Vanadyl porphyrins in sedimentary kerogens/asphaltenes: Estimation of the concentration

PAVLE I. PREMOVIĆ[1], THIERRY ALLARD[2], NIKOLA D. NIKOLIĆ[1], IVANA R. TONSA[1] and MIRJANA S. PAVLOVIĆ[3]

[1]Laboratory for Geochemistry and Cosmochemistry, Department of Chemistry, Faculty of Science, University of Niš, P.O.Box 91, YU-18000 Niš, FR Yugoslavia, [2]Laboratoire de Mineralogie-Cristallographie, Universités de Paris VI et VII, Place Jussieu - 75252 Paris Cedex 5, France, and [3]Institute of Nuclear Sciences Vinča, P.O.Box 522, YU-11001 Belgrade, FR Yugoslavia

A new, rapid method for determining the concentration of vanadyl porphyrins (VO^{2+}-P) associated with the kerogen of bituminous sedimentary rocks, using electron spin resonance (ESR) is described. The method is simple, straightforward and inexpensive. Several concentrations of a vanadyl (VO^{2+}) standard dissolved in glycerol/lignite mixture were prepared. The VO^{2+} concentrations ranged from 100–1000 ppm. The anisotropic ESR spectra of both the standards and kerogen samples were recorded at room temperature and the integrated areas of the pre-selected ESR line (attributed to nuclear spin $m_1 = -5/2$) were computed. The concentrations of VO^{2+} found in the kerogen samples were calculated using the relative ratio of the integrated areas for the standards and the kerogen samples. The VO^{2+}-P concentrations of the kerogen materials were then calculated using 450 as the mean molecular weight of these species. The quantitative determination of VO^{2+}-P in the kerogen fractions in the range 800 ppm and 8000 ppm and higher is feasible by the method reported. The method of analysis was also extended to asphaltene samples (enriched with VO^{2+}-P) and a coal sample containing non-porphyrin VO^{2+} associated with its organic fraction.

Key words: vanadyl porphyrins, kerogen, estimation, concentration.

The occurrence of alkyl vanadyl (VO^{2+}) porphyrins (P) in geological bitumen samples was first demonstrated by the work of Treibs[1] and now they are known to be present in a wide range of sedimentary rocks and petroleums. VO^{2+}-P, first biomarkers identified in sedimentary bitumens, are molecular fossils of tetrapyrrolic pigments such as chlorophylls/bacteriochlorophylls.[2] Today, over 50 years after Treibs' discovery, there is considerable interest in sedimentary alkyl VO^{2+}-P as biomarkers of depositional environments,[3] thermal history[4] and original organic input into the sedimentary milieu.[5] Sedimentary VO^{2+}-P can be arbitrarily divided according to their physiochemical properties into the following two groups: (a) extractable (alkyl) VO^{2+}-P with relatively low moleuclar weight and (b) VO^{2+}-P

associated with high molecular weight geopolymers: extractable asphaltene and insoluble kerogen.[4]

Many analytical methods have been developed for the determination of the total alkyl VO^{2+}-P in sedimentary bitumens, but no method has been reported for the determination of VO^{2+}-P associated with the kerogen fraction. This paper presents an analytical procedure than has been developed to quantify VO^{2+}-P in the kerogens. The method has been tested with kerogen samples from various sedimentary rocks of marine origin with relatively high VO^{2+}-P concentrations ($\geq$800 ppm). The results should aid the interpretation of the process of VO^{2+}-P genesis and contribute to our understanding of the importance of redox processes in VO^{2+}-P genesis.

Present methods for the determination of the concentration of alkyl VO^{2+}-P in sedimentary bitumens utilize spectrophotometric techniques.[6] Spectrophotometric methods allow the determination of alkyl VO^{2+}-P of sedimentary bitumen by measuring the absorbance at the absorption maximum of alkyl VO^{2+}-P, and are therefore, not applicable to a kerogen system with VO^{2+}-P. Recently, Holden *et al.*[7] developed method for the estimation of the porphyrin concentration in the kerogen fraction of sedimentary rocks using high-resolution reflectance spectroscopy. This method is, however, not applicable to kerogen systems enriched with VO^{2+}-P when other metalloporphyrins (such as nickel(II) porphyrins) are present.

ESR has now become a popular and useful tool in the hands of geochemists and geologically oriented scientists. A large number of investigators working on paramagnetic ions in geological materials have utilized this method in probing into the structural and dynamic aspects of these ions. Furthermore, ESR is especially advantageous in sensitivity to the paramagnetic ions besides being powerful in the resolution and reproducibility of the signals. For instance, the discovery by O'Reilly[8] of the ESR signals of VO^{2+}-P in petroleums and asphaltenes prompted researchers to apply the technique for the detection and approximate quantification of low concentrations of alkyl VO^{2+}-P in various carbonaceous geological materials without recourse to extraction.[9] Hocking and Premović[10] used for the first time this technique to study VO^{2+}-P in the coal/coal-like inclusions of the Athabasca tar sand. In addition, Premović *et al.*[11] applied ESR to estimate the distribution of VO^{2+}-P in the kerogen fraction of ancient sedimentary rocks of marine origin: the La Luna limestone (Venezuela) and Serpiano marl (Switzerland). Finally, Nissenbaum *et al.*[12] detected by ESR VO^{2+}-P in the asphalt float from the Dead Sea Basin (Israel).

In view of the high ESR sensitivity, this investigation was undertaken with a specific objective in mind: to evaluate a possible rapid and accurate quantitative method for the determination of VO^{2+}-P in sedimentary kerogen without chemical pretreatment. This communication describes this new method which, in principle, is quite similar to the sample interchange method of Premović[13] and Premović *et al.*[11,14] The method has been tested with samples of sedimentary kerogens and asphaltenes, Table I. These materials were selected because their relatively high V content, ranging from 600 ppm up to 3000 ppm. The direct determination of VO^{2+}-P

was extended to both the asphaltenes of the floating asphalts from the Dead Sea Basin and the organic fraction of a Kentucky coal sample.

EXPERIMENTAL

Samples

In order to demonstrate the applicability of this method, ESR was used to determine the VO^{2+}-P contents of two kerogen samples (11-6x Corman and 35-1 Duncan) of the Denver: Powder River Formation (USA); six kerogen samples (AK 74, 76, 120; II D, IV D2, and DG 70) of the Akkuyi Formation (Turkey); two asphaltene samples (A1, 2) of the Dead Sea floating asphalt and a Kentucky coal sample (Providence mine, Kentucky, USA).

Electron spin resonance (ESR) analysis

The ESR measurements were performed on finely-ground powders of kerogen/asphaltene samples that were transferred to an ESR quartz tube. The spectra were recorded on a Bruker ER-200 series ESR spectrometer with a Bruker ER-044 X-band bridge using standard 100 kHz field modulation. X-band measurements were made at 9.3 GHz utilizing a rectangular TE cavity.

Emissions spectrometry

A PGS-2 plane grating spectrograph (Carl Zeiss, Jena) was used with an attachment for photoelectric detection, an arc plasma excitation source, and a Bausch and Lomb diffraction grating as the monochromator.[15]

Isolation of kerogen/asphaltene

The procedure for the isolation of various organic fractions of bituminous rocks, asphalts and coals, as well as their analysis has been presented in previous publications.[4,11,16]

RESULTS AND DISCUSSION

Within the method employed, the VO^{2+}-P concentration, [K], is given by the following equation

$$[K] = C \, A_k/A_{st} \, \rho_k/\rho_{st} \, [ST]$$

where the subscripts k and st indicate the kerogen sample and the standard, respectively, A is either the intensity (the ESR line height) or the integrated area under the first derivative of the corresponding ESR line, ρ is the density and [ST] the concentration of the standard. C is mainly an instrumental constant. The areas and concentrations were evaluated by means of a Daewoo computer system that performed the integrations with baseline corrections, and computed the VO^{2+}-P concentrations from the above expression.

A glycerol solution was prepared by first dissolving a known amount of $VOSO_4 \times 5H_2O$ in a solution containing 1.5 mL of concentrated H_2SO_4 + 0.5 mL of deionized H_2O and then diluting it with glycerol to the desired VO^{2+} concentration (8000 ppm) with thorough agitation. Changes in the efficiency (Q) of the ESR cavity can result with samples that have different dielectric properties of surfaces. The above glycerol VO^{2+} solution has a high dielectric constant (56 D) and so cannot be used as a reliable comparison of the relative VO^{2+} concentration in kerogen. For this reason, standards were prepared by mixing/diluting the glycerol VO^{2+} solution

with lignite (or, of course, any kerogen-like material containing no VO^{2+}-P) to the desired VO^{2+} concentration. The preparation of this (hereinafter called glycerol/lignite) mixture has the effect of maintaining the dielectric medium of the standards close to that of the kerogen samples, thus keeping Q similar. The standards prepared by mixing the glycerol VO^{2+} solution and lignite (using a vibrating mill: Perkin-Elmer) covered the VO^{2+} concentration range from 100 ppm to 1000 ppm of VO^{2+}. The lignite used in these standards was Kostolac coal (Serbia) which contains no VO^{2+}.

The VO^{2+}-P have characteristic anisotropic ESR spectra. The anisotropic ESR spectra of VO^{2+}-P in the kerogen fractions of the studied sedimentary rock were similar to that of La Luna kerogen (Fig. 1a). In general, these spectra gave a 16-line anisotropic pattern, due to the interaction of the ^{51}V nucleus with its unpaired electron, and
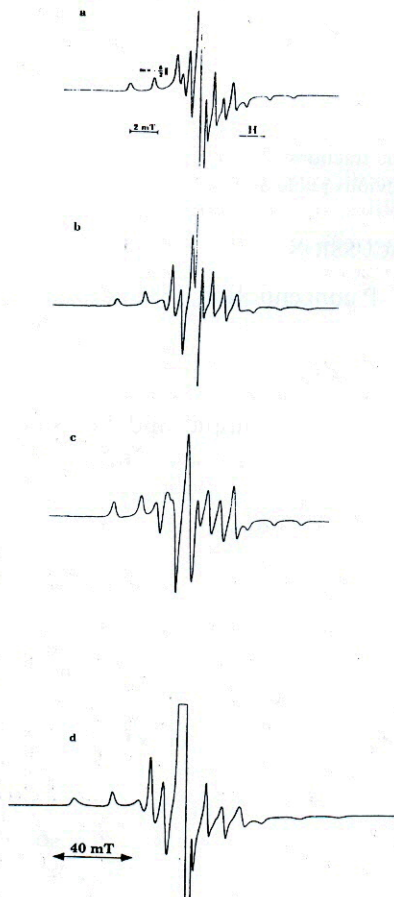

Fig. 1. First derivative, room temperature, anisotropic ESR spectrum of: (a) the La Luna kerogen enriched with VO^{2+}-P; (b) a standard (the glycerol/lignite mixture) containing 1000 ppm of VO^{2+}; (c) the initial glycerol solution containing 8000 ppm of VO^{2+}; and (d) the insoluble organic fraction of the Kentucky coal containing VO^{2+}-non-P.
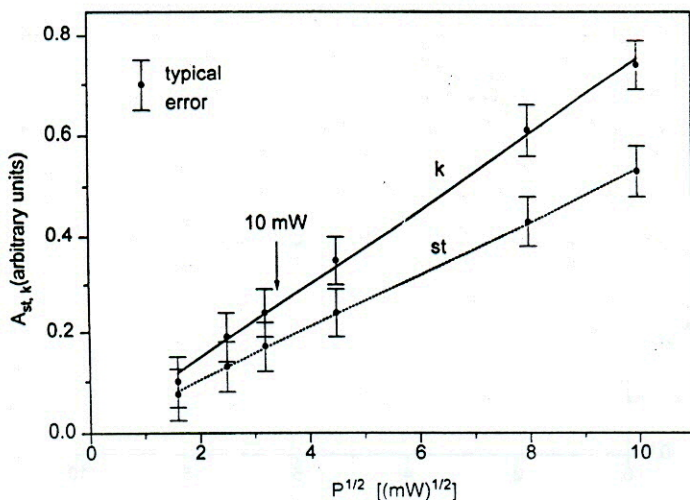
Fig. 2. Saturation behavior of the $-5/2 \parallel VO^{2+}$ resonance line of: (st) a standard containing 1000 ppm of VO^{2+} and (k) the Duncan kerogen.

displayed parallel and perpendicular features characteristic of polycrystalline (amorphous) samples. A sharp intense peak near $g = 2.003$ is assigned to polyaromatic paramagnetic species, which are always present in the kerogen materials.[17]

At least three sources of error affect the precision of the estimation: (1) the error in recording the spectrum which depends upon the instrument used; (2) the error in mixing the glycerol VO^{2+} solution with lignite; and (3) the error in measuring the area under the appropriate line of the VO^{2+} ESR spectrum.

Figure 1 also illustrates the anisotropic ESR spectrum of: (b) a standard containing 1000 ppm of VO^{2+} and (c) a solution of $VOSO_4 \times 5H_2O$ dissolved in

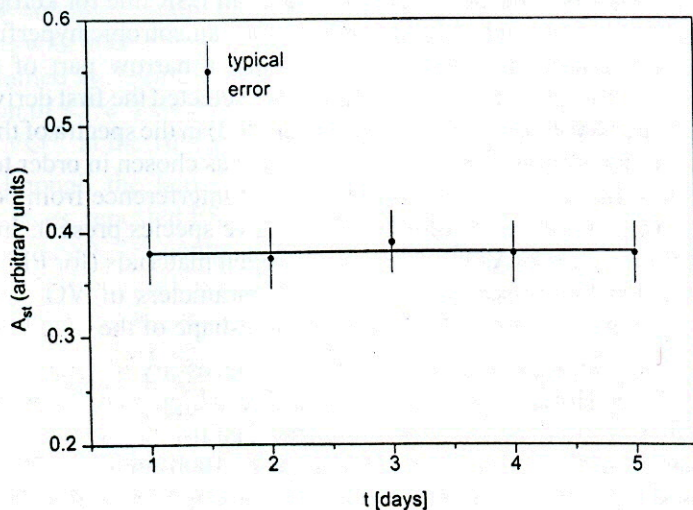Fig. 3. The repeatability of the integrated area of the $-5/2 \parallel VO^{2+}$ resonance line using a standard containing 1000 ppm VO^{2+}.
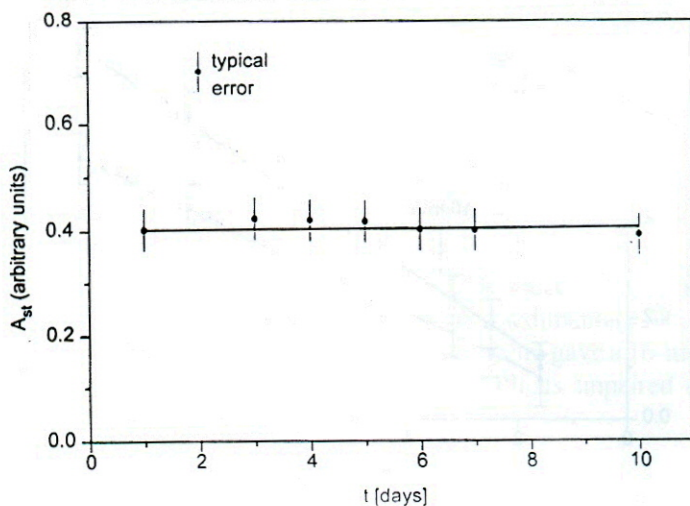
Fig. 4. Effect of time on the −5/2 ∥VO^{2+} resonance line of a standard (with 1000 ppm of VO^{2+}) stored in air.

the H_2SO_4/H_2O system which was used for the preparation of the glycerol solution. The anisotropic spectrum is typical of those previously reported for VO^{2+} in powder (polycrystalline) solids (b) or extremely high-viscous liquids (c).[18] It must be understood here that the relative intensity (the ESR line height) in this case is not proportional to the VO^{2+} concentration and one cannot make use of the ESR line intensity for a reliable comparison of the relative VO^{2+} concentrations in both the standards and kerogen samples. Such a comparison requires the integrated areas. Thus, the technique employed to measure the VO^{2+} concentration in the kerogen samples was a comparison of the integrated area of an ESR line for kerogen to that of a standard sample. Since only one line of the VO^{2+} anisotropic hyperfine pattern is necessary for obtaining the integrated area, just a narrow part of the VO^{2+} spectrum needs to be recorded. For this purpose, we selected the first derivative ^{51}V hyperfine line marked with $m_I = -5/2$ ∥(hereinafter −5/2) in the spectra of the kerogen samples (Fig. 1a) and standards (Fig. 1b). This line was chosen in order to keep the linewidth and lineshape similar and to minimize the interference from both neighbouring VO^{2+} lines and the lines of other ESR active species present. In addition, from our continuing study of VO^{2+} in various kerogen materials (for PIP 20 years), we have found that the anisotropy of the ESR parameters of VO^{2+} in various kerogens has little or no effect on linewidth and lineshape of the −5/2 line.

In order to obtain maximum sensitivity, it is necessary to record a spectrum at a high power level. However, saturation is possible at high power. For this reason, we plotted the integrated area of the −5/2 line against the square root of the microwave power ($P^{1/2}$) for both the standard (with 1000 ppm VO^{2+}) and the La Luna kerogen samples (Fig. 2). The linear relationship shows that it is safe to perform quantitative work at the 10 mW power employed for these measurements.
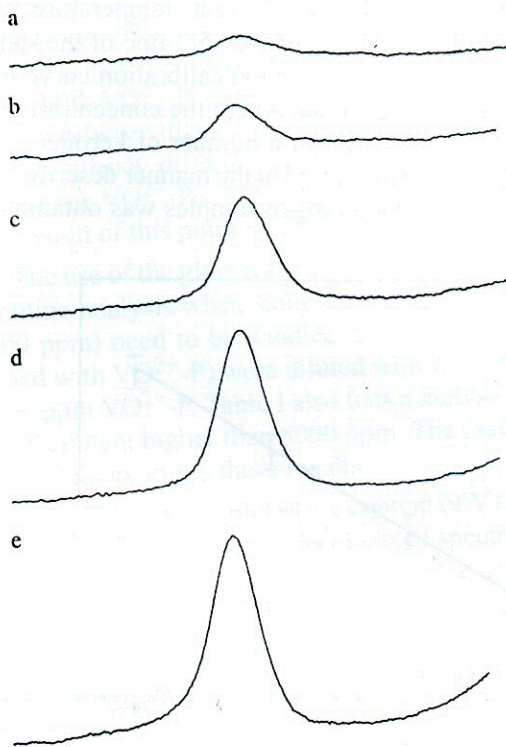
Fig. 5. The $-5/2$ $||VO^{2+}$ resonance line of the Kostolac glycerol/lignite mixture for the following concentrations of VO^{2+}: (a) 100 ppm; (b) 250 ppm; (c) 500 ppm; (d) 750 ppm; and (e) 1000 ppm.

Figure 3 shows a plot of the integrated area of the $-5/2$ line (*vs.* days) for five standard samples containing 1000 ppm of VO^{2+} derived from five different glycerol solutions with 8000 ppm of VO^{2+} prepared on five different days. A scatter of points was obtained averaging to a straight line (parallel to the day axis in Fig. 3) with a deviation of <5%. This figure indicates that the repeatability of these results is <30 ppm of VO^{2+} at the 1000 ppm level.

Although the kerogen samples were not collected from freshly exposed outcrop faces, repeated ESR analyses over the course of several months showed no change in their VO^{2+} contents. Similar experiments on VO^{2+} standards showed that after several weeks no oxidation had occured. Typical results (standard with 1000 ppm of VO^{2+}) are shown in Fig. 4. The ESR analysis at zero time corresponds to a fresh sample stored under N_2. After six weeks of exposure to air, the VO^{2+} concentration was virtually unchanged from the initial value of 1000 ppm. A part of the sample was stored in a cloth bag to allow complete exposure to air.

Finally, the packing densities of the kerogen samples did not vary by more than 5% but the standards had densities anywhere between 0.50–0.90 g cm^{-3} and appropriate corrections were made.

Figure 5 shows a series of −5/2 ESR lines at room temperature for five concentrations of standards. If the integrated area of the −5/2 line of the standards is simply plotted against the VO^{2+} concentration a good calibration curve in itself is possible. Figure 6 shows the linear plot obtained where the concentration range 100 to 1000 ppm is covered. The VO^{2+} spectra of a number of kerogen samples were recorded and the −5/2 line areas were measured in the manner described. From these areas the concentration of VO^{2+} in the kerogen samples was obtained using the calibration curve in Fig. 6.
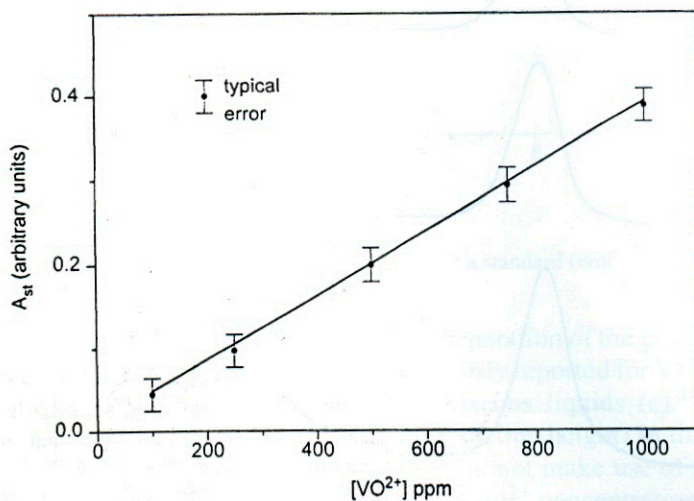

Fig. 6. The glycerol/lignite mixture as a standard for VO^{2+} in the concentration range from 100 ppm up to 1000 ppm.

Table I lists a number of kerogen samples for which the VO^{2+}-P concentration was determined. The calibration curve shown in Fig. 6 was used in obtaining these results. The use of the glycerol/lignite mixture as a standard is suitable, especially for routine analysis when many samples with relatively low concentrations of VO^{2+}-P (<8000 ppm) need to be handled, as it is often the case with most kerogen samples. All the concentration results were confirmed by two or more experiments on different days using more than one kerogen sample in each case. Figure 7 indicates that the repeatibility of these results is <30 ppm of VO^{2+}-P at the 5400 ppm level (the Duncan kerogen).

In fact, there are implicit assumptions in our approach that should be considered. The VO^{2+}-P are assumed to be the only species VO^{2+} present in each sample. While these are the dominant species in sedimentary bitumens,[2] very little is known about those VO^{2+} species incorporated into the kerogen framework.[4] Occasionally, the ESR spectrum of VO^{2+} non-porphyrins (VO^{2+}-non-P) are noted in the kerogen spectra.[16,19] The presence of these VO^{2+}-non-P, however, can not affect in anyway the determination of VO^{2+}-P in a particular kerogen sample.

It is also assumed that the VO^{2+}-P in each kerogen sample consists of equivalent alkyl VO^{2+}-P species with similar ESR spectral properties and molecular weights (*ca.* 450).[11] To obtain almost identical ESR spectra for extractable alkyl VO^{2+}-P and VO^{2+}-P incorporated into the kerogen matrix,[4] a high degree of similarity between these VO^{2+}-P structures must exist. If there are kerogen VO^{2+}-P which are grossly different in structures than the (exractable) alkyl VO^{2+}-P (say, polyaromatic VO^{2+}-P structures) then their ESR spectra should be quite different.[11] A discussion of this point is, however, beyond the scope of this report.

The use of the glycerol/lignite mixture as a standard is not suitable, especially for routine analysis when samples with relatively high concentrations of VO^{2+}-P (>8000 ppm) need to be handled. For this reason, some kerogens (exceptionally enriched with VO^{2+}-P) were diluted with Kostolac lignite to lie in the range of 800 to 8000 ppm VO^{2+}-P. Table I also lists a number of sedimentary kerogens having a VO^{2+}-P content higher than 8000 ppm. The calibration curve shown in Fig. 6 was, also, used in obtaining these results.

Figure 8 depicts a plot of the content of V (as VO^{2+}-P) of the kerogen samples against the total content of V, as obtained spectrochemically, Table I. These results support the view that most of the V (>80%) exist as kerogen VO^{2+}-P recognized by ESR.[11]

TABLE I. The V [ppm], VO^{2+} [ppm] and VO^{2+}-P [ppm] contents of the organic fractions of selected bituminous rocks, asphalts and Kentucky coal

Lithology/Sample	VO^{2+}	VO^{2+}-P*	V as VO^{2+}-P	Total V**	V as VO^{2+}-P [% of total V]
Black shale:					
11-16× Corman	3000	24000[a]	2300	2900	80
35-1 Duncan	675	5400[a]	500	600	83
AK 74	1625	13000[a]	1200	1400	86
AK 76	2125	17000[a]	1600	1900	84
AK 120	1125	9000[a]	900	1000	90
II D	1625	13000[a]	1200	1400	86
IV D2	1000	8000[a]	800	1000	80
DG 70	3000	24000[a]	2300	2800	82
Floating asphalt:					
A1	925	7400[b]	700	850	82
A2	1250	10000[b]	950	1100	86
The Kentucky coal[c]	850	–	650[d]	675	95[e]

*Determined by ESR. **Determined by emission spectrometry. [a]In kerogen. [b]In asphaltene. [c]V as VO^{2+}; [d]V as VO^{2+} [% of total V].

Essentially, a similar procedure was applied to the asphaltene samples of the floating asphalts from the Dead Sea Basin. From our set of VO^{2+}-P standards, we estimate that the VO^{2+}-P concentrations of the floating asphalts to be about 1000
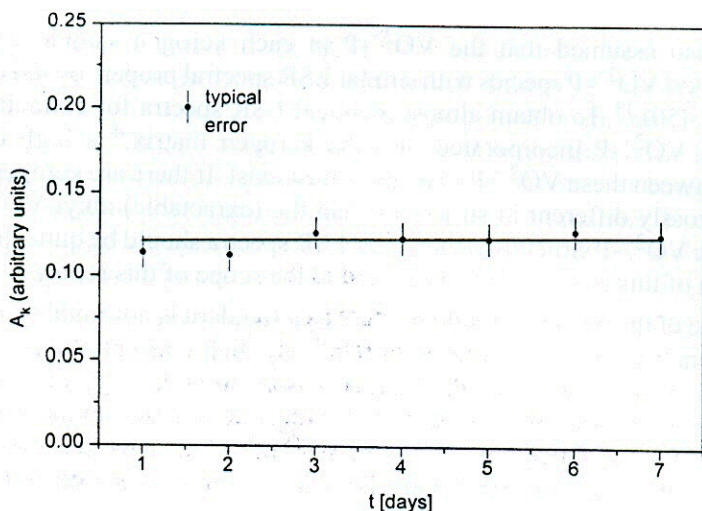
Fig. 7. The repeatability of the integrated area of the $-5/2$ ‖VO^{2+} resonance line of the Duncan kerogen sample.

ppm, while the VO^{2+}-P contents of their asphaltene fractions are considerably higher, Table I.

Finally, our method of analysis was extended to VO^{2+}-non-P species associated with the organic insoluble fraction of a Kentucky coal sample containing a relatively high concnetration of V (675 ppm), Table I. The complete ESR spectrum of this fraction is shown in Fig. 1d. The VO^{2+} concentration in the Kentucky coal sample was found to be 850 ppm, *i.e.*, in this coal fraction 95% of total V appeared
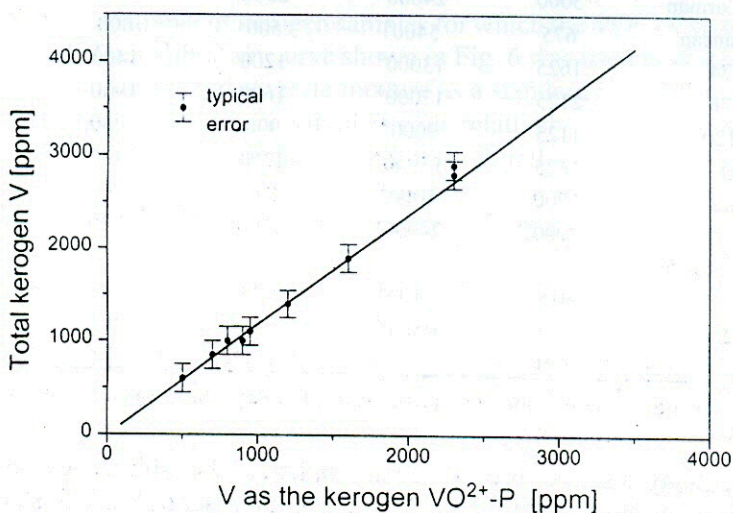

Fig. 8. V as kerogen VO^{2+}-P *vs.* the total kerogen V of the kerogen samples studied.

to be as VO^{2+}, Table I. Thus, the proposed method for the determination of VO^{2+}-P in various organic fractions of various bituminous rocks is suitable of providing good analytical data for non-porphyrin VO^{2+} in organic, as well as inorganic components of these geological materials. In addition our recent work indicates that the quantitative analysis of other ESR-active transition metal ions (*e.g.*, copper (II)) could also be facilitated by this method.

Our analyses of bituminous rocks indicate that the present method will be useful in basic studies of the VO^{2+} content and type in their various organic fractions. In additon, studies of this type should allow the determination of the concentration and, thus, the ratio of VO^{2+} incorporated into the inorganic (predominantly clay) fraction[13] to that associated with the organic fraction of sedimentary rock, thereby enhancing investigations of paleoenvironmental preferential enrichment of both VO^{2+} and VO^{2+}-P.[16] These measurements should allow the determination of the general paleo-environment during the formation of bituminous sedimentary rocks (*e.g.*, marine *vs.* terrestrial).[19]

CONCLUSION

The direct method of determination of the kerogen/asphaltene VO^{2+}-P (using a mixture of glycerol VO^{2+} solution and lignite coal) is a simple and rapid procedure and exhibits good precision for kerogen/asphaltene samples with relatively low VO^{2+}-P content ($\geq$800 ppm). This method is, also, applicable to similar materials but with relatively high concentrations of VO^{2+}-P (>8000 ppm).

ИЗВОД

ВАНАДИЛ ПОРФИРИНИ У СЕДИМЕНТНИМ КЕРОГЕНИМА/
АСФАЛТЕНИМА: ПРОЦЕНА КОНЦЕНТРАЦИЈЕ

ПАВЛЕ И. ПРЕМОВИЋ,[1] THIERRY ALLARD,[2] НИКОЛА Д. НИКОЛИЋ,[1] ИВАНА Р. ТОНСА[1] и МИРЈАНА С. ПАВЛОВИЋ[3]

[1]*Лабораторија за геохемију и космохемију, Философски факултет, Универзитет у Нишу, п.пр. 91, 18000 Ниш,*
[2]*Laboratoire de Mineralogie-Cristallographie, Universités de Paris VI et VII, Place Jussieu – 75252 Paris Cedex 5, France u*
[3]*Институт за нуклеарне науке Винча, п. пр. 522, 11001 Београд*

Описали смо нову, брзу методу за одређивање концентрације ванадил порфирина (VO^{2+}-P) удружених са керогеном битуминозних седиментних стена употребом елек-троноспинске резонанције (ЕСР). Метода је проста, директна и јефтина. Припремљено је неколико стандардних концентрација ванадила (VO^{2+}) у глицерол/лигнитној смеши.

Концентрације VO^{2+} су се кретале од 100–1000 ppm. Анизотропни ЕСР спектри и станд-ардних и керогенских узорка су записани на собној температури и интегрисане површине предходно одабране ЕСР линије (приписане нуклеарном спину $m_I = -5/2$) су израчунате коришћењем релативног односа интегрисаних површина за стандардне и керогенске узорке. Концентрације VO^{2+}-P керогенских материјала су онда израчунате коришћењем 450 као средње молекулске тежине ове врсте. Овом методом могуће је квантитативно одређивање VO^{2+}-P у керогенским фракцијама у опсегу од 800 ппм до 8000 ппм и већих. Метода анализе је проширена такође и на асфалтенске узорке (обогаћене VO^{2+}-P) и узорка угља који садрже не-порфиринске VO^{2+} који су удружени са његовом органском фракцијом.

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