ELSEVIER

Fuel 79 (2000) 813–819

FUEL

www.elsevier.com/locate/fuel

Estimation of vanadyl porphyrin concentration in sedimentary kerogens and asphaltenes

P.I. Premović[a,*], T. Allard[b], N.D. Nikolić[a], I.R. Tonsa[a], M.S. Pavlović[c]

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

Received 18 November 1998; received in revised form 14 August 1999; accepted 4 September 1999

Abstract

We describe 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). 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 to 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 $m_I = -5/2$) 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. Quantitative determination of VO^{2+}–P in the kerogen fractions in the range of 800–8000 ppm and higher is feasible by the method reported. The method of analysis was also extended to the asphaltene samples (enriched with VO^{2+}–P) and a coal sample containing non-porphyrin VO^{2+} associated with its organic fraction.

Keywords: Vanadyl porphyrins; Kerogen; Estimation; Concentration

1. Introduction

The occurrence of alkyl VO^{2+}–P in geological bitumen samples was first demonstrated by the work of Treibs [1]; they are known to be present in a wide range of sedimentary rocks and petroleums. VO^{2+}–P was the first biomarker identified in sedimentary bitumens and they 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 a biomarker 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 physicochemical properties into the following two groups: (a) extractable (alkyl) VO^{2+}–P with relatively low molecular 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 total alkyl VO^{2+}–P in sedimentary bitumens, but no methods have been reported for determination of VO^{2+}–P associated with the kerogen fraction. This paper presents an analytical procedure that 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 (≥ 800 ppm). The results should aid in 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.

The current methods for the determination of the concentration of alkyl VO^{2+}–P in sedimentary bitumens utilize spectrophotometric technique [6]. Spectrophotometric methods allow a determination of alkyl VO^{2+}–P of sedimentary bitumen by measuring absorbances at the absorption maxima of alkyl VO^{2+}–P, and therefore are not applicable to a kerogen system with VO^{2+}–P. Recently, Holden et al. [7] developed a method for estimation of porphyrin concentration in the kerogen fraction of sedimentary rocks using high-resolution reflectance spectroscopy. This method is, however, not applicable to a kerogen system

---

[*] Corresponding author. Universidad Central de Venezuela, Instituto de Ciencias de la Tierra, Facultad de Ciencias, Aptdo 3895, Caracas 1010-A, Venezuela.

E-mail address: pprem@gea.ciens.ucv.ve (P.I. Premović).

0016-2361/00/$ - see front matter
PII: S0016-2361(99)00205-7

Table 1
The V (ppm), VO^{2+} (ppm) and VO^{2+}–P (ppm) contents of the organic fractions of selected bituminous rocks, asphalts and the Kentucky coal

Lithology/sample	VO^{2+} [a]	VO^{2+}–P	V as VO^{2+}–P	Total V [b]	V as VO^{2+}–P (% of total V)
Black shale					
11-16x Corman	3000	24 000 [c]	2300	2900	80
35-1 Duncan	675	5400 [c]	500	600	83
AK 74	1625	13 000 [c]	1200	1400	86
AK 76	2125	17 000 [c]	1600	1900	84
AK 120	1125	9000 [c]	900	1000	90
II D	1625	13 000 [c]	1200	1400	86
IV D2	1000	8000 [c]	800	1000	80
DG 70	3000	24 000 [c]	2300	2800	82
Floating asphalt					
A1 [d]	925	7400	700	850	82
A2 [d]	1250	10 000	950	1100	86
The Kentucky coal	850	–	650 [e]	675	95 [f]

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

enriched with VO^{2+}–P, with other metalloporphyrins (such as nickel(II) porphyrins) present.

Electron spin resonance (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 for probing into the structural and dynamic aspects of these ions. Further, ESR is especially advantageous for its sensitivity to the paramagnetic ions besides being powerful in resolution and reproducibility of signals. For instance, the discovery of the ESR signals of VO^{2+}–P in the petroleums and asphaltenes by O'Reilly [8] 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 this technique for the first time 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 VO^{2+}–P, using ESR, in the asphalt float from the Dead Sea basin (Israel).

In view of high ESR sensitivity this investigation was undertaken with a specific objective in mind: to evaluate a possibly rapid and accurate quantitative method for the determination of VO^{2+}–P in sedimentary kerogen without chemical pretreatment. The previous ESR method [11,13,14] employed in our laboratory for the determination of the VO^{2+} concentration in geological materials utilized the standards prepared from a pulverized single crystal of $(NH_4)_2SO_4$ (as an isomorphous diamagnetic compound) containing Cu^{2+} as a paramagnetic impurity. The Cu^{2+} concentration of the $(NH_4)_2SO_4$:Cu^{2+} standard was determined by spectrochemical analysis (e.g. by employing atomic absorption spectrometry). In addition, the presence of multiple hyperfine lines in the ESR spectrum of both VO^{2+}, within the geological amorphous matrix, and Cu^{2+}, within the polycrystalline standard, requires a double integration of their entire spectra. The absolute error of measurement involving the spectrochemical determination of the Cu^{2+} content of the $(NH_4)_2SO_4$:Cu^{2+} standard, recording the spectrum and critical double integration processing of the entire complex spectra was estimated to be $> \pm 50\%$, which is quite high for the ESR technique.

While the above method is conceptually correct, one of its major disadvantages is that the ESR spectrum of Cu^{2+} is different from that of VO^{2+}. Namely, as Calas [15] pointed out for the quantitative estimation of paramagnetic species in the test sample by ESR, it is critical to refer to a standard having similar ESR characteristics as the test sample in order to obtain the correct estimation. In other words, in the ESR determination of the VO^{2+} concentration in the geological sample it is desirable to use a standard containing VO^{2+} (which has an ESR spectrum very similar to that of the particular geological sample) instead of Cu^{2+} (or any other paramagnetic metal) ion. This approach will eliminate many difficulties in consideration. For these reasons, the determination of VO^{2+} in geological samples by this method using the $(NH_4)_2SO_4$:Cu^{2+} standard was abandoned by our laboratory. There is, therefore, the need for a new method that utilizes the VO^{2+} standard. This communication describes a new method that, in principle, is quite similar to the sample interchange method of Premović [13] and

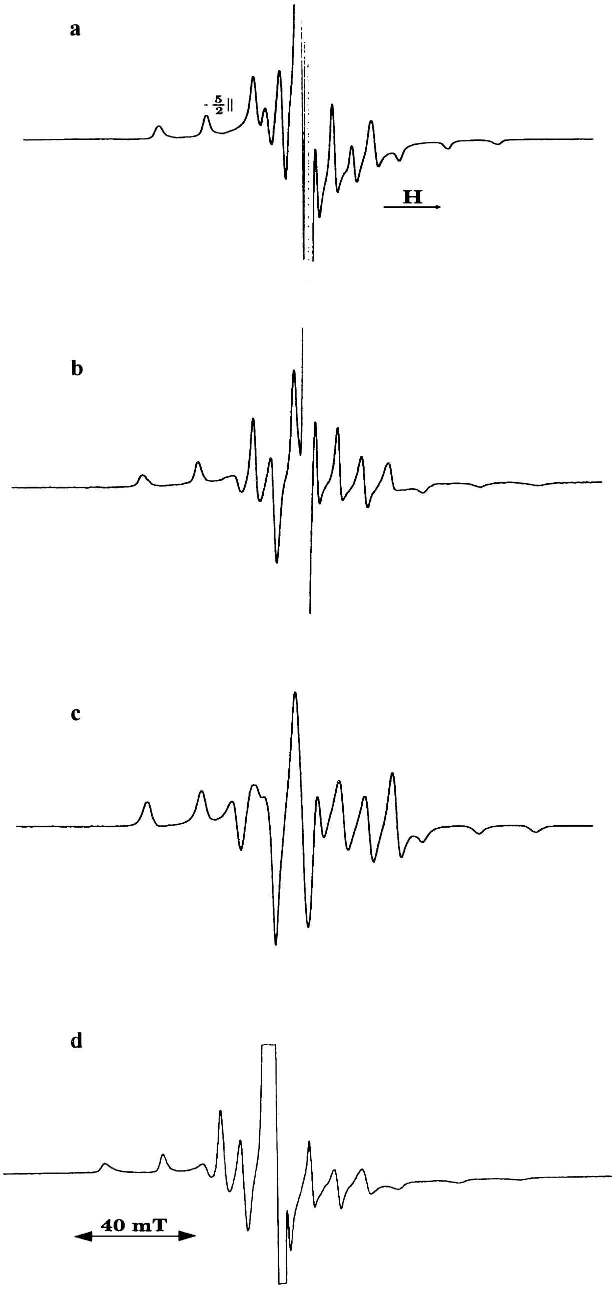

Fig. 1. First derivative, room temperature, anisotropic ESR spectrum of: (a) the La Luna kerogen enriched with VO^{2+}–P; (b) a standard (the glycerol/Kostolac lignite mixture) containing 1000 ppm of VO^{2+}; (c) initial glycerol solution containing 8000 ppm of VO^{2+}; and (d) the insoluble organic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

Premović et al. [11,14]. The method has been tested with samples of sedimentary kerogens and asphaltenes (Table 1). These materials were selected because their relatively high vanadium (V) content ranges from 600 up to 3000 ppm. This 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 the Kentucky coal sample.

2. Experimental

2.1. Samples

In order to demonstrate the applicability of this method, we used ESR to determine the VO^{2+}–P contents of two kerogen samples (11-16x 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 the Kentucky coal (Providence mine, KY, USA).

2.2. Electron spin resonance analysis

The ESR measurements were performed on finely ground powders of kerogen/asphaltene samples that were transferred to an ESR quartz tube. 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.

2.3. Emission 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 [16].

2.4. Isolation of kerogen/asphaltene

The procedure for isolation of various organic fractions of bituminous rocks, asphalts and coals and analysis has been presented in previous publications [4,11,17].

3. Results and discussion

In the new method employed, the VO^{2+} concentration is given by the following equation

$$[\mathrm{K}] = CA_{\mathrm{k}}/A_{\mathrm{st}}\rho_{\mathrm{k}}/\rho_{\mathrm{st}}[\mathrm{ST}]$$

where k indicates the kerogen sample and st indicates the standard, A is either the intensity (the ESR line height) or integrated area under the first derivative of the corresponding ESR line and ρ is the density. 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 first by dissolving known amounts of $VOSO_4 \cdot 5H_2O$ in a solution containing 1.5 ml of concentrated H_2SO_4 and 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

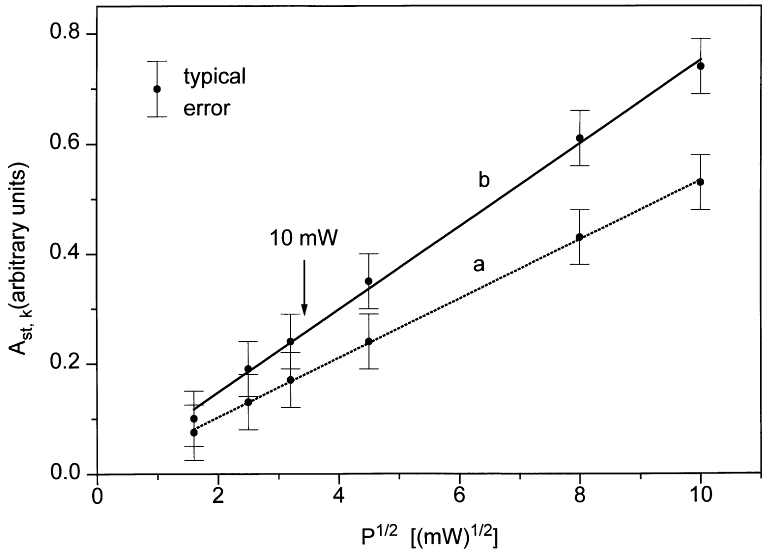

Fig. 2. Saturation behavior of the $-5/2\|$ VO^{2+} resonance line of: (a) a standard containing 1000 ppm of VO^{2+}; and (b) the La Luna kerogen.

samples that have different dielectric properties or surfaces. The above glycerol–VO^{2+} solution has a high dielectric constant (56 D) and it cannot be used as a reliable comparison of relative VO^{2+} concentrations of kerogen. For this reason, standards were prepared by mixing or diluting the glycerol VO^{2+} solution with lignite (or, of course, any kerogen-like material containing no VO^{2+}) to the desired VO^{2+} concentration. Preparing this mixture (hereinafter glycerol/lignite) has the effect of maintaining the dielectric medium of standards close with respect to the kerogen samples, thus keeping the *Q* similar. Standards prepared by mixing the glycerol VO^{2+} solution and lignite (using a vibrating mill: Perkin–Elmer), covered the range of 100–1000 ppm of VO^{2+}. Lignite used in these standards was the Kostolac coal (Serbia) which contains no VO^{2+}.

VO^{2+}–P have characteristic anisotropic ESR spectra. Anisotropic ESR spectra of VO^{2+}–P in the kerogen fractions of sedimentary rocks studied were similar to that of the La Luna kerogen (Fig. 1a). In general, these spectra gave a 16-line anisotropic pattern, due to interaction of the ^{51}V nucleus with its unpaired electron, and displayed parallel and perpendicular features characteristic of polycrystalline (amorphous) samples. A sharp intense peak near $g = 2.003$ is assigned to polyaromatic paramagnetic species that are always present in the kerogen materials [18].

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

Fig. 1 illustrates the anisotropic ESR spectrum of a standard containing 1000 ppm of VO^{2+} (Fig. 1b) and a solution of $VOSO_4 \cdot 5H_2O$ dissolved in H_2SO_4/H_2O system that was used in preparing the glycerol solution (Fig. 1c). The anisotropic spectrum is typical of those previously reported for VO^{2+} in powder (polycrystalline) solids (b) or extremely high-viscous liquids (c) [19]. 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 as a reliable comparison of relative VO^{2+} concentrations of both standards and kerogen samples. Consequently, such a comparison requires an integrated area. 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, only a narrow part of the VO^{2+} spectrum needs to be recorded. For this purpose, we select 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 line width and line shape similar and to minimize the interference from both neighboring 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 (P.I.P, 20 years) we have found that the anisotropy of the ESR parameters of VO^{2+} in various kerogens has little or no effect on line width and line shape of the $-5/2$ line.

In order to obtain maximum sensitivity it is necessary to record a spectrum at a high power level. However, at high power saturation is possible. 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 La Luna kerogen samples (Fig. 2). The linear relationship shows that it is safe to perform quantitative work at the power of 10 mW employed for these measurements.

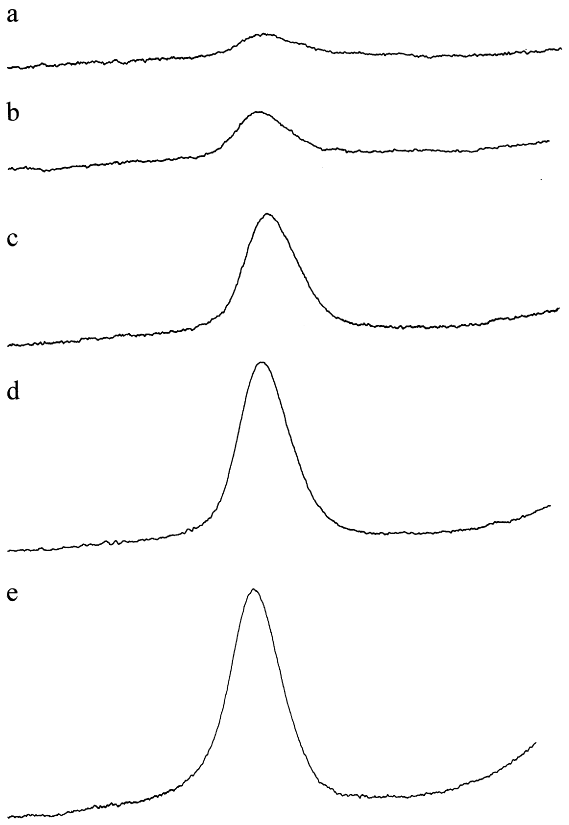

Fig. 3. The $-5/2\|$ VO^{2+} resonance line of the glycerol/Kostolac lignite mixture for the following concentrations of VO^{2+}: (a) 100 ppm; (b) 250 ppm; (c) 500 ppm; (d) 750 ppm; and (e) 1000 ppm.

In order to check the repeatability, we plotted the integrated area of the $-5/2$ line (vs. days) for five standard samples containing 1000 ppm of VO^{2+} (by the above-described procedure) each prepared on different days (the plot is not shown). A scatter of points was obtained averaging to a straight line (parallel to the day axis) with a deviation of $<5\%$. These results indicate 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 the VO^{2+} standards showed that after several weeks no oxidation had occurred. Typical results of the ESR examination show that after six weeks of exposure of the standards to air, their VO^{2+} concentrations were virtually unchanged from the initial value. A split 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 standards had densities of anywhere between 0.50 and 0.90 g cm^{-3} and appropriate corrections were made.

Fig. 3 shows a series of the $-5/2$ 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. Fig. 4 shows the linear plot obtained where the 100–1000 ppm concentrations ranges are covered. Using this plot as the calibration curve, a number of kerogen samples were recorded for the VO^{2+} spectrum and the integrated $-5/2$ line areas were measured in the manner described to obtain the concentration of VO^{2+} in the kerogen samples.

Table 1 lists the kerogen samples for which the VO^{2+}–P determinations have been made. The calibration curve shown in Fig. 4 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

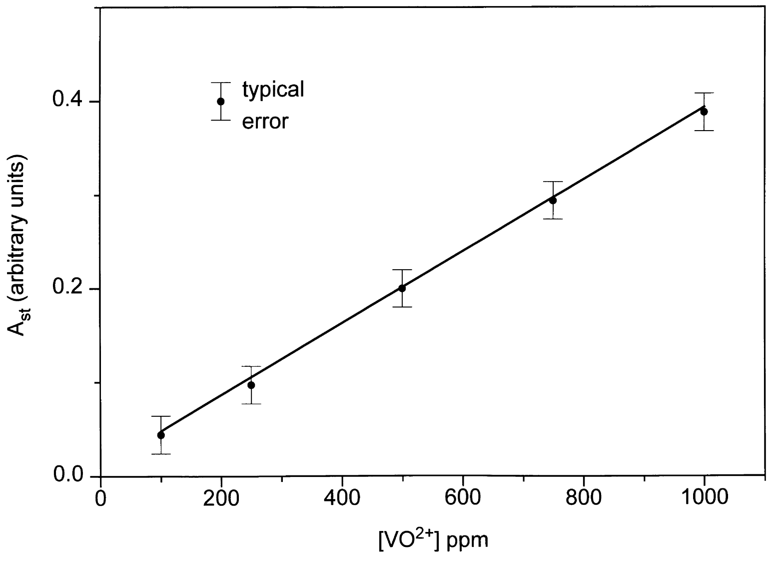

Fig. 4. The glycerol/Kostolac lignite mixture as a standard for the VO^{2+} concentrations range from 100 to 1000 ppm.

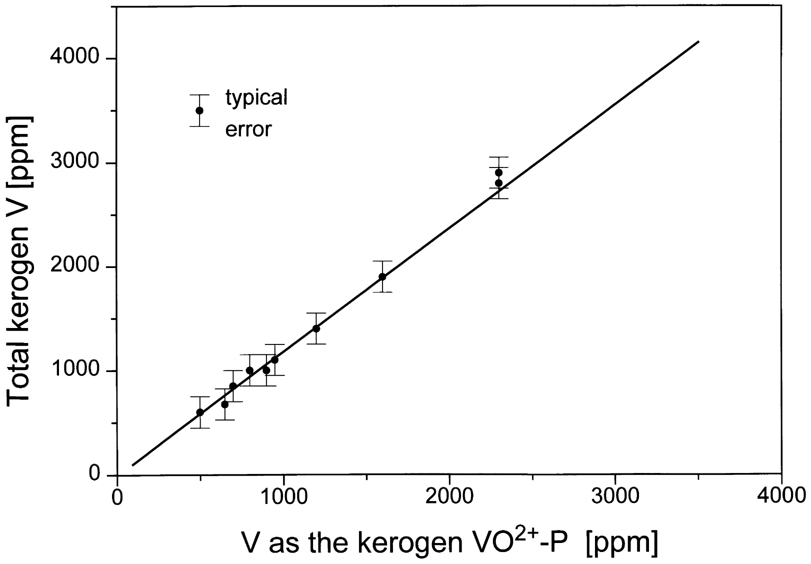

Fig. 5. V as the kerogen VO^{2+}–P vs. total kerogen V of the kerogen samples studied.

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 and the use of more than one kerogen sample in each case. We found that the repeatability 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. VO^{2+}–P are assumed to be the only VO^{2+} species present in each sample. While these are dominant species in sedimentary bitumens [2], very little is known about those VO^{2+} species incorporated into the kerogen framework [4]. Occasionally, ESR spectrum of VO^{2+} non-porphyrins (VO^{2+}–non-P) is noted in the kerogen spectra [16,20]. The presence of these VO^{2+}–non-P, however, could not affect in anyway the determination of VO^{2+}–P in a particular kerogen sample.

It is also assumed that 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 that are grossly different in structures from (extractable) alkyl VO^{2+}–P (say, polyaromatic VO^{2+}–P structures) then their ESR spectra should appear quite different [11]. Discussion of this point is, however, beyond the scope of this report.

The use of the glycerol/lignite mixture as a standard is, however, 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, we dilute the particular kerogen (exceptionally enriched with VO^{2+}–P) with the Kostolac lignite to fit the range of 800–8000 ppm. Therefore, Table 1 also lists a number of sedimentary kerogens having the VO^{2+}–P content higher than 8000 ppm. The calibration curve shown in Fig. 4 was also used in obtaining these results.

Fig. 5 depicts a plot of V (as VO^{2+}–P) of the kerogen samples against total V as obtained spectrochemically, Table 1. These results support the view that the most of V ($>80\%$) exist as the kerogens VO^{2+}–P recognized by ESR [11].

An essentially similar procedure was applied to the asphaltene samples of the floating asphalts from the Dead Sea basin. From our set of VO^{2+} standards we estimate the VO^{2+}–P concentrations of the floating asphalts to be about 1000 ppm, while the VO^{2+}–P contents of their asphaltene fractions is considerably higher, Table 1.

Finally, our method of analysis was extended to VO^{2+}–non-P species associated with the organic insoluble fraction of the Kentucky coal sample containing a relatively high concentration of V (675 ppm) (Table 1). Fig. 1d shows the complete ESR spectrum of this fraction. 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 to be as VO^{2+} (Table 1). Thus, the proposed method for the determination of VO^{2+}–P in various organic fractions of various bituminous rocks is capable 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 study 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 VO^{2+} content and type in their various organic fractions. In addition, studies of this type should allow determination of the concentration and thus the ratio of VO^{2+} incorporated into inorganic (predominantly clay) fraction [13] to that associated with organic fraction of sedimentary rock, thereby enhancing investigations of paleo-environmental preferential enrichment of both VO^{2+} and VO^{2+}–P [17]. These measurements should allow determination of the general paleo-environment of formation of bituminous sedimentary rocks (e.g. marine vs. terrestrial) [20].

Acknowledgements

We are thankful to both the IRD (previous ORSTOM) Institution (France) and Ministry of Science and Technology (Serbia) for the support of this work. Funding support from le Ministere francais de l'Education National, de l'Enseignement Superieur et de la Recherche to P.I.P. for his stay at Universite Pierre et Marie Curie (Paris) is gratefully acknowledged. We are also indebted to Drs J.Clayton (the Denver/Powder rocks), F. Baudin (the Akkuyi rocks), J.C. Hower (the Kentucky coal), A. Sandler (the floating asphalts) and the late V. Davidović (the Kostolac lignite) for providing the geological samples.

References

[1] Treibs A. Annales des Chemie 1934;509:103.
[2] Baker EW, Palmer SE. In: Dolphin D, editor. Porphyrins, 1. New York: Academic Press, 1978. p. 458.
[3] Barwise AJG. Energy and Fuels 1990;4:647.
[4] Premović PI, Jovanović LjS, Nikolić GS. Organic Geochemistry 1996;24:801.
[5] Lewan MD. Geochimica et Cosmochimica Acta 1984;48:2231.
[6] Hodgson GW, Baker BL, Peake E. In: Nagy B, Colombo U, editors. Fundamental aspects of petroleum geochemistry, Oxford: Elsevier, 1967. p. 177.
[7] Holden PN, Sundararaman P, Gaffey MJ. Geochimica et Cosmochimica Acta 1991;55:3893.
[8] O'Reilly DE. Journal of Chemical Physics 1958;29:1188.
[9] Premović PI. Proceedings of the Seventh Yugoslav Conference on General and Applied Spectroscopy, Serbian Chemical Society, 1978. p. 11.
[10] Hocking PB, Premović PI. Geochimica et Cosmochimica Acta 1978;42:359.
[11] Premović PI, Pavlović MS, Pavlović NZ. Geochimica et Cosmochimica Acta 1986;50:1923.
[12] Nissenbaum A, Aizenshtat Z, Goldberg M. In: Douglas AG, Maxwell JR, editors. Advances in Organic Geochemistry 1979, Oxford: Pergamon Press, 1980. p. 157.
[13] Premović PI. Geochimica et Cosmochimica Acta 1984;48:873.
[14] Premović PI, Jovanović LjS. Chemical Papers 1991;45:433.
[15] Calas G. Spectroscopic methods in mineralogy and geology. In: Hawthorne FC, editor. Reviews in mineralogy, Mineralogical Society of America, 1988. pp. 513 Washington, D.C.
[16] Marinkovic M, Vickers T. Applied Spectroscopy 1971;25:319.
[17] Premović PI, Nikolić ND, Pavlović MS, Jovanović LjS, Premović MP. European coal geology and technology, 125, 1997. p. 273 Geological Society Special Publication.
[18] Premović PI. In: Schidlowski M, editor. Early organic evolution: implications for mineral and energy resources, Berlin: Springer, 1992. p. 241.
[19] Goodman BA, Raynor JB. In: Emeleus HJ, Sharpe AG, editors. Advances in inorganic chemistry and radiochemistry, Advances in inorganic chemistry and radiochemistry, 13. New York: Academic Press, 1970. p. 135.
[20] Premović PI, Tonsa IR, Pavlović MS, López L, LoMonaco S. Fuel 1998;77:1769.