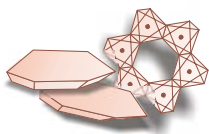


ANALYSIS OF LOW CONCENTRATION OF FREE FERRIC OXIDES IN CLAYS BY VIS DIFFUSE REFLECTANCE SPECTROSCOPY AND VOLTAMMETRY



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MECC '01

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(Manuscript received October 4, 2001; accepted in revised form December 13, 2001)

Abstract: Ferric oxide admixtures in the concentration range 0.1–10% in soils, sediments, and clay mineral samples can be conveniently characterized by Vis diffuse reflectance spectroscopy (DRS) in the region of d-d electron transitions close to 500 nm, voltammetry of microparticles, and voltammetry with carbon paste electroactive electrode (CPEE). DRS also detects Fe(III) in the clay mineral matrix equally sensitively. Voltammetry of microparticles is suitable for direct detection of free crystalline and amorphous ferric oxides. The determination limit of total free ferric oxides with CPEE is ~0.01%. The techniques were tested with six clay mineral samples. XRD was able to detect free FeOOH in only one of them (1.6%), DRS and CPEE also detected 0.19% FeOOH in Be-3 (bentonite of Rokle deposit, Bohemia) and 0.04% in reference montmorillonite SWy-2.

Key words: voltammetry, Vis spectroscopy, analysis, FeOOH, Fe₂O₃.

Introduction

Fe in oxic soils, sediments, and clay minerals is present in several forms. In the total amount of Fe, free ferric oxides are an important class of phases, and their analysis is a typical task of solid-state speciation. Speciation by XRD is complicated by poor crystallinity and low concentration of free ferric oxides, commonly below the detection limit of about 1% for well crystalline and >10% for poorly crystalline species. Chemical extraction by dithionite-citrate-bicarbonate (DCB) or ammonium oxalate solutions is conventionally used for quantification of the free ferric oxides, but the phase specificity of extractions is commonly overestimated. Mössbauer spectroscopy and selective chemical extraction can be used if the content of free ferric oxides is >0.1% (Komadel et al. 1998). Recently another two convenient experimental techniques were reported to be sufficiently sensitive and specific for this analytical task: Vis diffuse reflectance spectroscopy (DRS) and voltammetry. Although both these techniques are almost traditionally used in analysis of inorganic solids, they have been applied to ferric oxides in low concentrations for geochemical analysis as late as in the last decade. Vis spectroscopy was proposed to determine soil goethite and hematite in concentrations >0.1% (Malengreau 1996; Scheinost et al. 1998). DRS was also used for phase identification in poorly crystalline palagonitic soil (Morris et al. 1993). Voltammetry of microparticles (VMP) was found to be similarly sensitive to detect and semi-quantitatively analyze free ferric oxides in paleosoils (Grygar & van Oorschot 2002) and in lacustrine sediments (van Oorschot et al. 2001). Another electrochemical technique, voltammetry with a carbon paste electroactive electrode (CPEE) was used for quantitative analyses of pure synthetic ferric oxides (Lequire 1975) and pure natural ilmenites (Andriamanana et al. 1984), but it has not been used for analysis of sub-percent con-

centration in mixtures, although the detection limit of CPEE can be as low as 0.02% (Brainina & Vydrevich 1981). As it was shown by using rock magnetism methods, free ferric oxides in paleosoils and sediments bear information that can be related to the paleoenvironment in the Quaternary (Dekkers 1997). Such analyses are enabled by particular sensitivity of rock magnetic measurements to ferrimagnetic phases Fe₃O₄ and γ-Fe₂O₃. However, there is a clear lack of methods that would similarly sensitively detect antiferromagnetic and paramagnetic pigment ferric oxides, mainly hematite and goethite, whose ratio also has a well-established environmental diagnostic value (Cornell & Schwertmann 1996). The need for such methods is particularly relevant with respect to widespread occurrence of non-ferrimagnetic pigment ferric oxides in the environment.

The aim of this study was to apply Vis spectroscopy and voltammetry in analysis of free ferric oxides in selected well-characterized clay mineral samples to evaluate the sensitivity and specificity of these techniques, which are rather novel in geochemical analysis. DRS seems to be a very promising tool for detection of Fe(III) in free oxides as well as in clay mineral's skeleton. Our aim is hence to promote application of these techniques because their full utilization is conditioned by collecting more data for comparative purposes taking into account the large structural variability of clay minerals.

Experimental

Samples

The samples of clay minerals are described in Tables 1 and 2. X-ray powder diffraction (XRD) was used for mineralogical

analyses with SIEMENS D-5005 (CuK α radiation, secondary monochromator, 40 kV, 30 mA).

Samples KGa-2, PF-1, STx-1 and SWy-2 and their mineralogical and chemical composition were provided by Source Clay Repository of the Clay Minerals Society in Missouri, U.S.A. The content of clay minerals was also confirmed by additional XRD measurements under conditions described below.

Samples KIC-8 and Be-3 were separated from the raw material so that they would be representative and prepared for measurement as non-orientated mixtures (dried and powdered in an agate mill, measured in the 2θ range 3–80°, step 0.02° per 10 seconds). Then they were pre-treated by sedimentation in distilled water and the clay fraction (< 4 μm) was separated and sedimented on a glass slide to make clay aggregates orientated along their basal crystal planes. These orientated specimens were analyzed conventionally under air-dried conditions (in the 2θ range 3–70°, step 0.02° per 10 seconds) and under ethylene glycol-solvated conditions (in the 2θ range 3–40°, step 0.02° per 2 seconds). The raw data were processed by the ZDS program for Windows (Ondruš 1997) employing the diffraction pattern database (JCPDS 2000). Clay minerals were interpreted in detail according to Moore & Reynolds (1997). Chemical analyses of bulk clay samples were obtained in the analytical laboratories of Gematest Ltd. and Laboratories of the Geological Institutes of Charles University in Prague.

Voltammetry

The cell used for the electrochemical measurements is shown in Fig. 1. Working electrode, either with immobilized sample particles (VMP) or with carbon paste, saturated calomel reference and Pt-plate counter electrodes were used. In VMP samples were deposited mechanically on the surface of a paraffin-impregnated graphite rod (Grygar 1996; Grygar & van Oorschot 2002). The working electrode was then touched to the supporting electrolyte and fixed in the cell to minimize the wetting of the sides of the carbon rod. This is necessary to decrease the background current, which arises from oxygen and water reduction on the graphite surface. Because the actual amount of sample on the electrode surface in VMP is not known, the technique is suitable for the phase identification and relative comparisons.

For the quantitative analysis a carbon paste electroactive electrode (CPEE) was prepared as in reports by Lecuire (1975)

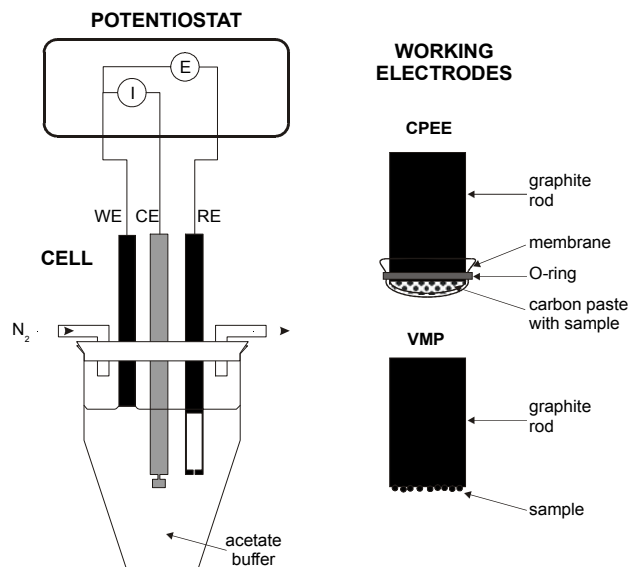


Fig. 1. The scheme of the measuring cell and electrodes for the voltammetric measurement. WE — working electrode, RE — reference saturated calomel electrode, CE — counter-electrode. CPEE electrode consists of the carbon paste with the sample, covered by a membrane (perforated microtene foil) fixed to a graphite rod by a rubber ring. In VMP the sample is mechanically attached to the graphite rod.

and Andriamanana et al. (1984). 2–15 mg sample, about 100 mg graphite powder (Electrocarbon Topoľčany, Slovakia), and 0.1 ml acetate buffer (acetic acid to Na-acetate 1:1, total acetate 1 M) were mixed in an agate mortar to obtain paste of characteristic butter-like consistency. An important prerequisite for quantitative analyses with CPEE is that the loading of the carbon paste with the ferric oxides must be a few percent or less to be completely involved in the electrochemical reactions. Immediately after mixing, 20–30 mg of the paste was spread over the surface of epoxide-resin impregnated graphite rod, weighed, covered by a piece of microtene foil secured by a rubber O ring (Fig. 1). The foil was laid on the paste not to leave any air bubbles between the paste and foil, and then the foil was perforated by a needle to ensure the electric contact between the electrode and supporting electrolyte. Acetate buffer (1:1, total acetate 0.2 M) was used as supporting elec-

Table 1: General description of clay samples. Parentheses stand for less than about 5% of the phase.

Sample	Origin	Grain size (μm)	Mineralogical composition (XRD)
KGa-2	Warren County, Georgia	< 2	poorly ordered kaolinite
KIC-8	Skalná nr. Cheb – ULK clay	< 4	poorly ordered kaolinite, illite, (goethite)
STx-1	Gonzales County, Texas	< 2	Ca-montmorillonite, (cristoballite)
SWy-2	Crook County, Wyoming	< 2	Na-montmorillonite, quartz, illite, (calcite)
Be-3	Rokle, Czech Republic	< 4	Ca-montmorillonite, illite, calcite, quartz (kaolinite)
PF-1	Gadsden County, Florida	< 2	palygorskite, quartz

Table 2: Elemental composition of clay mineral samples.

	KGa-2	STx-1	SWy-2	KIC-8	PF1-1	Be-3
SiO ₂	43.90	70.10	62.90	45.03	60.90	42.64
TiO ₂	2.08	0.038	0.09	0.62	0.49	3.72
Al ₂ O ₃	38.50	16.00	19.60	33.93	10.40	12.82
Fe ₂ O ₃	0.98	0.65	3.35	5.61	2.98	11.11
FeO	0.15	0.15	0.32	0.25	0.40	0.35
MgO	0.03	3.69	3.05	0.00	10.20	2.42
CaO	0.00	1.59	1.68	0.17	1.98	5.77
Na ₂ O	<0.005	0.27	1.53	0.59	0.058	0.21
K ₂ O	0.065	0.078	0.53	3.36	0.80	0.96
P ₂ O ₅	0.045	0.026	0.049	0.13	0.80	0.68
CO ₂	-	0.04	0.05	-	0.11	3.17

trolyte. PC-controlled potentiostat μ Autolab (EcoChemie Utrecht, the Netherlands) was used in linear-sweep (in VMP) or normal cyclic voltammetric mode (with CPEE). The software package GPES 4.4 supplied by EcoChemie was used for voltammetric data processing.

To distinguish goethite and hematite, sub-samples were heated at 320 °C to convert goethite to protohematite (Grygar 1996) and voltammograms of original and heated samples were compared (Grygar & van Oorschot 2002). Protohematite is more reactive than the original goethite, and hence the reductive dissolution peak of goethite is shifted to more positive values after heating (Fig. 2B). Hematite peak position is not affected by the heating.

Vis diffuse reflectance spectroscopy (DRS)

Spectra of homogenized powdered samples were recorded using Perkin-Elmer Lambda 19 UV-Vis-NIR spectrometer equipped with a standard device for measuring powder samples called “praying mantis”. Spectra were recorded in the region 200–900 nm with 1 nm increment and BaSO₄ as a reference. The remission function $F(R_{\infty})$ was calculated from the Schuster-Kubelka-Munk equation $F(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$, where R_{∞} is the diffuse reflectance from a semi-infinite layer. $F(R_{\infty})$ of solids is proportional to the concentration of absorbing species in solids as with absorbance in the case of dissolved compounds in solutions.

Two procedures were used for the characterization of samples: decomposition of the spectra to the Gaussian bands and analysis of the second derivative mode of the spectra. The signal noise was removed by application of Fourier filter (cross 5 points). The second derivative of the spectra was connected with smoothing by adjacent averaging cross 9 points. Data processing was carried out using the Microcal Origin 4.1 software (Microcal Software, Inc. U.S.A.).

The region of electron pair transition (EPT), (⁴T₁+⁴T₁) ← (⁶A₁+⁶A₁), around 500 nm (15,000–30,000 cm⁻¹) was used for the estimation and characterization of Fe(III) species in samples. The wavenumber of the Fe(III) EPT transition in hematite significantly differs from corresponding transitions of other Fe oxides (Scheinost et al. 1998). However, it is necessary to point out, that the d-d transition of Fe(III) does not allow us to distinguish goethite from other Fe oxides (ferrihydrite, lepidocrocite, maghemite, etc.). Spectral characteristics of the samples studied are collected in Table 3.

Results and discussion

The colour of the six studied samples varied from very pale grayish (samples with < 1 % total Fe₂O₃) to yellow (KIC-8) or yellowish brown (Be-3). As for the ferric oxides, XRD was only able to detect goethite in poorly ordered kaolinite sample KIC-8.

Table 3: Wavenumbers ν and integral intensities A of absorption bands of clay mineral samples in 2nd derivative diffuse reflectance spectra. Abbreviations: h — hematite, g — goethite, cl-1, cl-2, cl-3 — clay minerals' skeletal Fe.

STx-1	ν (cm ⁻¹)	18,100	18,750	19,600		20,500	21,000	21,800
	$10^7 \cdot A$	8.2	23	18		35	7.6	12
SWy-2	ν (cm ⁻¹)	18,250	18,700	19,400	19,900	20,600	21,300	21,700
	$10^7 \cdot A$	31	65	57	200	100	200	300
Be-3	ν (cm ⁻¹)	18,400		19,500	20,200		21,200	21,800
	$10^7 \cdot A$	660		3900	1680		2500	800
KIC-8	ν (cm ⁻¹)		18,700	19,500	20,300		20,900	21,800
	$10^7 \cdot A$		860	1640	660		7090	950
PF1-1	ν (cm ⁻¹)	18,100		19,600			20,800	
	$10^7 \cdot A$	1.7		300			78	
KGa-2	ν (cm ⁻¹)	18,400		19,300	20,200			21,800
	$10^7 \cdot A$	3.2		40	153			18
Identification		h	h	cl-1	cl-2	cl-2 or g	g	cl-3

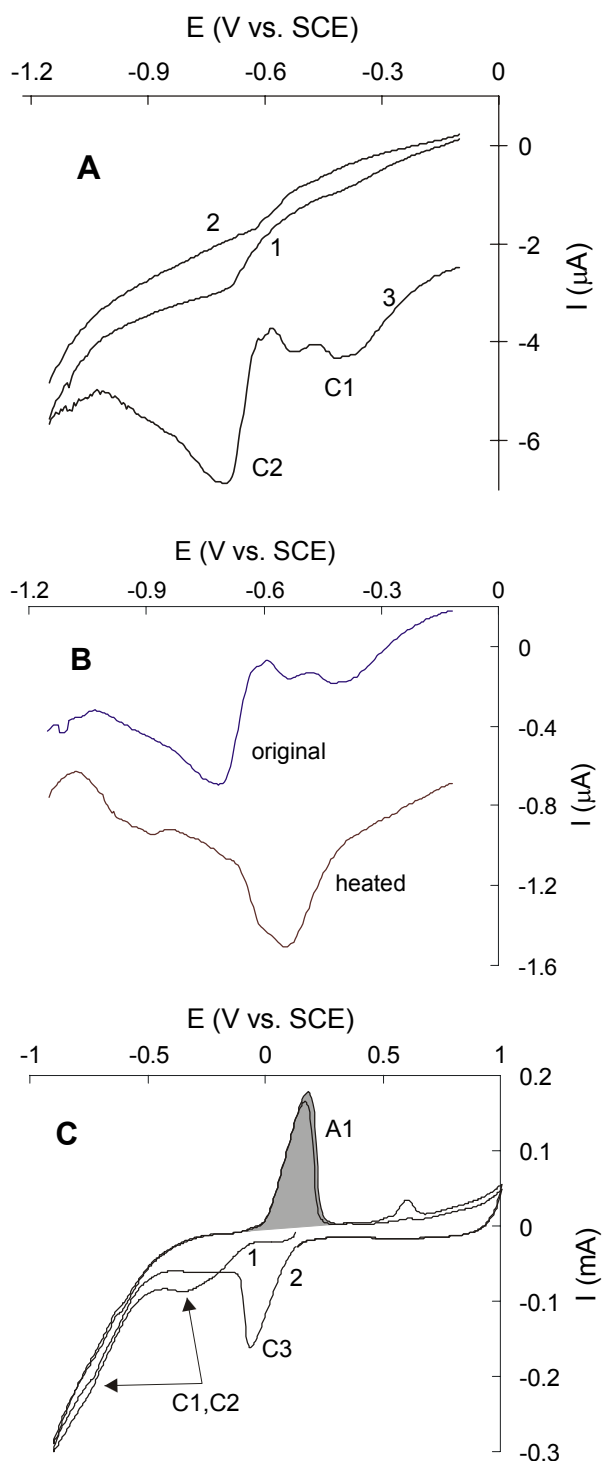
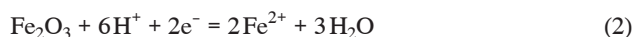


Fig. 2. The voltammetric curves of sample KIC-8. **A** — linear-sweep VMP of untreated sample, curve 1 and 2 are 1st and 2nd scans, curve 3 is the difference between the 1st and 2nd scans multiplied by 5. **B** — VMP of original and heated sample, curves were offset for clarity. **C** — cyclic voltammetry with CPEE, 1st and 2nd scans, grey area corresponds to the charge of Fe^{2+} oxidation. Peak denotation: C1 reductive dissolution of amorphous Fe(III) oxides, C2 reductive dissolution of crystalline Fe(III) oxides, A1: re-oxidation of Fe^{2+} dissolved from Fe(III) oxides, C3: reduction of Fe^{3+} in solution.

Voltammetry of Fe oxides can in principle use one of four electrochemical reactions: reductive dissolution to Fe^{2+} , reduction to metallic Fe and its re-oxidation to dissolved Fe^{2+} , and/or oxidation of total Fe^{2+} obtained by the previous reactions (Lecuire 1975; White et al. 1994; Grygar 1996). Reductive dissolution is suitable for identification of ferric oxide phases (Lecuire 1975; Grygar 1996), but the analysis must encounter problem of large background current of working electrode in the corresponding potential range (see the increasing absolute value of current with decreasing potential in curves 1 and 2 in Fig. 2A). Formation of metallic Fe is only typical as a side reaction in reduction of Fe_3O_4 (White et al. 1994) and α - and γ - Fe_2O_3 polymorphs, but we did not observe that reaction in the presented case. Re-oxidation of Fe^{2+} is most suitable for quantitative analysis of reducible Fe oxides (Lecuire 1975; Andriamanana et al. 1984), as in the corresponding potential range there is no significant background current (peak A1 in Fig. 2C).

VMP was used to directly detect reductive dissolution of free ferric oxides (Grygar 1996; Grygar & van Oorschot 2002; van Oorschot et al. 2001). Reductive dissolution:



is responsible for linear-sweep voltammetric peaks C1 and C2 in Fig. 2. Due to a large background current, the net electrochemical signal can only be obtained by subtracting the currents of the 1st and the 2nd scans (Grygar & van Oorschot 2002), as it is shown in Fig. 2A. Discrimination between goethite and hematite, which are of approximately the same electrochemical reactivity if their particles have the same size (Grygar 1996), can be done by heating a small fraction of sample at 320°C to produce the highly reactive form of hematite, and comparing their voltammograms (Grygar & van Oorschot 2002). Due to the thermal conversion, the voltammetric peak C2 of the heated sample is moved toward more positive potentials if goethite is present (Fig. 2B). In such a way VMP was able to detect goethite in samples KIC-8 and Be-3. Because in VMP soluble reaction products including Fe^{2+} can freely diffuse to the bulk of the surrounding solution, re-oxidation peak A1 cannot be observed using this technique.

The voltammograms of reductive dissolution C1 and C2 are worse developed using CPEE (Fig. 2C). However, contrarily to VMP, the ferrous salt produced by the reductive dissolution of ferric oxides according to equations (1) and (2) is retained in the bulk of the carbon paste and can be re-oxidized in subsequent anodic scans (peak A1 in Fig. 2C). Because the total amount of sample in the paste is known and the charge corresponding to this re-oxidation can be recalculated to weight of Fe using the Faraday law (Lecuire 1975), quantitative analysis is possible without any calibration. The charge is equal to the integral of the voltammetric peak, (the gray-highlighted area in Fig. 2C). Because of negligible background current and no side reactions in the potential range of A1, CPEE determination is more sensitive than the VMP detection of free ferric oxides. Using this approach, free ferric oxides were determined in samples KIC-8, Be-3, and SWy-2. The results were ex-

pressed as FeOOH because DRS identified goethite as the major free ferric oxide in the samples (Table 3). The results of the quantitative CPEE analysis are summarized in Table 4.

In contrast to the report by Xiang & Villemure (1995), we did not observe any signs of redox cycling of the clay mineral's skeletal Fe ions. Negligible electrochemical activity of skeletal Fe in montmorillonite enables its application as modifier in carbon paste electrodes for analysis of dissolved electroactive species (Navrátilová & Kula 2000).

The UV-Vis absorption spectra of ferric oxides exhibit strong charge-transfer absorption bands with maximum around $40,000\text{ cm}^{-1}$, followed by medium-intense d-d electron pair transition (EPT) bands around $25,000$ and $20,000\text{ cm}^{-1}$ and weak d-d bands around $14,000$ and $11,000\text{ cm}^{-1}$. The charge-transfer band is very sensitive but not phase specific. Although the hematite band at around $11,500\text{ cm}^{-1}$ is enough specific to hematite (Morris et al. 1993; Scheinost et al. 1998), it is too weak to be applied in trace phase analysis. The EPT bands are hence most appropriate for the characterization of Fe(III) oxides in soils (Scheinost et al. 1998). The EPT absorption bands were distinguished according to the minima in the 2nd derivative spectra as in the previous reports (Malengreau et al. 1996; Scheinost et al. 1998). Scheinost et al. gave wavenumber ranges of the bands by goethite ($20,300\text{--}20,900\text{ cm}^{-1}$) and hematite ($17,700\text{--}19,200\text{ cm}^{-1}$, median $18,800\text{ cm}^{-1}$). Ferrihydrite band occurs at $20,000\text{--}20,700\text{ cm}^{-1}$, but we have not got any proof of its presence in the samples studied.

The noise removal based on the application of Fourier filter followed by the second derivative of the spectra is significantly better for the spectra evaluation than the cubic spline fitting procedure applied by Scheinost et al. (1998) and Malengreau et al. (1996), as the Fourier filter does not alter the shape of the spectrum including weak bands (shoulders). The 2nd derivative spectra were decomposed into Gaussian curves corresponding to individual absorption bands and the areas of these Gaussian bands were used as a measure of the intensity of Fe(III) absorption bands in the spectrum; the results are collected in Table 3. Because the absorption coefficients of the individual species are not known, integral intensities can only be used to evaluate a relative order of concentration of the free ferric oxides in the samples. Their goethite content decreased in the following order:

$$\text{KIC-8} > \text{Be-3} > \text{SWy-2} \gg \text{PF-1} \gg \text{STx-1}$$

Goethite is absent in KGa-2. Hematite is only present in a small amount in Be-3 and in traces in SWy-2, STx-1. Ferric oxides found in samples are given in Table 4.

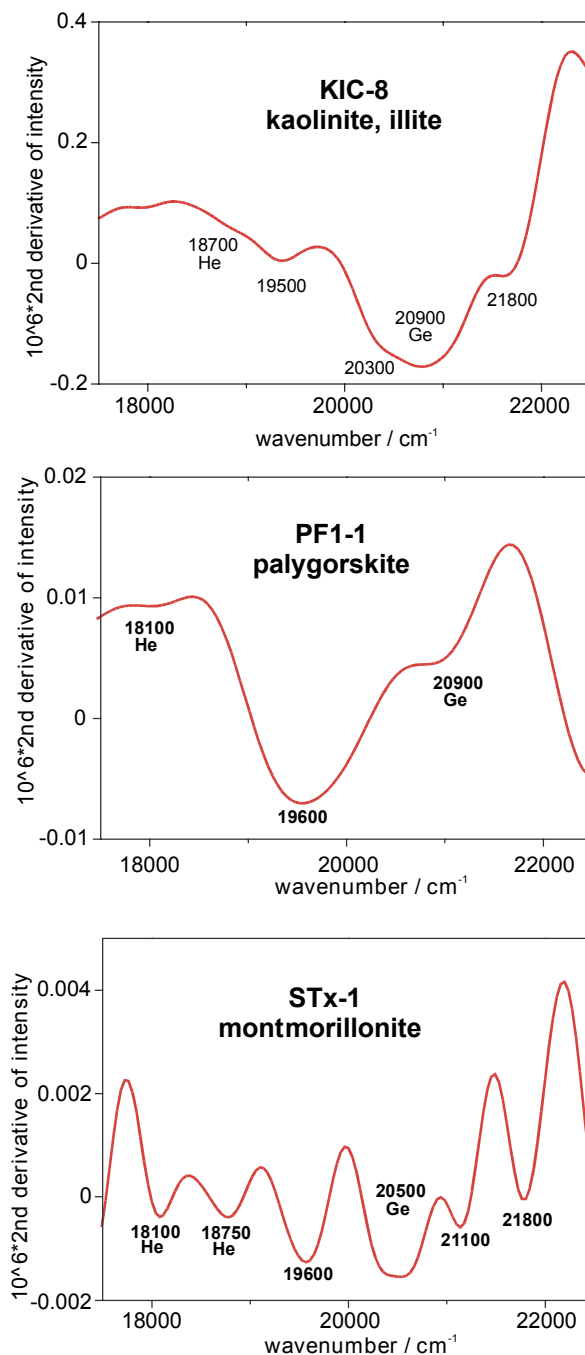


Fig. 3. 2nd derivative DR spectra of three samples. The wavenumbers of minima are given, Ge stands for goethite and He for hematite, further absorption bands are identified in Table 3.

Table 4: The evaluation of free ferric oxides in the clay mineral samples. Brackets denote a trace amount of the ferric oxide phase.

Sample	XRD	DRS	VMP	CPEE
KGa-2		goethite		
KIC-8	goethite	goethite	goethite	1.6 % FeOOH
STx-1				
SWy-2		(goethite)		0.04 % FeOOH
Be-3		goethite, hematite	goethite	0.19 % FeOOH
PF1-1		(goethite)		

Table 5: The overall evaluation of DRS and voltammetry as tools for analysis of admixtures of free ferric oxides.

Method	Specificity	Detection/determination limit
DRS ~500 nm	Directly distinguishing goethite and hematite, overlap of goethite with ferrihydrite and lepidocrocite	~0.1% (detection), semi-quantitative comparisons
VMP red. dissolution	Indirectly distinguishing goethite and hematite, distinguishing amorphous and crystalline ferric oxides	0.1–0.5% (detection)
CPEE Fe ²⁺ re-oxidation	Only for sum of reductively dissolved Fe oxides	~0.01% (determination)

Other Fe(III) octahedral species than free ferric oxides must be responsible for the other three absorption bands observed in the samples and denoted cl-1 to cl-3 in Table 3. As follows from the report by Bishop et al. (1993), Fe(III) montmorillonite also absorbs in this region. The Fe(II) and Fe(II)-Fe(III) electronic absorption bands are present at longer wavelengths (~800 nm, Komadel et al. 1990; Morris et al. 1993), and tetrahedral Fe(III) are also of different spectral properties than octahedral Fe(III) (Lever 1984).

Comparing the presence of bands cl-1 to cl-3 to the kind of clay minerals, we propose the following identification of those bands. Band cl-1 is mainly typical for 2:1 clay minerals, cl-2 for both 2:1 and 1:1 clay minerals, and cl-3 is dominant in samples with a significant content of mica-illite. It is noteworthy that 2nd derivative spectra enable resolution of as many as seven bands in SWy-2 in a relatively narrow bandwidth, however, the fact that all these bands are present in at least one of the other samples indicates that certain well-defined species are responsible for them. Further study would be necessary with a larger set of clay minerals with skeletal Fe(III) to identify those species.

Conclusions

The comparison of the methods described above is summarized in Table 5. Both Vis diffuse reflectance spectroscopy (EPT bands in the range approx. 17,500–22,500 cm⁻¹) and voltammetry can compete with XRD and other analytical techniques for speciation of Fe(III), especially in analysis of free ferric oxides in natural solid samples such as soils, sediments, and separated clay mineral fractions. Sensitivity of these techniques is generally much better than that of XRD. Furthermore, the simultaneous speciation of free ferric oxides and octahedral Fe(III) in the clay mineral structure is a unique and yet not exploited possibility of Vis spectroscopy.

Direct evidence of free ferric oxides by VMP can possibly be affected by a simultaneous presence of reducible species, such as Pb compounds and oxygen, which must be expelled from electrochemical system. On the contrary we are not aware of any interferences in the determination of total free ferric oxides by re-oxidation of Fe²⁺ in CPEE. The low determination limit of CPEE (~0.01%) is enabled by the fact, that charges of about 0.1 mC (~0.06 µg Fe₂O₃) can be conveniently determined with a common potentiostat and with the carbon paste containing only a few milligrams of sample.

Acknowledgment: The work on speciation of Fe oxides in a mineral matrix was solved in the framework of the project supported by Grant Agency of CR (Project 205/00/1349).

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