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A new method for determining the concentration of vanadyl ions in clays

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Abstract: A novel and simple method for quantitatively determining the concentration of vanadyl ions in clays using electron spin resonance data has been developed. Several vanadyl standards with concentrations between 200–1000 ppm were prepared in a mixture of glycerol and kaolinite (KGa-2). The anisotropic electron spin resonance (ESR) spectra were recorded at room temperature, and the specific intensity of the line (attributed to nuclear spin $m = -5/2\|$) was determined. For vanadyl concentrations between 50 ppm and 200 ppm, the standards must be prepared by mixing kaolinite with known vanadyl content (FBT2A-03) and kaolinite (GB1) containing no vanadyl. The method is applicable without modification to other clays and clay-rich sediments containing vanadyl ions. The whole procedure is very suitable for routine work.

Key words: clay, kaolinite, vanadyl, determination, electron spin resonance.

Introduction

Clays containing vanadium (V) have been described in a wide range of geological environments (Muller et al. 1995). In these materials, V is present in the +3, +4, and +5 oxidation states, which are closely related to the physicochemical conditions of the clay formation (Premović 1984; Premović et al. 1986). Chemical conversion of V to vanadyl (VO^{2+}) in natural waters is strictly determined by both the acidity (pH) and the redox potential (Eh). Therefore, VO^{2+} is an excellent indicator of the geochemical conditions of clay formation and may provide clues to the origin of the clay deposits of the past. In an investigation of these conditions, an accurate assessment of the portion of V that occurs as vanadyl (VO^{2+}) is necessary. Therefore, it is highly desirable to establish a relatively simple and practical method for VO^{2+} determination.

Electron spin resonance (ESR) has become a popular and useful tool for geochemists and geologically oriented scientists. A large number of investigators working on paramagnetic ions in geological materials have utilized this method to probe the structural and dynamic aspects of ions. ESR is especially sensitive to paramagnetic ions and has excellent resolution and signal reproducibility. Trace quantities of several transition metals may be detected and quantitatively measured by ESR. Quantitative analysis of clays containing these trace metals has not been as extensive by ESR as by other spectroscopic methods.

The use of ESR in the characterization of VO^{2+} compounds is well established. A part of the V in clays exists as VO^{2+} and ESR can be utilized to quantitatively determine VO^{2+} concentrations (Premović 1984; Premović et al. 1993a). In these studies, we compare the ESR signals from a sample containing an unknown amount of VO^{2+} to that from a reference sample with a known concentration of Cu^{2+} ions. This determination is based on the assumption that the VO^{2+} content of the analysed sample and the Cu^{2+} content in the reference sample (the standard) are related to each other by a simple ratio:

$$[C_{VO}{}^{2+}] = (SI_{VO}{}^{2+}/SI_{Cu}{}^{2+})\,[C_{Cu}{}^{2+}]$$

where SI is the specific signal intensity (the area under the corresponding ESR absorption per g of sample) of particular paramagnetic ions. This assumption may not be valid because the transition probabilities (i.e. the coefficients relating the specific signal intensity to the number of absorbing species) for VO^{2+} and Cu^{2+} ions might not be equal (Aasa & Vånngard 1975). This method is also long because it requires an integration of the whole spectrum and is somewhat complex; the absolute error is estimated to be at least >50 %, which is quite high for the ESR technique. Dielectric differences between some clays and standard samples may create additional discrepancies in analyses of VO^{2+} ions by the ESR method. The present report describes a new method for determining the concentration of VO^{2+} ions in clays which eliminates these obstacles. The method has been tested with samples of natural kaolinite containing V and VO^{2+}.

The investigation was undertaken with three specific objectives: (a) to determine the VO^{2+} content in kaolinite using ESR; (b) to evaluate ESR as a possible convenient, rapid, sensitive and accurate quantitative method for the determination of VO^{2+} in kaolinite and other clay minerals without chemical pretreatment, and (c) to better understand the application of ESR for analytical purposes.

Materials and methods

Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES) analysis. V of the whole rock samples were analysed by ICP–OES in the Laboratory for Physical Chemistry in the Institute of Nuclear Sciences Vinča. A Spectroflame ICP–OES instrument was employed, and Ar was used as the plasma gas.

ESR measurements. The ESR measurements were performed on finely-ground powders of the kaolinite samples in an ESR quartz tube. Spectra were recorded on a Bruker ER-200 series ESR spectrometer with Bruker X-band bridges using standard 100 kHz field modulation. The measurements were made at 9.3 GHz utilizing a rectangular TE cavity.

To maximize accuracy and precision, a sample tube was always kept inside the ESR cavity with an approximately uniform magnetic field, and the reproducibility of the sample positioning was achieved by using the same sample tube with a fixed holder. Tests verified that all spectra for the measurements were obtained with instrumental parameters that gave no instrumental effects on the peak height, shape, or width. The measurements were run at a modulation amplitude of 2 mT, a time constant of 100 ms, and a scan time of 16 min. The field was scanned at 200 mT when the entire spectrum was desired and at 20 mT when sensitive tracing of the –5/2|| resonance line (see below) was required. The instrument was carefully tuned according to the manufacturer's directions.

Samples and standards. Twenty one reference kaolinite samples were selected including the Nowa Ruda dickite. These samples, which originated from sediments and hydrothermal alteration, are listed in Table 1a together with their location, type, origin, total V content and references. These materials were selected because their total V content ranges from 15 ppm to 2475 ppm. Table 1a also lists the VO^{2+} concentrations of the kaolinite samples studied and the fraction of their V that occurs as VO^{2+}. Combined chemical, Fourier transform infrared analyses, X-ray diffraction, and microprobe analyses show that the samples studied contain 63–92 % kaolinite. Major impurities are illite and quartz.

A glycerol solution was prepared first by dissolving known amounts of VOSO$_4$×5H$_2$O (Merck) in a solution containing 1.5 ml concentrated H$_2$SO$_4$ and 0.5 ml deionized H$_2$O. This solution was then diluted to the desired VO^{2+} concentration (8000 ppm) with thorough agitation. Although the VOSO$_4$×5H$_2$O reagent had impurity content below 10^{-5} %, the real concentration of VO^{2+} ions in a weighted portion could be different from the theoretical concentration because of the loss of crystallization H$_2$O and partial oxidation of

Table 1a: Location, type, origin and V (ppm)/VO^{2+} (ppm) contents of the selected kaolinite samples.

Sample name	Location	Type	Origin	V[a] [ppm]	VO^{2+} [ppm]	V as VO^{2+} (wt. %)	Reference
KGa-1	Georgia (USA)	Well-ordered kaolinite	Sedimentary	95	100	80	Gaite et al. 1997
BCH5	Charentes (France)*	Poorly-ordered kaolinite	“	198	174	67	Delineau et al. 1994
BCH6	“	“	“	185	155	64	“
CHA2	“	“	“	95	68	55	“
LAP1	“	“	“	105	50	36	“
SGN2	“	“	“	131	155	90	“
SGN3	“	“	“	191	201	80	“
FBT2	“	“	“	280	120	33	“
FBT 4	“	“	“	210	65	23	“
FBT 2A-02	“	“	“	220	132	46	“
FBT 2A-03	“	“	“	250	200	61	“
FBT 3A-01	“	“	“	270	166	47	“
FBT 3A-02	“	“	“	250	175	53	“
FBT 3A-03	“	“	“	225	147	50	“
Provins	Paris Basin (France)	“	“	210	70	25	Muller et al. 1995
Aranđelovac	Belgrade Basin (Serbia)	“	“	170	85	38	This work
Kolubara	“	“	“	155	65	32	“
GB1	Cornwall (England)	Well-ordered kaolinite	“	15	n.d.	–	Cases et al. 1982
Cigar Lake	Saskatchewan (Canada)	“	Hydrothermal	2475	2700	83	Mosser et al. 1996
“	“	(3× diluted)	“	825	900	83	
“	“	(4× diluted)	“	619	675	83	
“	“	(5× diluted)	“	495	540	83	
Nopal	Chihuahua (Mexico)	Well-ordered kaolinite	“	115	85	57	Muller et al. 1990
Nowa Ruda	Silesia (Poland)	Well-ordered dickite	“	175	160	70	Balan et al. 2002

[a] The content determined by ICP–OES. **n.d.** — not detected. *Each of the Charentes samples is represented by three letters indicating the name of the open-pit and a number indicating its position.

Table 1b: Location, type and V (ppm)/VO^{2+} (ppm) contents of the selected kaolinite-rich sedimentary samples.

Sample name	Location	Type	V[a] [ppm]	VO^{2+} [ppm]	V as VO^{2+}(wt. %)	Reference
CNS[b]	New Mexico (USA)	shale	150	66	33	Pillmore et al. 1987
SVS[b]	“	“	175	72	31	Premović et al. 1993b
Fish Clay	Stevns Klint (Denmark)	marl	120	52	33	Premović et al. 1993a
Zvonce black shale	Zvonce (Serbia)	shale	100	50	38	Premović 1984

[a] The content determined by ICP–OES.

[b] The short notations for the Cretaceous-Paleogene boundary shales are: CNS — Canadian North Site and SVS — Starkville South Site.

VO^{2+} ions. Therefore, just before preparing the standards, the composition of $VOSO_4 \times 5H_2O$ was checked using the most precise gravimetric/titrimetric methods of chemical analysis. The relative standard deviation (RSD) was less than 5 %.

Changes in the loading Q factor of the ESR cavity can result in samples that have different dielectric properties or surfaces. The above glycerol solution has a dielectric constant (56 D) and cannot be used as a reliable comparison for the relative VO^{2+} concentrations in kaolinite. For this reason, standards were prepared by mixing and diluting the glycerol VO^{2+} solution with KGa-2, which contains a very low amount of VO^{2+} (<5 ppm), to the desired VO^{2+} concentration. This mixture has a similar dielectric medium and Q parameter as the kaolinite samples. For the first set of measurements, the VO^{2+} standards were prepared from the glycerol solution and KGa-2 using a vibrating mill (Perkin-Elmer) that covered the concentration range from 200 ppm to 1000 ppm. For the second set of measurements, standards were prepared from the FBT 2A-03 kaolinite, which contains 200 ppm of VO^{2+}, and diluted with GB1 kaolinite, which contains no VO^{2+} (a detection limit 1 ppm), covering the concentration range from 50 ppm to 200 ppm.

Results and discussion

The concentration of VO^{2+} (C) is given by the following equation:

$$[C_k] = (SI_k / SI_{st})\ [C_{st}]$$

where k indicates the kaolinite sample, st indicates the standard, and SI is the specific signal intensity (the integrated area under the corresponding ESR absorption per g of the sample). In the first approximation the discrepancy between the specific (signal) intensity of the VO^{2+} ions in the standards and kaolinite are considered to be analytically insignificant.

The kaolinite samples studied show multiline spectra similar to the spectra of VO^{2+} ions incorporated into the lattices of numerous kaolinite samples, including KGa-1 (Premović 1984; Muller & Calas 1993; Gehring et al. 1993). A representative X-band spectrum from KGa-l is shown in Fig. 1a. A preliminary Q-band measurement indicates that this spectrum is a superimposition of the spectra of VO^{2+} ions located in two different positions in the kaolinite structure. The spectrum shows an anisotropic pattern typical of axially symmetrical hyperfine coupling. A sharp intense peak near $g = 2.002$ is ascribed to defects that are always present in kaolinite (Muller et al. 1992).

Figure 1 also illustrates the anisotropic ESR spectrum of: (b) an initial solution of $VOSO_4 \times 5H_2O$ compound dissolved in H_2SO_4/H_2O and diluted with glycerol and (c) a standard containing 1000 ppm of VO^{2+}. These spectra are typical of those previously reported for VO^{2+} in either powder (polycrystalline) solids or extremely highly-viscous liquids (Goodman & Raynor 1970).

Because only one line of the VO^{2+} anisotropic hyperfine pattern is necessary for obtaining the integrated area, only a narrow part of the VO^{2+} spectrum needs to be recorded. We selected the first derivative ^{51}V hyperfine line marked with $m_I = -5/2\|$ in the spectra of the kaolinite samples (see, for example, Fig. 1a) and the 50–1000 ppm VO^{2+} standards (see, for example, Fig. 1c). This line was chosen to keep the linewidth and lineshape similar and to minimize the interferences from both neighbouring VO^{2+} lines and other ESR active species present. The anisotropy of the ESR parameters of VO^{2+} in various clays has little or no effect on the linewidth and lineshape of the $-5/2\|$ resonance line.

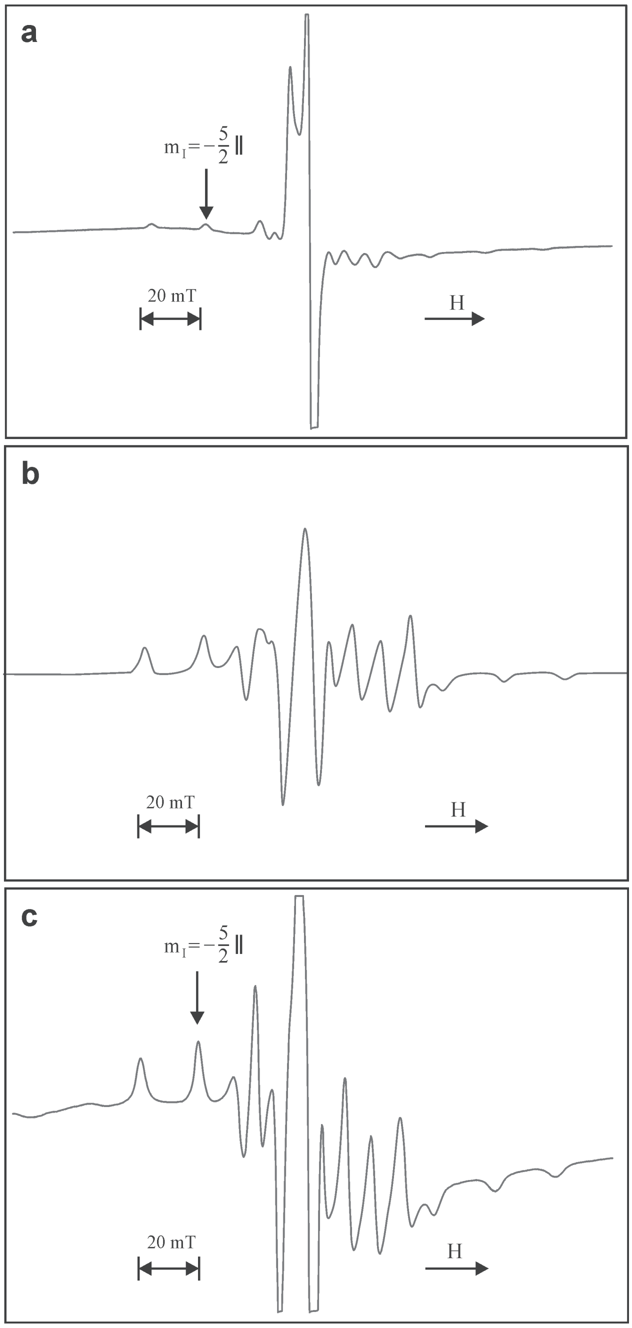

Fig. 1. First derivative, room temperature, anisotropic ESR spectrum of: **a** — KGa-1; **b** — An initial solution of $VOSO_4 \times 5H_2O$ dissolved in H_2SO_4/H_2O and diluted with glycerol; **c** — A standard containing 1000 ppm of VO^{2+}.

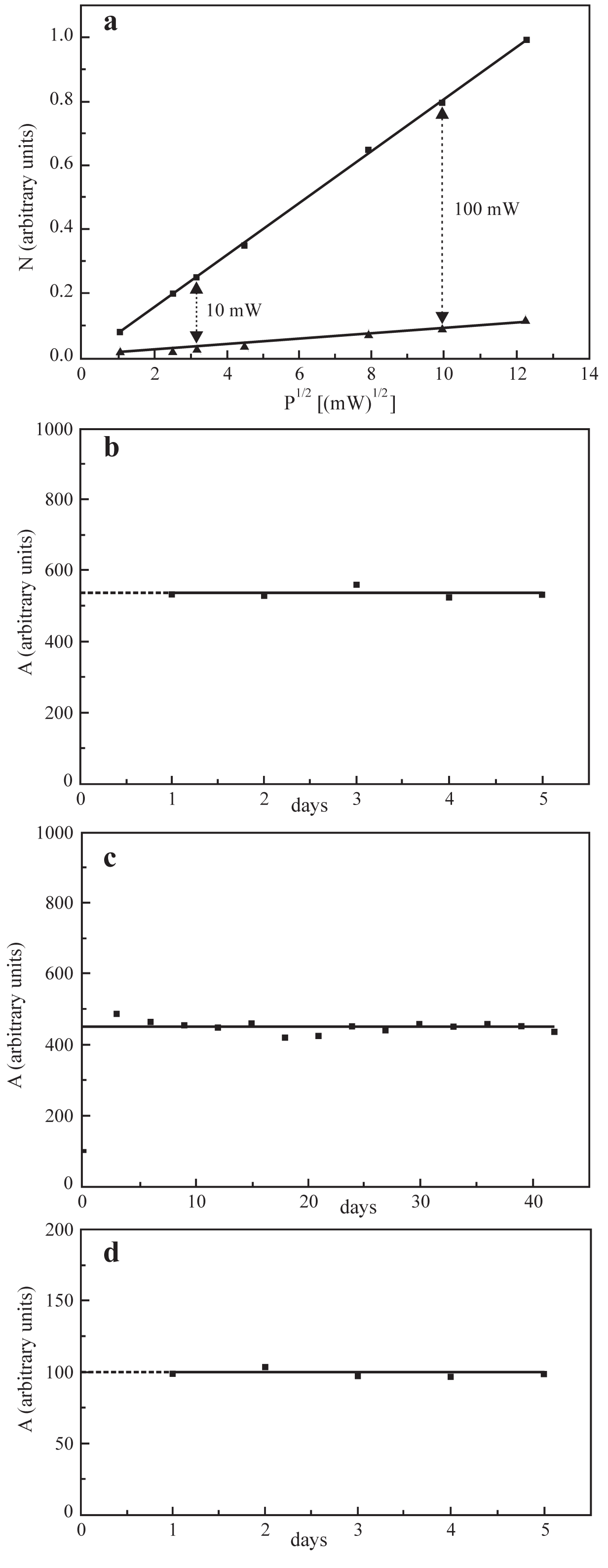

Fig. 2. Saturation behaviour of the –5/2|| VO^{2+} resonance line in: **a** — A standard containing 1000 ppm of VO^{2+} and KGa-l; **b** — The repeatability of the integrated area using the 1000 ppm standard; **c** — Effect of time on the –5/2|| VO^{2+} resonance line of the 1000 ppm standard stored in air; **d** — The repeatability of the integrated area using a secondary standard at the 100 ppm level. N is the normalized intensity of the –5/2|| line; A is the integrated area of this line.

To obtain maximum sensitivity, the spectrum must be recorded at a high power level. However, at high power, saturation is possible. Therefore, we plotted the normalized integrated area (A) of the –5/2|| line against the square root of the microwave power ($P^{1/2}$) for both the 1000 ppm standard and the KGa-l sample (Fig. 2a). The linear relationship shows that quantitative work can be safely performed at 100 mW. At this power, no saturation broadening of the signal was observed for either the standards or the kaolinite samples. Consequently, a high power of 100 mW was selected for measurement, ensuring a high absolute intensity of the –5/2|| line.

Figure 2b shows a plot of the integrated area of the –5/2 line (vs. days) for five 1000 ppm standards prepared on five different days. The scatter of obtained points averaged to a straight line (parallel to the day axis in Fig. 2b) with deviations of <5 %. The repeatability of these results is <30 ppm of VO^{2+} at the 1000 ppm level.

The spectrometric procedure described enabled us to achieve sufficient reproducibility of the specific signal from the standard and kaolinite samples with a VO^{2+} anisotropic ESR spectrum. The RSD was less than 10 %. Although VO^{2+} concentrations as low as 5 ppm were detected, the best results were achieved for concentrations of about ≥50 ppm.

Although the kaolinite samples were not collected from freshly exposed mine faces, repeated ESR analyses over the course of several months showed no change in VO^{2+} content. This result is consistent with previous studies of VO^{2+} stability in kaolinite (Muller & Calas 1993; Gehring et al. 1993). Similar experiments on VO^{2+} standards show that after six weeks no oxidation had occurred (Fig. 2c).

The calibration curves were prepared by determining the area under the peak of the –5/2|| resonance line and multiplying or dividing that line by factors required to put all of the standard and kaolinite sample peak areas on the same setting. The peak areas were evaluated using the built-in computer of the spectrometer. This computer performed the appropriate integrations with baseline corrections.

A linear calibration curve was obtained by plotting the specific intensities of the –5/2|| lines of the standards against the VO^{2+} concentrations. Fig. 3a shows this plot in the 200–1000 ppm range. Using this plot as the calibration curve, the concentration of VO^{2+} was determined for the kaolinite samples (Table 1a) by recording the VO^{2+} spectrum and the specific intensity of the –5/2|| line. It should be noted that the calibration curve obtained by plotting the specific intensities of the –7/2, +5/2 and +7/2 lines gave similar results but with less accuracy and precision.

A rough ESR estimate indicates that the VO^{2+} content of the Cigar Lake kaolinite sample is much higher than 1000 ppm. Therefore, this sample was diluted three, four and five times with the KGa-2 kaolinite. The calibration curve shown in Fig. 3a was then used to determine the VO^{2+} contents of these diluted samples (Table 1a). The VO^{2+} content in the Cigar Lake kaolinite sample is 2700±100 ppm (Table 1a).

The use of the KGa-2/glycerol mixture as a standard is not suitable, especially for routine analysis when many samples with relatively low concentrations (<200 ppm) of VO^{2+}

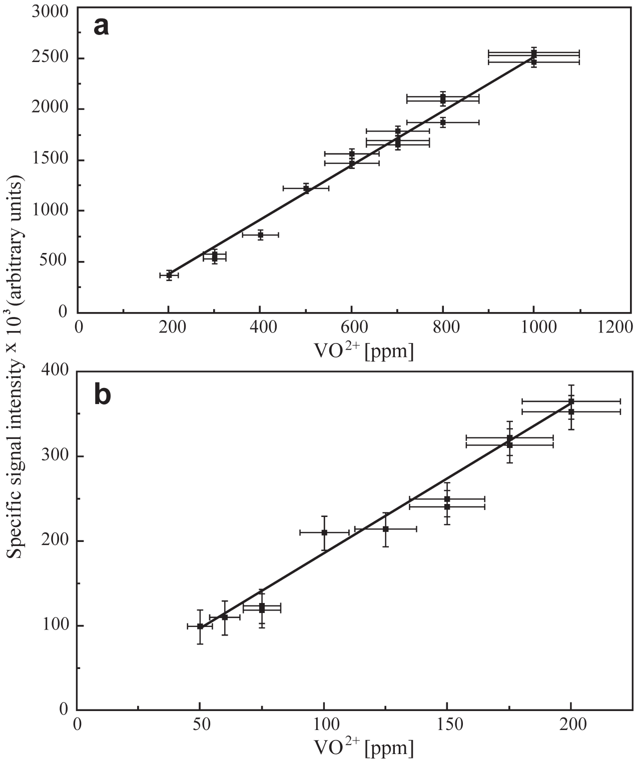

Fig. 3. Specific signal intensities of the –5/2|| lines of the standards against the VO^{2+} concentration. **a** — The standards of 200–1000 ppm. Experimental error bars for the data points are ±10 % for VO^{2+} and $\pm 50\times10^3$ for specific intensity; **b** — The standards of 50–200 ppm. Error bars for the data points are ±10 % for VO^{2+} and $\pm 20\times10^3$ for specific signal intensity.

need to be handled. For this reason, new (hereinafter secondary) standards were prepared by mixing GB1, which has no detectable VO^{2+}, and the FBT 2A-03 kaolinite, which is relatively enriched with VO^{2+} (Table 1a).

Eight secondary standard samples were prepared with 50, 60, 75, 100, 125, 150, 175 and 200 ppm of VO^{2+}. A very good linear relation was obtained as is shown in Fig. 3b. The linearity shows that these secondary standards are a good tool for the quantitative determination of VO^{2+} in the range of 50 to 200 ppm. Table 1a also lists the number of kaolinite samples with VO^{2+} content lower than 200 ppm. The calibration curve shown in Fig. 3b was used to obtain these results.

All secondary standard concentration results were confirmed by performing two or more experiments in five days and through the use of more than one GB1 and FBT 2A-03 sample in each case. Fig. 2d indicates that the repeatability of these results is < 10 ppm of VO^{2+} at the 100 ppm level.

The above method of VO^{2+} determination was extended to the kaolinite-rich Cretaceous-Paleogene boundary shales CNS/SVS, the smectite-rich marl Fish Clay and the kaolinite-rich Zvonce black shale, (Table 1b). The calibration curve shown in Fig. 3b was also used to obtain the results listed in Table 1b. Preliminary results indicates that a similar method can be used to determine the concentration of other paramagnetic ions, such as Cu^{2+} and Mn^{2+} in clays.

Conclusions

A new, fast, simple and straightforward method for determining the concentration of VO^{2+} in clays and clay-rich sediments using ESR is described. This method eliminates difficulties of the previously reported method employing the Cu^{2+} standard. In addition, the proposed method does not require any pretreatment of the clay and tedious/complex integration of the whole spectrum. The newly developed method is sensitive enough to enable quantization of VO^{2+} at low (≥50 ppm) and high (>2500 ppm) concentrations. These advantages encourage the application of the proposed method in routine clay analysis of VO^{2+}.

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