Field Screening Test for Iron Leached from Well Bore Rock Samples by Using Color Development of Iron(III)-Xylenol Orange System

Akihiko Ishida, Emiko Kaneko, and Takao Yotsuyanagi*
Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-yama 07, Sendai 980-8579

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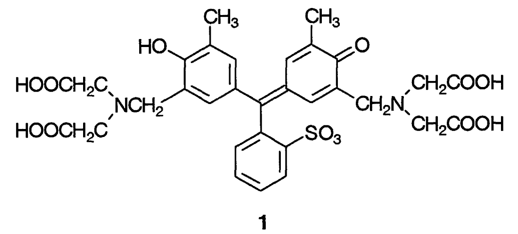
A field test for iron leached from rocks has been developed by using a purple blue iron(III)-Xylenol Orange (XO) complex formed at the iron(III) concentrations above the molar concentration of XO. The test is performed in an aqueous drop on a Tefron® plate. When the iron content exceeds a criterion, a distinct color change from yellow to purple blue appears in the drop containing a 10-mg rock sample, HCl, XO, and $(NH_4)_2S_2O_8$. This method was applied to the prediction of water quality in aquifers.

In the field of well construction, a reliable and rapid method for the prediction of water quality in groundwater has been urgently needed. Groundwater quality depends on the nature of aquifers. Since water sample of aquifers cannot be available during well construction, the rocks are the only sample that can be analyzed. Water quality has been predicted indirectly by the geological survey around the well site and also roughly by observations of bore rocks obtained from each depth of the drilled hole. These prediction methods, however, are not sufficient to select aquifers that have high quality water among several aquifers across the borehole. Furthermore, aquifers should be selected immediately after drilling and before setting the well casing.

One of the important factors in water quality in wells is iron content. Iron that causes a bad taste and brown precipitates of iron(III) hydroxide at the high concentration is often an obstacle to practical use. In addition, iron is accompanied by the other undesired components such as manganese and arsenic. Chemical composition in groundwater generally relates to that in rocks of aquifers. Therefore, iron contents in rocks will effectively indicate iron concentrations in groundwater. However, common laboratory methods for rock samples, such as X-ray fluorescence analysis, are impracticable for on-site analysis in terms of its portability, cost, and analysis time. Commercially available test kits for iron ion in water sample provide simple and rapid methods but are not applicable for the test of rock samples.

In this study, a simple, rapid, and inexpensive method has been developed for the determination of iron in rock samples. This method is based on the color development property of iron(III)-Xylenol Orange **1** (XO) system that gives yellow, red, and purple blue with an increase in iron concentration. In particular, the purple blue color that develops in the presence of excess iron contrasts with other colors in the iron(III)-XO system. The purple blue color assists the visual detection for higher content of iron in samples, responsible for the quality criterion of drinking water. Moreover, for the visual screening tests, sensing with distinguishable colors will be advantageous rather than the comparison of the color intensity with standard series. Xylenol Orange has never been used as in the proposed method though the reagent is frequently used for the determination of iron.[1–3] Drop-based methods are important approaches to simple tests for metal ions, such as spot test,[4] ring oven technique,[5] TLC,[6,7] and ring fluorometry with hydrophobic substrates.[8,9] In the proposed procedure, as described below, a drop-based method with a water-repellent plate has been employed, where many samples are tested simultaneously on the single plate without any vessels and laboratory equipments.



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The recommended procedure is as follows: add 40 μl of 0.02 M (1 M = 1 mol dm^{-3}) hydrochloric acid to about 10 mg of rock sample or almost the same volume of rock sample as 10 mg of model rock samples (size, 0.5–2 mm) on a poly(tetrafluoroethylene) plate (80 x 150 x 2 mm). The rock sample is engulfed in a hemispherical drop on the plate throughout this test. Stand the reaction mixture for 5 min to leach out iron ions from the rock. Add 10 μl of 0.1 M ammonium peroxodisufate and 40 μl of 250 μM XO (Dojin Co. Ltd. Kumamoto, Japan) and then stand the drop for 1 min for the color development. The level of iron(III) concentration is evaluated from the color of the drop. When the color of the drop is yellow, it indicates a low iron content (< 44 μM in the final drop) in the rock sample. The color from deep reddish yellow to dark red indicates a significant content (44–110 μM). A purple blue drop indicates an even higher iron content (> 110 μM).

Figure 1 shows the absorption spectra of iron(III)-XO system at pH 2 with various iron(III) concentrations. The absorption maximum shifts from 430 to 585 nm without isosbestic points with an increase in iron(III) concentration. The reagent has the absorption maximum around 430 nm. The absence of the isosbestic points resulted from the formation of

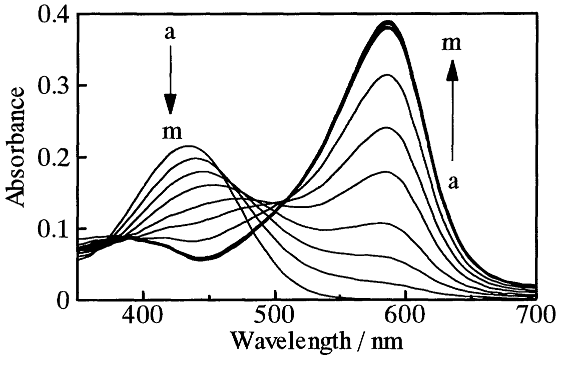

Figure 1. Absorption spectra of 110 μM XO with varied amounts of total iron(III) at pH 2. [Fe(III)] / μM: a, 0; b, 22; c, 44; d, 66; e, 88; f, 110; g, 130; h, 150; i, 180; j, 200; k, 220; l, 330; m, 440. $[(NH_4)_2S_2O_8]$ was 11 mM. One-millimeter length path cells were used.

three color components including two complexes with an absorption maximum approximately at 540 nm and 585 nm, respectively, according to spectra obtained by using the reagent blank as a reference. The former is formed in the presence of excess reagent and the latter in the presence of excess iron(III).

We investigated relationship between molar ratio and absorbance at 585 nm and 540 nm, respectively at pH 2, even though the commercially available reagent contains impurities such as semi-XO and iminodiacetate.[10–12] The two bending points were obtained. The results suggested the existence of 1 : 1 and 2 : 1 (M : L) complexes as given by following equilibria (XO is denoted as L and charges were omitted):

$$\mathrm{Fe^{III}} + \mathrm{L\ (Yellow)} \rightleftharpoons \mathrm{Fe^{III}L\ (Red)} \qquad (1)$$

$$\mathrm{Fe^{III}L} + \mathrm{Fe^{III}} \rightleftharpoons \mathrm{Fe^{III}{}_2L\ (Purple\ Blue)} \qquad (2)$$

The reagent, which has two geometrically isolated coordination sites in a molecule, probably forms a 2 : 1 complex. More details with a purified reagent will be reported elsewhere.

The absorbance at 585 nm in the presence of excess iron(III) remained constant and maximum value in the pH range 1.5–2.5. The reaction of XO with iron(III) is selective and rapid under acidic conditions. Full color development was accomplished within 1 min under the analytical conditions. Xylenol orange reacts not only with iron(III) but also with a variety of other metal ions including aluminium ion. An appropriate choice of pH conditions (below 2) considerably improves the selectivity. Aluminium ion forms a red purple chelate with an absorption maximum at 555 nm under the same conditions. However, the reaction of aluminium ion with XO was slow enough, so that up to 1 mM of aluminium ion was tolerated when the colors due to iron(III)-XO complexes was detected within 3 min at the conditions of the proposed method.

Iron(II) ion hardly reacts with XO under the conditions. The oxidation of iron(II) ion by dissolved oxygen at pH 2 is very slow. For the measurement of total iron, iron(II) ion is oxidized to iron(III) ion by ammonium peroxodisufate. Hydrogen peroxide is not suitable for the field use because of storage difficulty.

Leaching technique with 0.02 M hydrochloric acid solution was used for the determination of water-soluble iron species that are closely related to iron in groundwater. In preliminary investigations with rocks of aquifers, iron concentration in well water was higher than 0.3 mg/L (the criterion for drinking water in Japan) when iron leached from rock samples is higher than 110 μM for leaching time of 5 min. On the basis of these findings, the reagent XO at the concentration of 110 μM in a final drop was used in the recommended procedure.

The proposed method was applied to the determination of iron in rock samples from aquifers of wells in five different locations (Table 1). Rock samples were offered by Geological Survey of Hokkaido. Water samples were taken after the wells were drilled and left for more than one week undisturbed. Iron contents in well water were determined by 1,10-phenanthroline method. At the positions of the strainers of the wells 1–4 in Table 1, there were several layers. Iron in well water is brought about from all the layers. When the results by the proposed method show purple blue, iron concentrations in well water were higher than the quality criterion of 0.3 mg/L (see the well No.2 in Table 1).

Table 1. Application to rock samples of aquifers

Well[a]	Rock samples from aquifers (Geological nature)	Sampling depth / m	Analytical result by proposed method[b]	Total iron in well water / mg L^{-1}
1	Volcanic breccia	32	Y	0.03–0.05
	Tuff breccia	35, 37, 38, 39, 40	Y	
	Volcanic breccia	45, 47, 50	Y	
2	Pebbly conglomerate	53.5, 59.5, 63.4	PB	1.01
	Slate	67	PB	
3	Pumiceous tuff	55, 60	Y	0.26
	Tuff breccia	70	O	
	Volcanic breccia	75	Y	
4	Volcanic breccia	21, 23, 24, 25, 26, 27, 28	Y	0.24[c]
	Volcanic sandy conglomerate	29, 30	Y	
	Andesite lava	32, 33, 34, 35, 36, 37, 38	Y	
5	Sandy conglomerate	43, 44, 45, 46, 47, 48	Y	0.08–0.18

[a] Positions of strainer / m: 1, 32.0–54.0; 2, 51.0–67.4; 3, 51.5–62.5 and 68.0–79.0; 4, 21.5–38.0; 5, 42.5–48. [b] The resulting color of drops: Y, yellow; O, orange; PB, purple blue. [c] Migration of iron species from upper or lower aquifers is speculated.

Therefore, the proposed method has been verified to be able to use as a key method for drillers to find an aquifer giving good quality water.

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References

1 B. Budesinsky, *Z. Anal. Chem.*, **188**, 266 (1962).
2 M. Otomo, *Bunseki Kagaku*, **14**, 677 (1965).
3 H. Nishida, T. Nishida, and T. Segawa, *Bunseki Kagaku*, **28**, 379 (1979).
4 F. Feigl and V. Anger, "Spot Tests in Inorganic Analysis," 6th English ed, Elsevier, Amsterdam (1972).
5 H. Weisz, "Microanalysis by the Ring Oven Technique," 2nd ed, Pergamon Press, Oxford (1970).
6 K. Oguma, Y. Takeda, and K. Ishida, *Bunseki*, **1993**, 661.
7 H. Mizuguchi, H. Yasuda, E. Kaneko, and T. Yotsuyanagi, *Chem. Lett.*, **1997**, 895.
8 E. Kaneko, A. Ishida, Y. Deguchi, and T. Yotsuyanagi, *Chem. Lett.*, **1994**, 1615.
9 A. Ishida, E. Kaneko, and T. Yotsuyanagi, *Chem. Lett.*, **1999**, in press.
10 M. Murakami, T. Yoshino, and S. Harasawa, *Talanta*, **14**, 1293 (1967).
11 S. Nakada, M. Yamada, T. Ito, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **50**, 1887 (1977).
12 H. Sato, Y. Yokoyama, and K. Momoki, *Anal. Chim. Acta*, **94**, 217 (1977).