Each matrix may require different pretreatment steps. Please see the general protocols below for: (1) Dilution, (2) pH Adjustment, (3) Filtration, and (4) Environmental Water On-site Calibration. Matrix-specific instructions, including necessary protocols, are presented following the protocols.

Note: Our tests have shown that the percent recovery for lead in environmental samples is ~60 % for less than 25 ppb lead and 75-125 % for 25-100 ppb lead. The percent recovery for uranium in environmental samples is > 60% for less than 30 ppb uranium and 75 – 125 % for 30 – 60 ppb uranium. Copper is less well characterized in environmental matrices, though the copper sensor is tolerant of high salt conditions.

General Protocols

(1) General Protocol - Dilution

Dilution is needed for accurate readings if the target metal ion is present at a concentration higher than the linear detection range stated in the *Testing and Calibration* manuals and below:

Lead – 2-100 ppb

Uranium – 2-60 ppb

Copper High Range – 0.6-3 ppm

Copper Low Range – 40-200 ppb

Mercury – 2-50 ppb

Zinc – 1-15ppm

Note: The ANDalyze Copper sensor is available in two ranges and therefore dilution is usually not required.

1. **Dilution is best performed using standard laboratory glassware** and reagent grade water – one volume sample to nine volumes reagent grade water.
2. **Dilution may also be performed in the field**, with a decrease in accuracy, by withdrawing 5 mL sample with a 5 mL fixed volume pipette, adding the aliquot to a 50 mL self-standing tube, and filling to the 50 mL mark with reagent grade water. Shake well. With this method, the concentration indicated after the test on the fluorimeter screen must be multiplied by 10 to account for the dilution (ie. 22ppb Lead = 220ppb in original solution).
3. **If the sample is diluted**, on-site calibration must be performed with the diluted sample.

(2) General Protocol - pH Adjustment

ANDalyze Lead, Mercury and Copper sensors perform best when the sample pH is between 5 and 8 (pH 4-7 for Uranium). Samples with a pH greater than 8 or below 5 will not test reliably for Lead, Mercury, or Copper (greater than 7 or below 4 for Uranium). It is required to adjust the pH into this range before sample preparation steps and testing can continue. Samples above pH 10 should not be tested even with pH adjustment.

1. **Check the sample pH** using pH paper.
2. **Prepare the following solutions** if pH adjustment is required
 1. Sodium Hydroxide Neutralization Solution, 1% (w/w) sodium hydroxide
 2. Nitric Acid Neutralization Solution, 1.5% (v/v) nitric acid
3. **Adjust the sample pH**
 1. **If the sample is below pH 5** (or pH 4 for U) addition of a dilute sodium hydroxide solution is necessary. To a 50 mL volume of sample add the Sodium Hydroxide Neutralization Solution dropwise with stirring or with shaking between addition of each drop. Do not titrate beyond pH 5 for Lead, Mercury, and Copper and pH 4 for Uranium.

Note: pH change from 4-5 is rapid, requiring a half drop or less. **Check the pH multiple times during titration.** The number of drops required depends heavily on matrix constituents. As few as four drops may be sufficient to increase pH from 3 to 4, or many more may be required.

2. **If the sample is above pH 8** for Lead, Mercury, and Copper (above pH 7 for Uranium) addition of a dilute nitric acid (1.5 %) solution is necessary. Samples above pH may be unsuitable for testing even with pH adjustment as metal ion may have already precipitated out.

Note: pH change from 9-8 is rapid, requiring a half drop or less depending on matrix. **Check the pH multiple times during titration.** The number of drops required depends heavily on matrix constituents. As few as four drops may be sufficient to decrease pH from 10 to 7, or many more may be required.

Note: For highly basic water samples, acidification may be insufficient to solubilize precipitated metals.

(3) – General Protocol - Filtration

- 1. Obtain an ANDalyze Filtration Kit.** Before testing or spiking any environmental water sample, it must be filtered to remove suspended solids.
- 2. Filter the water sample.** Draw ~20 mL water sample into a 20 mL syringe, securely attach the filter, and dispense into the self-standing vial.



Note: If the sample is collected off-site and transported to a laboratory for testing, ensure that the sample is stirred (*e.g.*, stir-bar in the bottom of a 1 L HDPE Nalgene bottle filled with sample on a stir plate) while filling the syringe to ensure homogeneity.



- 3. The sample should be clear and the filter may no longer be white.**

Note: If a sample contains a great deal of suspended solids the syringe filter may clog after elution of 10-20 mL sample. In this case, discard the clogged filter and use a fresh filter to continue filtering the sample.



(3) General Protocol - Environmental Water On-site Calibration

On-site calibration is performed for all new samples and any time a matrix may have changed, *e.g.* new sampling day, change in matrix composition, new sensor batch, temperature change, etc. If in doubt, perform On-site Calibration.

Important: For environmental samples, it is required to incubate the calibration spike with the sample for at least 5 minutes as the spiked metal takes some time to reach equilibrium between dissolved and bound states. Failure to allow spike incubation in the sample will lead to lower recovery.

- 1. Perform on-site calibration as described in the Product Manual.** After adding the 100 μL standard metal solution spike as per the instructions in the product manual, shake, and **let it sit for ~ 5 minutes** before the analysis is performed.
- 2. Use all spiked solutions** within 15 minutes.

Note: The ANDalyze test kit is designed to test for bioavailable metals and not total metals without acid digestion, which is beyond the scope of this procedure.

Matrix-Specific Protocols

Surface Water Testing Protocol

ANDalyze has performed extensive testing of our kits in surface waters such as rivers, lakes, and streams. Some surface waters, such as runoff from industrial sites, heavily contaminated bodies of water, mine runoff, or areas affected by acid rain may exceed interference levels and the acceptable pH range. Special care may be needed in handling as well as testing these samples. Please contact ANDalyze with any questions.

Important: Testing of surface waters from rivers, lakes, and streams usually does not require dilution, pH adjustment, or iron interference removal. If required, perform those steps as stated in the protocols. Filtration, however, is always required.

1. **Check the pH using pH paper** and adjust if required.
2. **Filtration** is required as per the Filtration Protocol.
3. **Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol (with incubation of calibration spike) and instructions in the *Testing and On-site Calibration* manual.

Groundwater Testing Protocol

Important: Testing of raw or treated groundwater usually does not require dilution or pH adjustment. If required, perform those steps as stated in the protocols. Iron interference may be an issue and the solution color should be noted – yellow/orange color may be indicative of iron. Filtration is always required.

- 1. Check the pH using pH paper** and adjust if required.
- 2. Verify that iron interference is not an issue.** If interference is suspected, follow the Iron Interference Solution Note.
- 3. Filtration** is required as per the Filtration Protocol.
- 4. Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol (with incubation of calibration spike) and instructions in the *Testing and On-site Calibration* manual.

Note: ANDalyze has performed extensive testing of our kits in ground waters from across the U.S.A as well as in artificial matrices based on those in Standard Methods for the Examination of Water & Wastewater, Centennial Edition. As a general rule, performance in soft waters exceeds that of very hard waters, which are much more likely to exceed the interference level or pH range.

Hard Water Testing Protocol

ANDalyze, Inc. has performed extensive testing of our kits in simulated hard waters, including hard and moderately hard waters according to Standard Methods for the Examination of Water & Wastewater, Centennial Edition.

Important: Testing of hard waters usually does not require dilution, pH adjustment, or iron interference removal. If required, perform those steps as stated in the protocols. Filtration, however, may be required.

- 1. Check the pH using pH paper** and adjust if required.
- 2. Filtration** is required as per the Filtration Protocol **IF** the water is cloudy.
- 3. Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol (with incubation of metal spike) and instructions in the *Testing and On-site Calibration* manual.

Wastewater Testing Protocol

Important: ANDalyze has tested multiple **finished or treated** wastewater matrices and analysis can be challenging depending on matrix constituents. **Raw wastewater** is **NOT** suitable for testing. Dilution of the sample (1:10) is absolutely required, which increases the **effective detection range tenfold**, *e.g.* the detection range for Lead after dilution is 20-1000 ppb. Analyte concentrations measured at the low end of the sensor ranges are **qualitative** rather than quantitative and the relative standard deviation of results is larger than experienced in drinking water.

1. **Precautions!** Wastewaters are complicated matrices and may contain interferences beyond other metal ions.
 - **Chelators** such as EDTA will cause false negatives. Chelators are present in many cleaning products and industrial processes, so check wastewater components carefully.
 - **Fluorescent compounds** will give a high background signal and results may be unreliable
 - **Very high concentration of other metal ions** – Example: Known metals from a metal finisher plant
 - **Wear personal protective equipment.** Wastewaters may have extreme pH values and contain hazardous components. Wear appropriate laboratory attire and use a fume hood as appropriate.
2. **Follow the Dilution Protocol to dilute the sample tenfold.** Remember that your effective detection range has increased tenfold.
3. **Check the pH using pH paper** and adjust if required.
4. **Verify that iron interference is not an issue.** If interference is suspected, follow the Iron Interference Solution Note.
5. **Filtration** is required as per the Filtration Protocol. If filters clog rapidly then pre-filtration through Whatman 3MM paper or acid digestion may be necessary.
6. **Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol and instructions in the *Testing and On-site Calibration* manual.
 1. **If on-site calibration fails, repeat.**
 2. **If on-site calibration fails again,** further dilution may be necessary. Dilute the sample another tenfold (total 100-fold dilution). Be aware that the analyte concentration may be out of the linear detection range upon 100-fold (total) dilution.

Note: Some waste water matrices have many interferences and cannot be effectively analyzed without acid digestion or other treatment procedures, which are beyond the scope of this solution note.

Seawater Testing Protocol

Important: Sample preparation steps for seawater are normally not necessary beyond filtration unless the sample is taken from a polluted area. This protocol is intended for analysis of seawater from the surface or water column with minimal sediment. Analyte concentrations measured are **qualitative/ semi quantitative** rather than quantitative and the relative standard deviations of results are larger than experienced in drinking water.

1. **Filtration** is required as per the Filtration Protocol.
2. **Perform Environmental Water On-site Calibration** following the Environmental Water On-site Calibration Protocol and instructions in the *Testing and On-site Calibration* manual.
3. Dilution (tenfold) may be performed if spike recovery is very low.

Note: Bittern Water is a concentrated solution left over after crystallization of NaCl from seawater. It contains very high concentrations of interfering ions, notably magnesium. ANDalyze test kits may work in bittern water upon dilution of the sample by at least ten-fold if not 100-fold. Contact ANDalyze for further details.