

## ELECTROCHEMICAL DISSOLUTION OF GOETHITE BY ABRASIVE STRIPPING VOLTAMMETRY

Tomas GRYGAR, Jan SUBRT and Jaroslav BOHACEK

*Institute of Inorganic Chemistry,*

*Academy of Sciences of the Czech Republic, 250 68 Rez near Prague, The Czech Republic*

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Abrasive stripping voltammetry was applied to the investigation of the reductive dissolution of some iron(III) oxides and hydroxy-oxides, particularly goethite ( $\alpha$ -FeOOH), in acid media. The electrode reaction directly involves the solid phase, and the reaction pathway depends on the phase composition and particle shape. This can be used for a qualitative and quantitative characterization of goethite. The results of a quantitative analysis of a mixture of goethite ( $\alpha$ -FeOOH) and lepidocrocite ( $\gamma$ -FeOOH) are compared with those of IR and Moessbauer spectroscopic examination. The effects of the particle appearance (shape, crystal intergrowth) on the results of the voltammetric and chronoamperometric measurements are discussed.

Direct analysis of powdered solids by electrochemical methods complements nicely conventional phase analysis methods such as powder X-ray analysis, IR spectroscopy and, for iron compounds, Moessbauer spectroscopy. In fact, each of the methods places some specific requirements on the phase crystallinity and particle size and the procedures are instrumentally demanding and time consuming and so that the possibility of resorting to alternative analytical methods is very appealing.

A method which does not place very high demands on instrumentation, is well suited to routine phase analysis, and moreover, can be used on a micro scale, has been suggested by Scholz and coworkers<sup>1,2</sup>. The method is based on voltammetric measurement with a carbon electrode to which analyte particles are fixed by rubbing against sample, the authors named the technique "abrasive stripping voltammetry" (henceforth AbrSV). The method is useful for the analysis and characterization of metal alloys<sup>1</sup>, minerals<sup>2</sup>, various inorganic binary mixtures<sup>3</sup>, pigments<sup>4</sup>, for the study of high-temperature superconductors<sup>5</sup>, for the calculation of thermodynamic constants of low soluble compounds<sup>6,7</sup>, etc. (a survey of applications has been presented in ref.<sup>8</sup>). Since electrode processes can generally involve higher order electrochemical reactions, diffusion, adsorption, and chemical reactions of the substance in the surroundings of the electrode, the overall reaction pathway is very complex<sup>8</sup> and interpretation of the voltammograms requires prior understanding of the conversion mechanism of the substance on the electrode and/or in its surroundings.

Basic rules for the analysis of binary mixtures of inorganic phases by AbrSV have been summarized by Scholz and coworkers<sup>3</sup>, who presented examples of analyses of  $\alpha$ -FeOOH–MnO<sub>2</sub>, HgO–PbO, HgS–HgO and AgCl–AgI mixtures. The components do not interact with each other, and therefore the calibration curves possess simple shapes, and the absolute amount of sample deposited on the electrode need not be known provided that the amount is sufficiently low to have no effect on the voltammetric peak shape. Since the amount of analyte reacting on the electrode is, according to the authors, on the order of  $10^{-10}$  mol, a perfect chemical homogeneity of sample is a basic pre-requisite.

Iron oxides and hydroxy-oxides find wide application as magnetic storage media, pigments, etc. Of importance is, in addition to the phase composition of their mixtures, the character of the crystals. For this reason we attempted to use AbrSV to analyze them. We chose goethite,  $\alpha$ -FeOOH, as the model phase to test the applicability of the technique. Synthetic goethite finds use as a pigment and the starting material for the manufacture of magnetic storage media. The substance also forms rather large particles of various shapes, which often intergrow<sup>9</sup>, and this manifests itself, among other things, in their dissolution patterns in acid solutions<sup>10</sup>.

Within the present study we examined whether AbrSV is capable of detecting other phases in synthetic goethite and/or of providing information on the character of goethite particles.

## EXPERIMENTAL

### Preparation of Iron Oxides and Oxide-Hydroxides

Goethite samples were synthesized by two different procedures. The one procedure was based on the transformation of ferrihydrite formed from Fe<sup>3+</sup> in basic medium<sup>9</sup>, whereas the other procedure, which is applied in the manufacture of goethite pigments, was based on the oxidation of an aqueous solution of iron(II) sulfate with air at 40–80 °C and pH 3–4; goethite germs were added to the sulfate solution with a view to obtaining particles uniform in size, shape, and phase composition. Natural goethite samples from Dachstein, Austria; Harz, Germany; and Příbram, Czech Republic sites were only ground in an agate mortar.

Ferrihydrite was prepared by hydrolysis of an aqueous solution of iron(III) nitrate at various pH values<sup>11</sup>, or from iron(III) sulfate at pH 13.

Magnetite was prepared by oxidation of iron(II) sulfate solutions with potassium nitrate<sup>9</sup> or by reaction of iron(II) sulfate and jarosite<sup>12</sup>.

Hematite was obtained by heating magnetite at 600 °C in air for 2 h. In addition, the commercial BAYER 130 HB pigment and hematite prepared by transformation of ferrihydrite in water at temperatures near 200 °C were also used.

Maghemite was obtained by heating magnetite at 180 or 250 °C in air for 2 h. Commercial SCP-21 maghemite for magnetic information storage (Societe de Chimique de Provance) was also used for comparison.

Lepidocrocite was synthesized by oxidation of aqueous solutions of iron(II) sulfate with air oxygen at a temperature not exceeding 20 °C and at pH 7–8 (ref.<sup>13</sup>). A goethite–lepidocrocite mixture was obtained at pH < 6 and a temperature lower than 80 °C.

Acaganeite was obtained by hydrolysis of an iron(II) chloride solution<sup>14</sup>.

### Sample Characterization

Phase purity of all phases and their mixtures was checked by powder X-ray diffractometry (sample identity: a DRON 2.0 instrument equipped with a CoK $\alpha$  source and an Fe filter; Burevestnik, U.S.S.R.), by Moessbauer spectroscopy (in particular, quantitative phase analysis: an KFKI 512-channel instrument, Hungary), and by IR spectroscopy (quantitative and qualitative analysis of mixtures: a Pye Unicam 9512 spectrophotometer, U.K.). The sample particle shape was evaluated based on TEM photographs (BS 242E, 60 kV, Tesla, Czech Republic).

### Voltammetric Measurements

Voltammetric measurements were performed on a PA-4 polarograph interfaced to an XY 4106 plotter; a TZ 4620 recorder was employed for chronoamperometric measurements (all Laboratorni pristroje, Prague, Czech Republic). An Ag/AgCl reference electrode in a saturated KCl solution was used, and all potentials reported are relative to that electrode.

The graphite working electrode was prepared by impregnation of a spectral graphite rod 5 mm in diameter (Elektrokarbon Topolcany, Slovak Republic) either with silicone oil (OIGE) (Lukoil M-15 methysilicone oil, Synthesia Kolin, Czech Republic), or with molten paraffin (PIGE) (m.p. 54–55 °C, Paramo, Pardubice, Czech Republic). Before impregnation, the lateral area of the rod was coated with an epoxy resin to ensure that only defined areas of the electrode would come into contact with the electrolyte. Prior to each measurement, the measuring surface of the electrode was polished either with a paste based on silicone oils and Si and Cr oxides (for OIGE) or with dry SiO<sub>2</sub> (for PIGE). Where this procedure was insufficient to remove all of the unreacted sample, a fine grinding paper was used. Subsequently, the working electrode was rubbed vigorously for some 10 s against several milligrams of the sample powder on a filter paper in order to force the particles to penetrate into the electrode surface. Loose particles on the electrode surface were then wiped off with cotton. This sample fixing procedure, which is more forceful than as described in refs<sup>1-3</sup>, proved to suit well also for fixing large platelets of goethite and lepidocrocite particles, which was rather difficult by other means.

The voltammetric curves were recorded in the differential pulse (DP) mode, because DC voltammetric curves mostly exhibited round peaks or poorly resolved waves only. The scan rate was within the range of 1 to 50 mV s<sup>-1</sup>, pulse of -12.5 mV in 0.2 s intervals.

The calibration curve for the determination of the composition of the mixture of goethite (G) and lepidocrocite (L) was set up based on current values at the potentials of the maxima of the pure components,  $E_{GI}$  and  $E_L$  ( $GI$  denotes the first of the two observed goethite maxima  $GI$  and  $GII$ ). Following ref.<sup>3</sup>, the  $i_L/(i_L + i_{GI})$  ratio was used as the dependent variable, and the lepidocrocite percentage content was the independent variable. The calibration curve shape was consistent with published data<sup>3</sup>.

Chronoamperometric measurements were performed by using the same working electrode as in the voltammetric measurements. Chronoamperometry was employed to examine the process of particle dissolution at a constant potential.

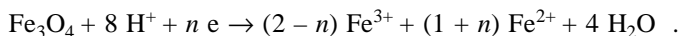
The current values during the voltammetric measurements depend, as well as on the amount of sample applied to the electrode, also on the actual state of the electrode surface. A reasonable reproducibility is achieved when determining the relative currents at the two maxima or the  $GI$ -to- $GII$

peak height ratio ( $s_r < 10\%$ ) or the potential of the voltammetric maximum ( $s_n < 20$  mV). Such reproducibility is attained after running approximately 10 measuring cycles if applying the above electrode cleaning and sample fixing procedures.

## RESULTS AND DISCUSSION

### *Qualitative Analysis*

We found that Fe oxides and hydroxy-oxides on the working electrode can be reduced at potentials that are quite typical of the phase in question (Table I). Cyclic voltammetric measurements gave evidence that the reaction involved is electrochemically irreversible. Typical DP voltammograms are shown in Fig. 1. It can be assumed that the process occurring at the electrode-sample-electrolyte interface consists in a reductive dissolution of sample, analogous to the dissolution of magnetite from a magnetite electrode in a weakly acid solution, which has been described as<sup>15</sup>



In a noncomplexing system this reaction is irreversible and magnetite dissolves at  $n = 2$ . This mechanism describes the behaviour of magnetite in dilute  $\text{HClO}_4$  at potentials up to  $-0.8$  V vs SCE. Reduction of  $\text{H}^+$  on the magnetite surface and, presumably, also reduction of the oxide to iron metal occur at more negative potentials. We suppose that other oxidic iron compounds react similarly in AbrSV conditions. Table I gives the positions of the DP voltammetric maxima at pH 1. At scan rates higher than  $20 \text{ mV s}^{-1}$ ,

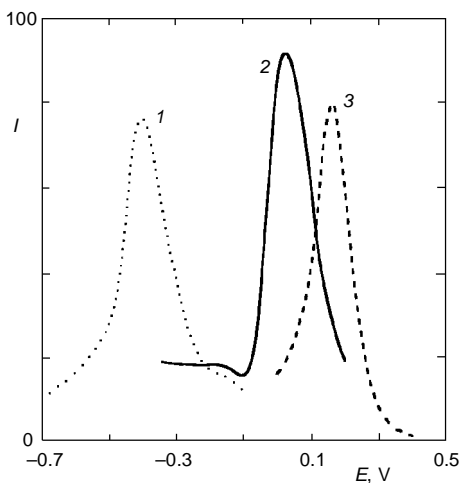


FIG. 1

Comparison of positions of DP voltammetric peaks of hematite (1), maghemite (2) and ferrihydrite (3). Working electrode: OIGE, electrolyte:  $0.1 \text{ M HCl} + 0.4 \text{ M KCl}$ , scan rate:  $50 \text{ mV s}^{-1}$ , potentials vs  $\text{Ag/AgCl}$  electrode. The peak heights are normalized, the actual peak height ratio is roughly  $10 : 2 : 1$

those maxima – which are largely phase specific – are complemented with a nonselective maximum at  $E < -0.7$  V.

### Effect of Particle Shape

For the majority of substances studied, the voltammograms did not differ considerably with respect to the conditions of their synthesis (Table I). Appreciable differences were

TABLE I  
Potentials of DP voltammetric maxima  $E_{\max}$  of synthetic iron oxides and hydroxy-oxides vs Ag/AgCl reference electrode; working electrode: OIGE, scan rate:  $10 \text{ mV s}^{-1}$ , electrolyte:  $0.1 \text{ M HClO}_4 + 0.1 \text{ M NaClO}_4$

| Compound                                      | $E_{\max}, \text{V}$                                   |
|---|--|
| $\alpha\text{-Fe}_2\text{O}_3$ (hematite)     | -0.4   |
| $\gamma\text{-Fe}_2\text{O}_3$ (maghemite)    | 0.0  |
| $\text{Fe}_3\text{O}_4$ (magnetite)           | -0.06  |
| $\alpha\text{-FeOOH}$ (goethite) <sup>a</sup> | GI <sup>b</sup> -0.08<br>GII <sup>b</sup> -0.2 to -0.4 |
| $\beta\text{-FeOOH}$ (acageneite)             | - <sup>b</sup>   |
| $\gamma\text{-FeOOH}$ (lepidocrocite)         | +0.05  |
| Ferrihydrite <sup>c</sup>                     | +0.15 to 0.0   |

<sup>a</sup> Positions of the maxima depend on the properties of the particles; <sup>b</sup> no pronounced maximum; <sup>c</sup> in dependence on pH during preparation.

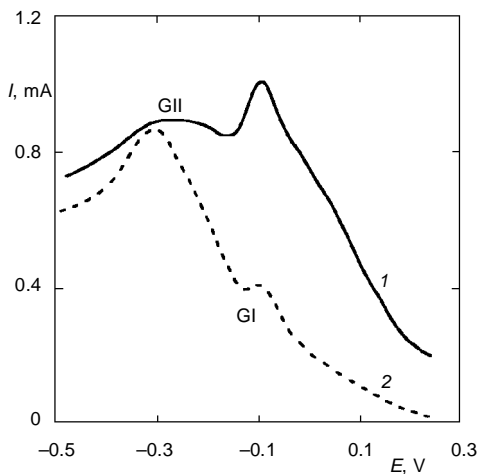


FIG. 2  
Shapes of the GI ( $\approx -80 \text{ mV}$ ) and GII DP voltammetric peaks of goethite samples containing single-domain needles (1) and particles with (021) planes (2). Other conditions as in Fig. 1

observed for ferrihydrite in dependence on the pH at which the precipitation was conducted, and, in particular, for goethite. As with other analytes which possess a crystal structure and whose electrochemical behaviour is not reversible, the electrochemical dissolution of goethites is governed by their structure. A nonequivalence of the crystal planes during the dissolution of goethites in mineral acids has been reported<sup>10</sup>.

Also, several crystal planes exhibiting different physico-chemical properties are well-developed on goethite particles<sup>9,10,16</sup>.

The extent to which the various planes are developed is very difficult to quantify, and preparation of particles of a homogeneous shape is only possible for some shapes and requires a good optimization of conditions<sup>9,16</sup>. Therefore, we used real crystal mixtures and applied cluster analysis and linear regression to the comparison of the electrochemical behaviour and the conditions of preparation, shape, and specific surface area of the goethites.

Table I and Fig. 2 document that the DP voltammogram displays two peaks, labelled GI and GII (the latter lies at more negative potentials than the former). The GI peak position (about  $-0.08$  V) is basically independent of the sample origin, whereas the GII peak is more specific but its position is also affected by the measuring conditions. For each sample, the relative height of the GII peak,  $i_r^{\text{GII}} = i_{\text{GII}} / i_{\text{GI}}$  is higher if the supporting electrolyte contains perchlorate ions than if it contains chloride ions (at the same pH). Furthermore, the  $i_r^{\text{GII}}$  value increases with decreasing concentration of hydrogen ions and with increasing scan rate, and also varies with the electrode surface quality; it is higher with the OIGE than with the PIGE.

The processes giving rise to the GI and GII peaks are mutually linked. If the analyte crystals are dissolved to a considerable extent as early as the first step (GI), the relative height of the GII peak decreases. Based on the findings by Siddhu and coworkers<sup>17</sup>, the

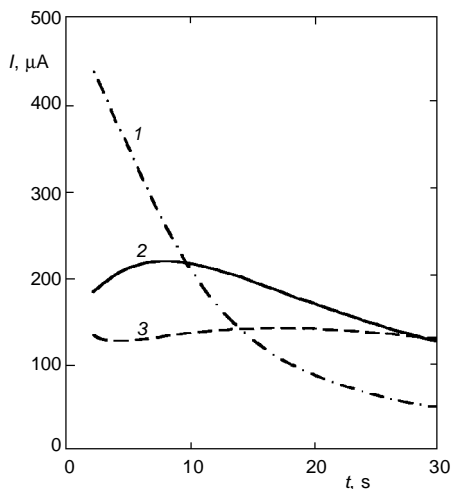


FIG. 3

Chronoamperometric curves for the starting dissolution of goethite samples consisting of single-domain needle-shaped particles (1), TEM-opaque parallelepipedic particles of pigment size (2) and particles with (021) planes (3). Working electrode: PIGE, potential:  $-0.13$  V vs Ag/AgCl electrode

dissolution rate of iron(III) oxides and hydroxy-oxides in acids increases linearly with the concentration of hydrogen ions and exponentially with the concentration of chloride ions, while the effect of perchlorate ions is negligible. This implies that the  $i_r^{\text{GII}}$  value is affected by the overall reaction rate and that the dissolution process rate is lower for the OIGE than for the PIGE. These facts can account for the necessity of adhering strictly to the working electrode maintenance procedure during the measurement of  $i_r^{\text{GII}}$ .

The chronoamperometric curve shape (Fig. 3) gives information on the dissolution rate and on the occurrence of intergrowths, if any, on the crystal surfaces. If suitable measuring conditions (working electrode potential between the GI and GII maxima, pH between 1 and 1.3) are chosen, a plateau in the current decrease or even a maximum can be observed on the chronoamperometric curves of samples with larger particles. The current maximum can only be explained by the occurrence of particle intergrowths, which break down relatively quickly and the reacting area thus temporarily increases (Fig. 3). If a more negative voltage and/or a higher concentration of hydrogen ions in the electrolyte are applied, the chronoamperometric curves are monotonous for all samples and their comparison can only serve a qualitative assessment of the dissolution rate of different samples.

As an outcome of the analysis of the relation between the electrochemical behaviour and properties of the goethite samples, the samples could be categorized into groups with identical behaviour patterns, as given in Table II.

TABLE II

Positions of the GI and GII maxima and shape of the chronoamperometric curve in dependence on the shape and origin of the goethite particles. DP voltammetry, working electrode: OIGE,  $E_{\text{GI}}$  and  $E_{\text{GII}}$  potentials vs Ag/AgCl electrode  $\pm$  confidence interval, scan rate: 50 mV s<sup>-1</sup>, electrolyte: 0.1 M HCl + 0.4 M KCl

| Particle size (origin)  | DP voltammetry                  |  |                    |
|---|---------------------------------|--|--------------------|
|   | $E_{\text{GI}}$ , mV            | $E_{\text{GII}}$ , mV                  | $i_r^{\text{GII}}$ |
| Tiny or irregular particles (Fe <sup>3+</sup> , Fe <sup>2+</sup> ) <sup>a</sup>                       | -50 $\pm$ 20                    | - <sup>b</sup>                         | <1 <sup>b</sup>    |
| Longitudinally intergrown needles (Fe <sup>3+</sup> , $t < 25$ °C)                                    |                                 | single maximum $\sim -90$ <sup>c</sup> |                    |
| Longitudinally intergrown and/or isolated needles (Fe <sup>3+</sup> , $t > 40$ °C; Fe <sup>2+</sup> ) | -80 $\pm$ 20                    | -220 $\pm$ 40                          | <1.2               |
| Opaque parallelepipedic particles (Fe <sup>2+</sup> )   | -80 $\pm$ 20<br>or <sup>b</sup> | -290 $\pm$ 20                          | >1.3               |
| Particles with (021) planes and irregular particles   | - <sup>b</sup>                  | -280                                   | >1.6 <sup>d</sup>  |

<sup>a</sup> Oxidation of Fe<sup>2+</sup> in a weakly acid solution in the presence of carboxylic acids or precipitation of Fe<sup>3+</sup> with urea; specific surface area >80 m<sup>2</sup> g<sup>-1</sup>; frequent occurrence of ferrihydrite impurities;

<sup>b</sup> no pronounced maximum; <sup>c</sup> unresolved GI and GII maxima; <sup>d</sup>  $i_r^{\text{GII}}$  value calculated as the current ratio in the GII maximum and at -80 mV.

Our findings concerning the goethite particle dissolution mechanism can be summarized and generalized as follows.

1. Single-domain needle-shaped particles dissolve rapidly at potentials corresponding to G1; the GII maximum is not very well developed in the DP voltammogram. In agreement with the literature<sup>9,10</sup>, the (110) plane, and perhaps the (010) plane, is the dominant reaction plane with respect to the relative abundance and reactivity.

2. Longitudinally intergrown needle-shaped particles (width larger than 0.05  $\mu\text{m}$ ) exhibit a very pronounced GII maximum. There is a smooth transition between the single-domain and so intergrown particles: the broader the particles, the higher the  $i_r^{\text{GII}}$  value and the larger shift of the GII peak to more negative potentials. The dissolution rate as indicated chronoamperometrically increases substantially with increasing cathodic overvoltage to attain a maximum at a potential near GII. At potentials near G1, some chronoamperometric curves exhibit a local maximum. The (010) and (110) planes and intergrowths of the (110) planes are presumably the dominant planes in the dissolution.

3. Particles with well-developed (021) planes, whose formation was observed during a slow oxidation of  $\text{Fe}^{2+}$  at elevated temperatures, dissolve extremely slowly at the G1 potential (like goethites of mineral origin). The GII maximum dominates in the DP voltammogram. Such behaviour was also observed for samples whose specific surface area was comparable to that of the more reactive partly intergrown needle-shaped par-

TABLE III

Lepidocrocite percentage in mixtures with goethite as determined by AbrSV and by other analytical techniques (in %)

| Sample | Abrasive voltammetry | IR spectroscopy | Moessbauer spectroscopy |
|--------|----------------------|-----------------|-------------------------|
| Z45/1  | 79 $\pm$ 6           | 68              |                         |
| Z47/1  | 16 $\pm$ 4           | 33              | 11                      |
| Z49/1  | 89 $\pm$ 3           | 76              |                         |
| Z51/1  | 94 $\pm$ 2           | 90              |                         |
| Z51    | 65 $\pm$ 6           | 85              | 69                      |
| Z52/1  | 67 $\pm$ 6           | 67              | 47                      |
| Z55    | 100 $\pm$ 5          | 97              |                         |
| Z57/1  | 29 $\pm$ 5           | 48              | 28                      |
| Z72/1  | 95 $\pm$ 5           | 99              |                         |
| Z72    | 80 $\pm$ 5           | 97              | $\leq$ 92               |



ticles, so that the low dissolution rate for particles with (021) planes at the G1 potential cannot be accounted for by the lower specific surface area solely.

4. Somewhat peculiar is the behaviour of the group of goethites synthesized from  $\text{Fe}^{3+}$  in alkaline solutions at temperatures of 4 to 25 °C. Their TEM photographs display needle-shaped particles intergrown into platelets, transparent in one direction, whereas needle-shaped particles obtained at temperatures higher than 50 °C form longitudinal particles which are less transparent and considerably more homogeneous in width and whose specific surface area is more than one-half lower. The platelet-like shape of particles intergrown through the (010) planes is also presumed in the literature<sup>16</sup>; this implies that the free reactive (110) planes dominate during the dissolution.

Some pigments with particles which are opaque in the TEM photographs constitute a transition between groups 1 and 2. With regard to their particle size (specific surface area  $<20 \text{ m}^2 \text{ g}^{-1}$ ), a high number of intergrowths of the needle-shaped building units can be assumed for them. Here the occurrence of maxima in the chronoamperometric curves is very frequent. Both of the G1 and GII maxima are well developed in the DP voltammogram. Details of crystal shapes are not available from the literature in this case.

### *Quantitative Analysis*

Quantitative analysis by AbrSV can be employed, for instance, to examine the phase purity of goethite. Possible impurities in synthetic goethite include ferrihydrite (an intermediate product during the synthesis from  $\text{Fe}^{3+}$ ) and lepidocrocite (in unsuitable conditions of synthesis from  $\text{Fe}^{2+}$ ). Although the DP voltammetric maxima of the two impurities ( $i_A$ ) are not very well resolved from the G1 maximum ( $i_{\text{G1}}$ ) (Table I), the  $i_A/(i_A + i_{\text{G1}})$  ratios, serving to construct the calibration curve, are fairly well reproducible at scan rates not exceeding  $10 \text{ mV s}^{-1}$  (see Experimental).

The feasibility of applying AbrSV to quantitative phase analysis was examined on goethite-lepidocrocite mixtures obtained from  $\text{Fe}^{2+}$  solutions at various rates of oxidation with air, various pH values and various  $\text{Fe}^{2+}$  concentrations. The mixtures were analyzed by AbrSV, IR spectroscopy, and Moessbauer spectroscopy. The results are given in Table III. Calibration curves were set up by using pure goethite and lepidocrocite of a similar particle shape and size. At scan rates  $<10 \text{ mV s}^{-1}$  the effect of the goethite particle shape on the shape of the voltammogram decreases because the GII maximum is suppressed. Statistical processing shows that the results of the AbrSV technique are not systematically different from those obtained by the remaining techniques.

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