

ANALYSIS OF REFINERY WATERS FOR pH, IRON AND COPPER

UOP Method 314-97

SCOPE

This method is for determining the pH of, and iron and copper concentrations in, refinery waters. The data may be used to gauge the extent of corrosion caused by refinery waters. Copper and iron are determined at levels of 0.1 $\mu\text{g/mL}$ and higher using Atomic Absorption Spectrometry (AAS). The metals may be present as single dissolved ions, as complex ions with cyanide or other complexing agents, or as part of the suspended solids that are often present in such samples. Ammonia, hydrogen sulfide, hydrogen cyanide and organic matter do not interfere with this test. The pH of the water is determined because it usually correlates with the extent of corrosion.

OUTLINE OF METHOD

The pH of the original water sample is measured using a pH meter. For iron and copper determinations, clear, colorless samples are diluted with sulfuric acid and water and analyzed. Samples containing any suspended solids or sediment are digested with sulfuric acid and then treated with nitric acid to oxidize any organic material. If silica is present, it is removed using hydrofluoric acid. Aliquots of the sample stock solution thus prepared are taken for determinations of iron and copper by AAS. The sample solution is aspirated into the flame of the AAS instrument. The concentration of the elements is determined by comparing the sample stock solution to matrix-matched standard solutions. The method assumes that the analyst is familiar with the operation of a pH meter and an AAS instrument.

APPARATUS

References to suppliers and catalog numbers are included as a convenience to the method user. Other suppliers may be used, unless stated otherwise.

Balance, top-loading, readability 0.01-g

Beaker, 250-mL, VycorTM, Fisher Scientific, Cat. No. 02-541A

Beaker, 250-mL, TeflonTM, Fisher Scientific, Cat. No. 02-593-5B

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Cylinder, graduated, 10-mL, Nalgene, Fisher Scientific, Cat. No. 08-572A

Electrode, pH, gel-filled, pH/ATC combination, Fisher Scientific, Cat. No. 13-620-112

Flasks, volumetric, Class A, glass, 100-mL, Fisher Scientific, Cat. No. 10-210-8C

Funnels, plastic, 75-mm, Fisher Scientific, Cat. No. 10-347E

Hot plate, capable of 460°C, Corning Model PC-500, Fisher Scientific, Cat. No. 11-495-52A

Lamp, copper, hollow cathode, Perkin-Elmer, Cat. No. 0303-6024

Lamp, iron, hollow cathode, Perkin-Elmer, Cat. No. 0303-6037

pH meter, Accumet #15, Fisher Scientific, Cat. No. 13-635-15

Pipets, volumetric transfer, Class A, 5- and 10-mL, Fisher Scientific, Cat. Nos. 13-660-5E and -5F, respectively

Spectrometer, Atomic Absorption, Perkin Elmer, Model 4100

Stirring bar, 32-mm, Fisher Scientific, Cat. No. 14-511-94

Stirrer, economy, Fisher Scientific, Cat. No. 14-493-120S

Wash bottle, LDPE, 500-mL, Fisher Scientific, Cat. No. 03-409-22C

Watch glass, 90-mm, Fisher Scientific, Cat. No. 02-612C

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications exist, unless otherwise specified. References to water mean distilled or deionized water.

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Buffer, pH 4, Fisher Scientific, Cat. No. SB101-500

Buffer, pH 7, Fisher Scientific, Cat. No. SB107-500

Buffer, pH 10, Fisher Scientific, Cat. No. SB115-500

Copper standard solution, 1000- $\mu\text{g/mL}$, Spex Certiprep, Cat. No. PLCU2-2X

Copper standard solution, 50- $\mu\text{g/mL}$. Pipet 5 mL of 1000- $\mu\text{g/mL}$ copper standard into a 100-mL volumetric flask and dilute to the mark with water. Cap and shake well. Make up fresh each time the lower level standards are to be prepared.

Copper standard solution, 5.0- $\mu\text{g/mL}$. Pipet 10 mL of the 50- $\mu\text{g/mL}$ copper standard into a 100-mL volumetric flask, add 5 mL of concentrated sulfuric acid and dilute to the mark with water. Cap and shake well. Lifetime of this standard is three months.

Copper standard solution, 2.5- $\mu\text{g/mL}$. Pipet 5 mL of the 50- $\mu\text{g/mL}$ copper standard into a 100-mL volumetric flask, add 5 mL of concentrated sulfuric acid and dilute to the mark with water. Cap and shake well. Lifetime of this standard is three months.

Hydrofluoric acid, concentrated, Fisher Scientific, Cat. No. A147-11B

Iron standard solution, 1000- $\mu\text{g/mL}$, Spex Certiprep, Cat. No. PLFE2-2X

Iron standard solution, 50- $\mu\text{g/mL}$. Pipet 5 mL of the 1000- $\mu\text{g/mL}$ iron standard into a 100-mL volumetric flask and dilute to the mark with water. Cap and shake well. Make up fresh each time the lower level standards are to be prepared.

Iron standard solution, 5.0- $\mu\text{g/mL}$. Pipet 10 mL of the 50- $\mu\text{g/mL}$ iron standard into a 100-mL volumetric flask, add 5 mL of concentrated sulfuric acid and dilute to the mark with water. Cap and shake well. Lifetime of this standard is three months.

Iron standard solution, 2.5- $\mu\text{g/mL}$. Pipet 5 mL of the 50- $\mu\text{g/mL}$ iron standard into a 100-mL volumetric flask, add 5 mL of concentrated sulfuric acid and dilute to the mark with water. Cap and shake well. Lifetime of this standard is three months.

Nitric acid, concentrated, Fisher Scientific, Cat. No. A509-212

Sulfuric acid, concentrated, Fisher Scientific, Cat. No. A300-212

Sulfuric acid, 1:1, mix equal volumes of concentrated sulfuric acid and water by slowly adding the acid to the water while mixing.

Test strips, 0 to 14 pH, Fisher Scientific, Cat. No. 09-876-17

PROCEDURE

Refinery water pH values are typically in a range of 7 to 8, but may occasionally be higher or lower. The pH measurement is most accurate in a range of 3 to 10. Samples with a pH greater than 10 must be neutralized prior to analysis for iron and copper.

Refinery water samples may range in appearance from clear and water-white to colored with suspended solids or sediment present. They must be prepared and analyzed in a manner that ensures that the final results are representative of the total sample. A clear, colorless sample is assumed to be totally in solution. Colored samples may contain organics. A colored sample or a sample with suspended solids or sediment present needs to be shaken well and then sampled immediately.

pH Measurement

1. Insert a pH test strip into the sample and estimate the pH using the color guide on the test strip container.
2. Standardize the pH meter with a purchased buffer solution, the pH of which is nearest that of the sample as estimated in Step 1.
3. Pour approximately 100 mL of the well shaken sample into a 250-mL beaker, add a stirring bar, place on the stirrer and stir the sample for approximately three minutes.

4. Lower the pH electrodes into the beaker and read the pH value from the meter while the sample is being stirred. Record and report the pH to the nearest 0.1 unit.
5. Remove the electrodes from the sample, thoroughly rinsing the electrodes with water.
 - Proper maintenance of the pH electrodes is important. Due to the corrosive nature of the refinery water sample, it is important to thoroughly rinse the electrodes after use. Keep the electrodes in water between uses.
 - The use of the Automatic Temperature Compensating (ATC) probe on the pH electrode is highly recommended to obtain the best measurement precision.

Sample Preparation for Iron and Copper Determinations

Prepare a reagent blank in a manner identical to that used in preparing the sample. *CAUTION:* The following procedures involving the use of acid solutions and the heating of acid mixtures must be performed in a properly operating fume hood.

If the sample pH is less than 10, proceed to *Clear, Colorless Solutions* or *Colored Solutions or Solutions Containing Suspended Solids or Sediment*, depending on the appearance of the sample. If the sample pH is greater than 10, proceed with neutralization.

Neutralization Procedure for Samples with pH Values Greater Than 10

1. Weigh 50 ± 1 g, to the nearest 0.1 g, of well shaken sample into a 250-mL beaker.
2. Place a stirring bar in the beaker, and place the beaker on the stirrer of the pH meter.
3. Insert the electrode and add 1:1 sulfuric acid dropwise until the pH reads less than 10 on the meter.
 - A precipitate may form, but will be resolubilized during the digestion steps.
4. Remove the beaker from the pH meter, rising the electrode with water into the beaker. Proceed to step 2 of either *Clear, Colorless Solutions* or *Colored Solutions or Solutions Containing Suspended Solids or Sediment*, depending on the appearance of the sample at this point.

Clear, Colorless Solutions

1. Weigh 50 ± 1 g, to the nearest 0.1 g, of sample into a 250-mL beaker.
2. Add, carefully, 5 mL of concentrated sulfuric acid to the beaker.
3. Add water to bring the total mass to 100 ± 1 g, to the nearest 0.1 g. Swirl to thoroughly mix the contents. Transfer to a 100-mL volumetric flask. This is the sample stock solution for iron and copper determinations.

Colored Solutions or Solutions Containing Suspended Solids or Sediment

1. Weigh 50 ± 1 g, to the nearest 0.1 g, of well shaken sample into a 250-mL beaker.
2. Add, carefully, 5 mL of concentrated sulfuric acid to the beaker.
3. Place the beaker on a hot plate and digest until the evolution of sulfur trioxide fumes.
4. Allow the sample to cool slightly and carefully add 5 mL of concentrated nitric acid. Return to the hot plate and again take the sample to sulfur trioxide fumes.

5. Repeat Step 4 until a clear solution is obtained. Then, if silica is present in the sample, proceed to Step 6, otherwise proceed to Step 7.
 - The presence of organics is usually indicated by a solution that darkens as nitric acid is depleted through oxidation and evaporation. Continue the nitric acid additions until darkening does not occur upon concentration. Then proceed to the following steps as directed.
 - The presence of silica is indicated if a white haze or precipitate is present after the nitric acid additions have removed the organics.
6. Transfer the sample quantitatively, with water, to a Teflon beaker and add 2 to 3 mL of hydrofluoric acid. Digest the sample until the evolution of sulfur trioxide fumes. Repeat if necessary to remove all silica from the sample. *CAUTION:* Use appropriate precautions and wear appropriate personal protective equipment when working with hydrofluoric acid (see the MSDS).
7. Transfer the solution quantitatively, with water, to a 100-mL volumetric flask. Allow to cool and bring to a total mass of 100 ± 1 g, to the nearest 0.1 g with water. Cap and shake well to mix. This is the sample stock solution for iron and copper determinations.

AAS Instrument Setup

Set up the AAS instrument in accordance with the manufacturer's instructions, using the instrument settings in Table 1 as a guide.

Table 1
AAS Instrument Settings

<u>Parameter</u>	<u>Iron</u>	<u>Copper</u>
Wavelength, nm	248.3	324.8
Slit, nm	0.2	1.3
Background correction	On	On
Flame	Air and Acetylene for both (set to manufacturer suggested settings)	

Calibration and Sample Analysis

The AAS instrument used in this analysis must have a non-metallic spray chamber, or iron values will not be reliable due to corrosion in the spray chamber. After performing the following calibrations, check the concentration(s) of the sample stock solution(s) by aspirating it (them) into the AAS instrument. The sample(s) must be close to the standards in concentration. If not, take a mass aliquot from a sample stock solution, and dilute to a total mass that will bring the dilution within range of the calibration standards. Cap and shake well. Maintain the same acid levels in the sample dilution as in the blank and standards.

1. Calibrate the AAS instrument using an acid blank, a 2.5- $\mu\text{g/mL}$ and a 5.0- $\mu\text{g/mL}$ iron standard.
2. Run the sample(s) and then run the 2.5- $\mu\text{g/mL}$ standard as a sample at the end of the run to check the calibration. If the 2.5- $\mu\text{g/mL}$ standard does not return 2.3 to 2.7 $\mu\text{g/mL}$, rerun the calibration and samples until a value in that range is obtained.
3. Calibrate the AAS instrument using an acid blank, a 2.5- $\mu\text{g/mL}$ and a 5.0- $\mu\text{g/mL}$ copper standard.
4. Run the sample(s) and then run the 2.5- $\mu\text{g/mL}$ copper standard as a sample at the end of the run to check the calibration. If the 2.5- $\mu\text{g/mL}$ standard does not return 2.3 to 2.7 $\mu\text{g/mL}$, rerun the calibration and samples until a value in that range is obtained.

CALCULATIONS

Calculate the iron or copper concentration using the following equation. Report the results to one significant figure below one $\mu\text{g/mL}$, to two significant figures between 1 and 99 $\mu\text{g/mL}$, and to three significant figures at or above 100 $\mu\text{g/mL}$.

$$\text{Iron or Copper, } \mu\text{g/mL} = \frac{CV}{W}$$

where:

C = concentration of iron or copper in solution read by AAS, $\mu\text{g/mL}$

V = mass of sample stock solution, g

W = mass of original sample taken, g

If a dilution was required to bring the sample reading within range of the standards, multiply the dilution factor times the result obtained from the equation to obtain the iron or copper concentration in the original sample.

PRECISION

Repeatability

Based upon two tests performed by each of two analysts on each of two different days, the within-laboratory estimated standard deviations (esd) were calculated for pH, iron and copper at specific pH, iron and copper levels and are listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences listed in Table 2 at the concentrations listed (95% probability).

Table 2
Repeatability

<u>Component, Units of Measure</u>	<u>Level</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
pH, units	9.5	0.06	0.2
Iron, µg/mL	2.5	0.05	0.2
Copper, µg/mL	2.5	0.06	0.2

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

TIME FOR ANALYSIS

The elapsed time is three hours per sample, the labor requirement is one hour per sample.

SUGGESTED SUPPLIERS

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-562-8300)
 Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 06859-0012 (203-762-1000)
 Spex CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840-1253 (908-549-7144)