Field Methods for Ferrous Iron (and Dissolved Manganese) Analysis in Monitoring Wells

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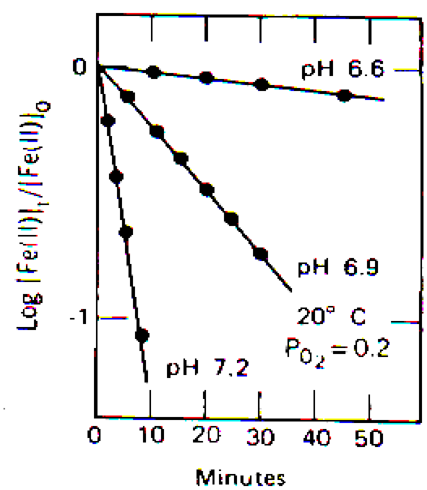
Introduction. Ferrous iron analysis is used at natural attenuation as well as other bioremediation sites to determine the predominant terminal electron accepting process. An accurate quantification of ferrous iron for environmental samples is difficult because exposure to oxygen can rapidly oxidize the ferrous iron to ferric iron. As shown in Figure 1, samples at neutral pHs can oxidize so rapidly that it is unrealistic to analyze the sample before it has been compromised. Standard sampling methods do not address the rapid oxidation at neutral pH. The sample may be further compromised by delayed analysis because the coloring agent forms an unstable complex with ferrous iron.

Figure 1.
Ferrous Iron Oxidation Rate at Neutral pH



Source: Stumm & Morgan, Aquatic Chemistry

Ferrous iron analysis must be performed immediately in the field. The procedures described herein are recommended for all ferrous iron analysis; however, these procedures must be followed at sites where the pH is greater than 6 and/or the dissolved oxygen concentration is less 2 mg/l. The appropriate sampling method for iron analysis depends on the well configuration and the ferrous iron concentration. The following guidelines can be used to select an appropriate sampling method for iron analysis. Some well configurations may prevent strict adherence to these guidelines. In these cases rapid analysis is important to prevent anaerobic groundwater at neutral or higher pH from becoming contaminated with atmospheric oxygen.

Although this text discusses ferrous iron sampling and analysis specifically, the same principles would apply to dissolved manganese due to similar chemistry.

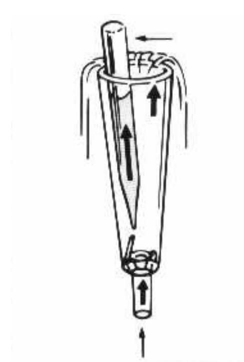
Sample collection location. If possible, samples should be collected from:

- within the screened interval of the well;
- near the center of the screened interval, unless a specific portion of the screened interval has been identified, through depth specific sampling, to be more appropriate;
- at least three feet below the water surface, which allows a concentration gradient to develop between the sample water and water exposed to oxygen in the atmosphere;
- at least three feet from the bottom of the well, primarily to avoid suspending silt that may interfere with the colorimetric test.

Sample collection technique. Samples for ferrous iron analysis should **<u>not</u>** be diluted. Samples may be collected using the following methods in order of preference.

1. Sample is collected **in-situ**. This is the preferred method as it limits potential contamination from atmospheric oxygen. In-situ sample collection is done using a **snapper sampling device (available from CHEMetrics)**. **In-situ sampling with a snapper is strongly recommended.**
2. Sample is collected from the water stream during well purging. The water must be sampled using an **overflow device**. The purpose of the overflow device is to limit potential contamination with atmospheric oxygen. An overflow device is any device that allows the sample to be taken while limiting contamination by atmospheric oxygen. An example of an overflow device designed by CHEMetrics for use with their CHEMets is shown in Figure 2. Any device that performs the same function is acceptable.
3. Sample is collected with a **bailer**. A bailed sample should only be used if the other alternatives are not available. Water must be removed from the bailer with a **slow**

Figure 2.
Sample overflow device



Source:
CHEMetrics

emptying device and the water used for analysis should come from the center of the bailer water volume. False positives are common when using a bailer.

Well purging. Wells should be purged prior to collecting water for ferrous iron analysis. Purging can be accomplished using a bailer or a pump.

1. **Pumping** should be done using a **micropurging** technique. Essentially, micropurging involves pumping at a flow rate that is comparable to the recharge rate of the well.
2. **Bailing** can cause mixing at the water surface as the bailer is introduced. Surface mixing can allow oxygen from the atmosphere into the groundwater. Also, if the well is bailed too quickly, the water drawn into the well may not be representative of the bulk aquifer in the screened interval. If the well is purged with a bailer, one should avoid a bailing rate greater than the well recovery rate by lowering the bailer carefully through the air water interface, and then collecting the sample at least three feet from the water surface.
3. Some wells have **dedicated pumps** that make other purging techniques impractical. Water samples should be collected from a discharge sampling port using **an overflow device.** Care should be taken to avoid excessive draw down, which can introduce water that is not representative of the bulk aquifer. In addition, pump cavitation can aerate the water and cause ferrous iron oxidation.

Equipment. Following is a list of recommended equipment for ferrous iron analysis:

- **Reaction vial**. Two companies, CHEMetrics and HACH, have auto-filling vials for collection of samples for iron analysis. Auto filling vials help protect the samples from oxidation by atmospheric oxygen once it is removed from the well.
- **Snapper**. A snapper is an in-situ sampling device made by CHEMetrics for use with CHEMets. HACH also makes a snapper-type device, but it only useful in shallow applications.
- **Overflow device**. An overflow device is any device that allows an oxygen

sample to be taken while limiting potential contamination by atmospheric oxygen.

- **Slow emptying device**. A slow emptying device is placed on the bottom of a bailer to produce a slow, controlled, steady water stream free from air entrainment. An example of a slow emptying device is the Aqua Bailer PVCEMP.
- **Spectrophotometer or colorimeter**. Ferrous iron analysis is a colorimetric method. The ferrous iron reacts with 1,10-phenanthroline creating a colored complex. Color change is proportional to the ferrous iron concentration, and is measured with a spectrophotometer or colorimeter. A spectrophotometer provides greater sensitivity and range, but a colorimeter or color comparator may be satisfactory in most cases.

Concentration range and choice of reaction vials. Samples for ferrous iron analysis should **not** be diluted because the dilution water may contain oxygen; therefore, results can only be reported within the range provided by the reaction vials. Table 1 shows two commercially available test kits for ferrous iron and dissolved manganese:

TABLE 1: Ferrous Iron and Dissolved Manganese Test Kits

Reaction vial	Range
HACH AccuVac – 25140-25 (ferrous iron)	0 – 3 mg/l
HACH AccuVac – 1467-00 (dissolved manganese)	0 – 3 mg/l
CHEMetrics CHEMet – K(R) -6210 (ferrous iron)	0 – 11 mg/l
CHEMetrics CHEMet - K-6502 (dissolved manganese)	0 – 2 mg/l

The CHEMetrics K–6210 is the same as the R-6210, but comes with a visual comparator, which can be used to estimate the ferrous iron concentration.

Summary. Both ferrous iron and dissolved manganese are susceptible to oxidation during field analysis. The procedures presented in this text are good guidelines to protect samples and avoid false negative results. However, field conditions vary greatly from site to site and analysis. The primary goal of this text is to educate and enable samplers to exercise judgment in properly collecting and analyzing samples on a case by case basis.