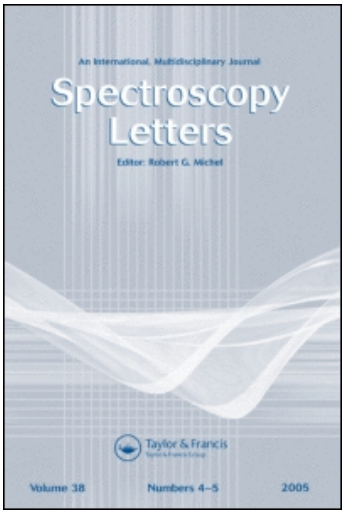

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Determination of Iron in Abandoned Mine Drainage by UV-Vis Spectrophotometry and Flame Atomic Absorption Spectrophotometry

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Abstract: This paper describes and compares the results obtained from determination of total iron in abandoned mine drainage (AMD) from selected sites in western Pennsylvania by UV-visible spectrophotometry (UV-Vis) and flame atomic absorption spectrophotometry (FAAS). As our laboratory possesses both methods, the accuracy and precision of iron results by UV-Vis, using iron (II) chelator 2,4,6-tripyridyl-1,3,5-triazine (TPTZ), and FAAS are of interest in the event of instrument problems with either method. Calibration curves show excellent linearity ($R^2 \geq 0.990$). The results show good accuracy (complete recovery of spiked iron) and precision (0.5–3.4% RSD by UV-Vis, 1.5–7.7% RSD by FAAS), indicating both methods are suitable for determination of iron in AMD. This comparison study is presented as a potential approach to teaching students about UV-Vis and FAAS and their advantages and disadvantages.

Keywords: Abandoned mine drainage (AMD), flame atomic absorption spectrophotometry (FAAS), iron, student project, 2,4,6-tripyridyl-1,3,5-triazine (TPTZ), UV-visible spectrophotometry (UV-Vis)

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INTRODUCTION

UV-visible spectrophotometry (UV-Vis)[1–3] and flame atomic absorption spectrophotometry (FAAS)[4–6] are perhaps the most widely used analytical methods for the determination of metal ions (e.g., iron) in a variety of sample types. UV-Vis and FAAS methods for the determination of iron [7–10] abound in the chemical literature. This is no surprise, as iron is the fourth most abundant element in Earth's crust [11] and plays a critical role in the physiologies of humans and other animal species.[12,13] Iron is still one of the leading metals of use in manufacturing processes, especially in the steel industry.[14]

The environmental impact of iron is witnessed in regions of the world in which coal mining was and is an active industry. Abandoned mine drainage (AMD) is a serious problem and a topic of high interest in western Pennsylvania due to extensive coal mining, numerous abandoned coal mines filled with groundwater, contamination of streams, and property subsidence.[15–17] AMD is the result of weathering of pyrite (FeS_2)-containing rocks by water to produce Fe^{2+}, SO_4^{2-}, and H^+ ions, which in turn lower the pH of runoff streams and precipitate iron oxides ("yellowboy").[17–20] The lowering of pH of streams contaminated by AMD can be harmful to aquatic life.[21,22] Milligram per liter (mg L^{-1}) concentrations of Fe in AMD impart a foul, metallic odor and taste to water as well as increase water hardness.[23] The chemistry involved in the production of yellowboy is summarized in Eqs. (1–4):[17–19]

$$2FeS_2(s) + 7O_2(g) + 2H_2O(l) \longrightarrow 2Fe^{2+}(aq) + 4\ SO_4^{2-}(aq) + 4H^+(aq) \quad (1)$$

$$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \longrightarrow 4Fe^{3+}(aq) + 2H_2O(l) \quad (2)$$

$$4Fe^{3+}(aq) + 12H_2O(l) \longrightarrow 4Fe(OH)_3(s) + 12H^+(aq) \quad (3)$$

$$FeS_2(s) + 14Fe^{3+}(aq) + 8H_2O(l) \longrightarrow 15Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 16H^+(aq) \quad (4)$$

In this study, our focus is on iron concentrations in AMD and the factors influencing those concentrations. Of particular interest to us are the accuracy and precision of iron results obtained by UV-Vis, using 2,4,6-tripyridyl-1,3,5-triazine (TPTZ)[7] as the iron chelator, and FAAS. Our laboratory possesses both analytical methods; thus, an idea of the suitability of these methods for determination of iron in AMD is required. UV-Vis and FAAS require that the sample be put into aqueous solution by an appropriate sample preparation technique. Similarities and differences between UV-Vis and FAAS are detailed in the literature.[1–10] The hypothesis is that both methods will

yield comparable results for iron and can be used interchangeably and reliably for determination of iron in AMD.

The comparison of UV-Vis and FAAS methods and results, along with AMD sampling protocols and analysis procedures, will be presented and discussed.

MATERIALS AND METHODS

Apparatus

Spectral measurements were made using a Hitachi Model U-3010 scanning, double-beam UV-Vis spectrophotometer (Hitachi Instruments, Inc., San Diego, CA, USA) and matched 1-cm quartz cuvets (NSG Precision Cells, Inc., Farmington, NY, USA) and a Perkin-Elmer A Analyst 100 atomic absorption spectrophotometer with air-acetylene flame, 10-cm single-slot burner head, and Lumina iron hollow cathode lamp model no. N3050126 (Perkin-Elmer Corporation, Norwalk, CT, USA). Adjustments of pH for optimum color formation were monitored with pH meters (Flinn Scientific, Inc., Batavia, IL, USA, and Fisher Scientific, Inc., Pittsburgh, PA, USA). AMD samples were collected in screw-cap plastic centrifuge tubes (Fisher Scientific, Inc.). A sample grabber for collection of AMD samples was constructed from a three-section hollow aluminum tube of approximately 6 ft (1.83 m) total length, to which was attached a ringstand clamp to secure the collection vessel.

Reagents and Solutions

The ligand 2,4,6-tripyridyl-1,3,5-triazine (TPTZ) was purchased from GFS Chemicals, Inc. (Powell, OH, USA) and used as is. Aqueous solutions of TPTZ, ca. 5.0×10^{-3} to 1.0×10^{-2} mol L^{-1}, were prepared according to published procedures.[7,8] Standard aqueous Fe stock solutions (1000 mg Fe/L or 1.79×10^{-2} mol Fe L^{-1} and working standard Fe solutions (10–100 mg Fe/L or 1.79×10^{-4} to 1.79×10^{-3} mol Fe L^{-1}) were prepared according to established procedures.[7,8] Calibration standards ranging from 0.05 to 10 mg Fe/L (or approximately 10^{-6} to 10^{-4} to mol Fe L^{-1}) were prepared from the working standard. Reagent grade hydroquinone (Fisher Scientific, Inc.) was used for reduction of Fe^{3+} to Fe^{2+} and was prepared at 1–2% (w/v) in aqueous solution. Reagent grade sodium acetate (Fisher Scientific, Inc.) was used as buffer component and prepared at 2 M in aqueous solution.[7,8] NIST-traceable pH 7 buffer solution (Fisher Scientific, Inc.) was used for calibration of pH electrodes. Dilute (0.1–1 M) aqueous HCl and NaOH were prepared from reagent grade concentrated HCl and NaOH pellets (Fisher Scientific, Inc.), respectively.

Protocol for Collection of AMD Samples

The collection tubes and screw caps were washed with 3 M HNO_3, then rinsed at least once with distilled or deionized water. One milliliter of ca. 3 M HNO_3 was added to each collection tube. At the collection site, the collection tube was secured by the sample grabber and lowered into the runoff stream. Concurrently, the date and time of collection, sample appearance, temperature, pH, and conductivity were measured and recorded.

Procedures for Determination of Iron in Abandoned Mine Drainage

UV-Visible Spectrophotometry[7,8]

Place 5–10 mL of deionized water into a small (e.g., 50 mL) beaker. Pipet between 0.20 and 5.00 mL of the AMD sample into the beaker. Treat the sample solution with the following reagents, added in the order given: 1.00 mL of ca. 5.0×10^{-3} mol TPTZ L^{-1} ligand solution, 1.00 mL of ca. 2% (w/v) hydroquinone solution, and 1.00 mL of 2 M sodium acetate solution. Then adjust the pH of the solution to 5.0 ± 0.05 with dilute HCl and NaOH, monitoring the adjustments with a pH meter. Transfer the solution to a clean 25 mL volumetric flask, dilute to volume with deionized water, and allow to stand for at least 5 min for optimum color development. Measure the absorbance at 593 nm versus deionized water. This procedure was used for all blanks, standards, and samples and for Fe determinations by standard addition.[2] Calibration curves are prepared using Fe concentrations ranging from 0.0 to 4.00×10^{-5} mol Fe L^{-1} (0.0 to 2.2 mg Fe L^{-1}).

Flame Atomic Absorption Spectrophotometry[9,10]

Add 10 mL of deionized water to a 25 mL acid-cleaned volumetric flask. Pipet 0.250 mL of concentrated H_2SO_4, HCl, or HNO_3 into the flask to produce a 1% (v/v) concentration of acid in the analysis solution. Pipet between 0.50 and 5.00 mL of the AMD sample into the flask, dilute to volume with deionized water, and analyze for iron by FAAS. This procedure was used for all blanks, standards, samples, and for Fe determinations by standard addition.[5] Calibration curves were prepared using Fe concentrations ranging from 1.00 to 10.0 mg Fe L^{-1}.

RESULTS AND DISCUSSION

Calibration Curves for Determination of Iron by UV-Vis and FAAS

Calibration slopes obtained from UV-Vis measurements are the product of molar absorptivity and cuvet pathlength (1.00-cm quartz cells were used in

these studies). The calibration slopes for the UV-Vis method ranged from 1.85×10^4 L (mol Fe)$^{-1}$ to 2.89×10^4 L (mol Fe)$^{-1}$ over the concentration range 1.00×10^{-6} to 4.50×10^{-5} mol Fe L^{-1} (0.056 to 2.5 mg Fe L^{-1}). For the FAAS method, the calibration slopes from 0.02233 L (mg Fe)$^{-1}$ to 0.03718 L (mg Fe)$^{-1}$ over the concentration range 0.0–10.0 mg Fe L^{-1}. The calibration curves obtained by both UV-Vis and FAAS possess R^2 values that are $\geq$0.990 in every case except one, indicating excellent linearity of absorbance with Fe concentration.

Determination of Iron in AMD by UV-Vis and FAAS: Precision and Accuracy

Table 1 compares results obtained by UV-Vis and FAAS for determination of iron in AMD samples collected at selected runoff sites near Elrama, Pennsylvania, during 2004. Overall, there is good agreement in the mg Fe L^{-1} obtained by both methods. The Fe concentrations of samples from sites 4S, 4 N, and 5 are the means of duplicate determinations. The agreement between the Fe concentrations obtained by UV-Vis and FAAS indicates that

Table 1. Determination of Fe in AMD from selected sites in the Mon Valley, Southwestern Pennsylvania, by UV-Vis[a,b] and FAAS[a,b]

	UV-Vis		FAAS	
Site no. (date[c])	Mean ± SD (mg Fe L^{-1})	%RSD	Mean ± SD (mg Fe L^{-1})	%RSD
5[a] (3/28/2004)	75.9 ± 1.5	2.0	61.1 ± 2.0	3.3
4S[a] (3/28/2004)	71.6 ± 0.2	0.2	76.9 ± 5.9	7.7
4S[a,d] (3/28/2004)	83.1 ± 0.4	0.5	82.8 ± 4.0	4.8
4N[a] (3/28/2004)	157.8 ± 5.4	3.4	161.6 ± 3.9	2.4
5[a] (4/30/2004)	100.2 ± 0.1	0.1	106.4 ± 4.0	3.8
4S[a] (4/30/2004)	89.0 ± 1.3	1.5	92.6 ± 2.0	2.2
4N[a] (4/30/2004)	216.3 ± 0.5	0.2	218.8 ± 2.0	0.9
1[b] (10/1/2004)	36.4 ± 0.2	0.5	39.0 ± 2.5	6.5
1[b] (10/7/2004)	45.9 ± 1.1	2.4	47.2 ± 2.4	5.1
1[b] (10/15/2004)	43.1 ± 0.5	1.2	46.3 ± 2.0	4.3
1[b] (10/29/2004)	37.4 ± 0.3	0.7	38.7 ± 1.5	3.8
1[b] (11/18/2004)	31.3 ± 0.1	0.3	35.5 ± 0.5	1.5
1[b,d] (11/18/2004)	36.7 ± 0.1	0.2	34.8 ± 0.8	2.3

[a]These samples were analyzed in duplicate.
[b]These samples were analyzed in triplicate.
[c]Date of sample collection.
[d]Additional sample collected from site 4S; repeat analysis of site 1 sample.

the two methods can be used interchangeably for determination of iron in abandoned mine drainage.

To better ascertain the precision of iron results obtained by both methods, AMD samples from site 1 were analyzed for iron in triplicate. These results are listed in Table 1. Overall, the precision obtained by UV-Vis is slightly better than that obtained by FAAS. The %RSD for samples analyzed for iron ranged from 0.1 to 3.4 by UV-Vis and 1.5 to 7.7 by FAAS. Possible sources of the higher percent relative standard deviation (%RSD) values obtained by FAAS include occasional instability of the air-acetylene flame produced by fluctuations in the gas flows, momentary variations produced by hollow cathode lamp emission, and errors in standard and sample preparations. Overall, the precision obtained in this study by both methods is acceptable for the ranges of iron concentrations determined.

Recovery of known amounts of Fe standard solution spiked into the AMD sample from site 1 (18 December 2004) was used as an assessment of the accuracy of the iron determination by both methods. The iron recoveries obtained by UV-Vis (102.0%) and FAAS (110.0%) are higher than expected; nonetheless, the results indicate that essentially complete recovery of iron by each method is feasible.

Determination of Iron in AMD by UV-Vis and FAAS: Using a Graphical Standard Addition Approach

The use of graphical standard addition[2, 5, 7–10] with both UV-Vis and FAAS for determination of iron in AMD was performed. For this study, the AMD sample from site 1 (1 October 2004) was used. Determination of iron in site 1 (1 October 2004) runoff water yielded 36.6 mg Fe L^{-1} by graphical standard addition and UV-Vis and 36.3 mg Fe L^{-1} by graphical standard addition and FAAS. The Fe concentration in the original sample was determined by conversion of the Fe concentration in the analysis solution from mol Fe L^{-1} to mg Fe L^{-1}, followed by correction for sample dilution. The results for mg Fe L^{-1} in the site 1 (1 October 2004) sample show excellent agreement and indicate that standard addition, combined with either UV-Vis or FAAS, is an alternative approach for determination of iron in AMD.

Environmental Significance of Iron Concentrations in AMD

The results given in Table 1 for Fe in AMD from sites 1, 4S, 4 N, and 5 show that sites 4S, 4 N, and 5 yielded higher Fe concentrations than site 1. Over the past 3 years, our results for Fe in mine drainage from these sites have confirmed this trend. For example, 21.6 and 32.8 mg Fe L^{-1} were found (by UV-Vis) in AMD collected from site 1 on 27 March 2004 and 29 April 2004, respectively, versus the corresponding Fe concentrations in AMD

from sites 4S, 4 N, and 5 (Table 1). Similarly, concentrations of 124, 209, and 189 mg Fe L^{-1} were found in AMD collected from sites 5, 4S, and 4 N, respectively, on 1 October 2004 versus the corresponding Fe concentration in AMD from site 1 (Table 1). This difference in mg Fe L^{-1} between site 1 and sites 4S, 4 N, and 5 may be due to greater amounts of water from surface streams and precipitation that entered and built up in the mines associated with sites 4S, 4 N, and 5 over time. A greater amount of water was observed to flow at sites 4S, 4 N, and 5 during the periods indicated in Table 1. It is possible that the runoff from the mine associated with site 1 may travel a greater distance to that site, increasing the possibility of lower Fe concentrations in the runoff via precipitation of Fe as insoluble oxides.

Environmentally, the concentrations of iron in AMD from the selected sites are a potential source of contamination for streams and aquifers that supply water for household use, into which runoff water might flow. Iron is generally not toxic to humans and higher mammals at the concentrations found in this study. Iron is a nuisance pollutant, in that iron in milligram per liter concentrations can contribute to increased water hardness and make household activities such as cooking and laundry difficult or nearly impossible. Milligram per liter concentrations of iron can impart an unpleasant metallic odor and taste to drinking water exposed to sources of iron contamination.[23] The maximum allowable concentration of iron in drinking water set by the U.S. Environmental Protection Agency (EPA) is 0.3 mg Fe L^{-1}.[24] Products of pyrite oxidation, for example, H^+ and SO_4^{2-} (as sulfuric acid) along with Fe^{2+} and Fe^{3+} [Eqs. (1–4)],[17–20] may lower the pH (e.g., $pH < 4$) of an otherwise clean stream (e.g., pH 6–7) and kill any aquatic life present.[21,22]

Comparison of UV-Vis and FAAS as a Potential Teaching Tool in Undergraduate Analytical Chemistry Laboratories or as an Undergraduate Research Project

The comparison study of UV-Vis and FAAS arose from our studies of iron concentrations in runoff water from abandoned mines. Our hypothesis was that both methods will produce comparable results for iron in AMD. Our laboratory possesses both UV-Vis and FAAS capability. Using either UV-Vis or FAAS reliably and interchangeably for determination of iron is important to us, should either instrument become incapacitated or be used for another project. Our results confirm our original hypothesis. Furthermore, our comparison study showed itself to be a research project within an existing one and can provide valuable experience to an undergraduate with an interest in spectroscopy and its quantitative applications. Such a project would be applicable to just about any analytical problem and involve any number of analytical methods. The scope of such a project is limited only by what the researchers are willing to do.

The comparison study of UV-Vis and FAAS described in this paper provides the basis for a laboratory project in an introductory quantitative or instrumental analysis course that allows students to establish whether two or more analytical methods for determination of the same analyte will yield comparable results and can be used interchangeably. Students would be exposed to similar yet different spectroscopic methods and method validation parameters, for example, calibration curve characteristics (linear range of concentration, best-fit straight line and slope, and R^2), accuracy (via standard addition), and precision (via replicate determinations) of results, and limits of detection and quantitation. Additionally, students would gain from this comparison of UV-Vis and FAAS for determination of iron in abandoned mine drainage in terms of the ability to assess suitability of analytical methods for specific applications.

With the introduction of instrumental analysis lecture and laboratory courses at our campus in spring 2006, we plan to incorporate this comparison study of UV-Vis and FAAS as a laboratory project similar in scope to the "Iron Project" in our introductory analytical chemistry course. Additionally, we plan to do comparison studies with other types of samples (e.g, beverages, foods, and soils) and focus on other metals of interest, such as copper, zinc, and aluminum.

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