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Trace metals characterisation of Niger delta kerogens

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Abstract

Ten trace elements were determined by graphite furnace atomic absorption spectrometry (GFAAS) in fifteen kerogen samples from five wells obtained from the paralic sequence Agbada formation in the Niger delta basin. The concentrations of the elements (As, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb and V) determined ranged from 0.374 to 667.340 ppb with a mean value of 77.434 ppb (%RSD < 5) for the kerogen samples analysed. These metals were selected for analysis for exploration and environmental considerations. The concentrations of the metals in the kerogen were in excess of those obtained for the Niger delta oils except for Ni and V, which followed the expected trend (i.e. there should be more trace metals in the kerogen than in the oil since kerogen is a precursor of petroleum). The results indicate that concentrations of the metals decrease with depth. Also, concentrations of the metals decrease with increase thermal maturity of the kerogens. Although, this trend could be altered in horizons with low organic richness. The ratios calculated from the metals are comparable with those obtained for the Niger delta oils and indicate that the kerogens were derived from terrestrial origin. Kerogens of similar organic matter type from different geographic sedimentary basins can be distinguished by the fingerprints of their metal contents.

Keywords: Kerogen; GFAAS; Origin

1. Introduction

The Niger delta contains post-Cretaceous sediments that become progressively younger towards the south west. It is a mature petroleum province and covers an area of 75,000 km^2 in southern Nigeria. The lithologies represent a variety of environments, ranging from marine through deltaic and estuarine with coastal swamps, to lagoonal and even fluvio-lacustrine.

The Niger delta sedimentary sequences consists of three litho-stratigraphic units consisting, in order of succession, the Akata formation, which is massive continuous shale deposited under marine conditions, the Agbada formation, a paralic sequence of inter-bedded sand and shale laid down in transitional environment and the Benin formation, mainly fluviatile gravels and sands [1,2]. The main hydrocarbon habitat in the Niger delta is the Eocene to Pliocene sandstone reservoirs in the Agbada formation [2].

Studies on organic geochemistry of Niger delta oils and rocks are fairly well documented in the literature [3–9]. Many reports on geochemical evaluation of this sedimentary basin indicated that the organic matter of the Niger delta to be mainly type II/III and type III [5,6,10–13], which indicates substantial terrestrial organic matter input. It has also been indicated that the oils from the Niger delta are from one source type, such that one superfamily of oils occurs in the delta [14,15]. This superfamily of oils is characterized by abundant of higher plant input as evident with high terrestrial biomarkers like oleanane, C29 steranes and high pristane/phytane ratio [6,7,10,12].

Trace metal contents of oils and kerogens are of significant importance in the determination of origin of oil, type

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of organic matter, and maturity of oils and organic matter. Barwse [16] used trace metals; particularly nickel and vanadium to classify oils of different origins, thermal maturity and depositional environment were also predicted. A few papers have discussed the trace metal contents of Niger delta oils [17–21]. In all these papers, successive oil–oil correlations were made with trace metals. The ratios of the metals were used to predict the environment of deposition and thermal maturity of the oils. However, no particular study was devoted for investigation of trace metal contents of Niger delta kerogens. Because kerogen is the direct precursor of petroleum and constitutes the bulk of organic matter in source rocks, it is expected that the trace metal contents of kerogen should be reflective of those in the oil. Therefore, characterisation of Niger delta kerogens in terms of their trace metal contents becomes very important. In this study, we characterize the Niger delta kerogens for their trace metal contents. We adopted a method of analysis that we recently used for the determination of metal contents of oils to afford a basis for comparison.

2. Experimental

Fifteen shale samples from five wells from the paralic Agbada formation in the Niger delta were analysed (Fig. 1). The samples were recovered in the depth range of 8005–11580 ft (2440–3530 m). Soxhlet extraction of the rock samples with a mixture of toluene and methanol for removal of soluble organic matter (bitumen) was initially carried out. Kerogen was isolated from the rock samples by crushing it to fine powder and treated with HCl for removal of carbonates and HF to destroy the silicates, and reduction with lithium aluminium hydride for removal pyrites. The kerogen was separated from the remaining residue by gravity separation. The resulting kerogen has ash content of about 5%.

The kerogen samples were prepared for analysis by digestion with HNO_3, $HClO_4$ and HF. Standard solutions of the elements with an analyte concentration of 1000 ppm were used. The stock solutions were diluted with deionized distilled water to prepare each working solution for calibration.

Graphite furnace AAS analysis of the replicate digested samples was performed using A Schimadzu model GFA-EX7 graphite furnace atomizer with a Schimadzu AA-6800 atomic absorption spectrophotometer. A deuterium-arc lamp was used for background correction. An aliquot of the digested sample was injected into the graphite furnace containing pyrolytic coating graphite tube by using a Schimadzu ASC-6100 auto sampler. The analysis was performed according to the Schimadzu manual.

3. Results and discussion

The trace element contents of the kerogen samples are summarised in Table 1. The concentrations of trace metals in the kerogen samples varied from 0.718 to 667.340 ppb with an average of 77.434 ppb. Iron is the most abundant among the trace metals determined. Among the biophile metals (i.e. metals of proven association with organic matter), Ni was the most abundant, followed by V and Co in that order. This is in a good agreement with distribution patterns of these metals in Niger crude oils [19–21].

The concentrations of the trace metals determined were compared with those obtained for Niger delta oils, which were determined using the same analytical technique (GFAAS), which had been reported [21]. As stated earlier, since kerogen constitutes the bulk of organic matter in source rocks, it is expected that trace metals should be more abundant in kerogens than in crude oils.

Arsenic concentration ranged from 0.718 to 138.618 ppb with a mean value of 56.755 ± 43.106 ppb. Cadmium concentration ranged from 5.592 to 37.606 ppb with a mean value of 14.768 ± 8.883 (Table 1). These two elements are rarely determined in oils and kerogens, yet they are of environmental importance in terms of pollution. Arsenic, apart

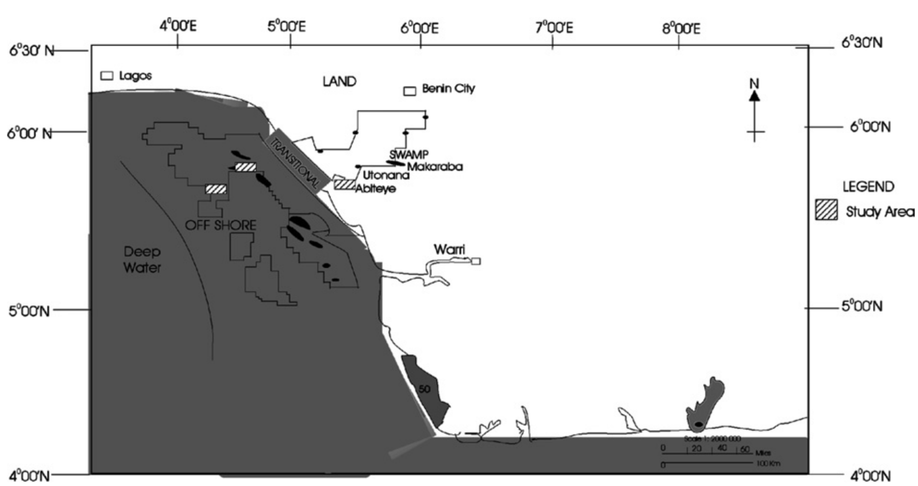

Fig. 1. Map of Niger delta showing location of study.

Table 1
Elemental composition of Niger delta kerogen (in ppb)

Sample	Depth (ft)	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V
A3	8005	62.128 ± 0.013	13.288 ± 0.0.022	3.64 ± 0.001	33.555 ± 0.021	24.362 ± 0.003	590.001 ± 0.031	43.897 ± 0.017	15.606 ± 0.0.006	168.384 ± 0.014	16.829 ± 0.003
A4	8390	27.891 ± 0.001	12.032 ± 0.020	5.273 ± 0.002	20.39 ± 0.012	15.554 ± 0.002	608.982 ± 0.004	46.624 ± 0.028	1.367 ± 0.001	79.925 ± 0.021	10.749 ± 0.002
A8	11060	9.683 ± 0.008	14.327 ± 0.003	3.946 ± 0.002	2.722 ± 0.003	19.357 ± 0.008	310.668 ± 0.034	42.591 ± 0.051	37.801 ± 0.003	19.767 ± 0.006	10.094 ± 0.002
B1	10190	91.547 ± 0.001	5.592 ± 0.005	2.347 ± 0.001	3.734 ± 0.006	13.963 ± 0.000	308.146 ± 0.016	39.620 ± 0.059	5.982 ± 0.000	7.207 ± 0.002	10.000 ± 0.002
B2	10390	93.864 ± 0.022	9.309 ± 0.010	2.136 ± 0.001	7.451 ± 0.003	17.941 ± 0.001	593.852 ± 0.011	42.390 ± 0.024	7.407 ± 0.006	4.267 ± 0.000	12.900 ± 0.000
B4	10590	8.872 ± 0.003	6.283 ± 0.007	1.735 ± 0.000	3.691 ± 0.003	18.387 ± 0.009	295.282 ± 0.011	41.266 ± 0.030	5.177 ± 0.000	28.130 ± 0.001	9.112 ± 0.002
C4	10128	138.618 ± 0.031	24.756 ± 0.024	6.531 ± 0.001	26.488 ± 0.003	47.395 ± 0.004	667.340 ± 0.357	44.361 ± 0.098	18.217 ± 0.010	80.881 ± 0.001	9.252 ± 0.000
C5	10199	110.913 ± 0.022	22.434 ± 0.016	0.511 ± 0.000	2.496 ± 0.028	8.998 ± 0.001	283.184 ± 0.059	40.644 ± 0.000	2.733 ± 0.000	69.576 ± 0.005	9.065 ± 0.002
C7	10249	0.718 ± 0.000	7.741 ± 0.012	0.374 ± 0.000	1.587 ± 0.001	17.146 ± 0.001	562.313 ± 0.012	40.720 ± 0.099	2.551 ± 0.001	172.284 ± 0.021	8.228 ± 0.001
D4	9680	108.574 ± 0.002	6.475 ± 0.001	2.619 ± 0.001	13.279 ± 0.002	39.487 ± 0.006	612.987 ± 0.047	40.414 ± 0.021	9.200 ± 00.003	37.449 ± 0.008	9.626 ± 0.001
D5	10100	47.720 ± 0.009	19.244 ± 0.007	6.225 ± 0.000	26.139 ± 0.009	27.298 ± 0.001	602.167 ± 0.167	190.191 ± 0.063	9.731 ± 0.003	8.112 ± 0.000	12.620 ± 0.001
D8	11580	38.407 ± 0.003	11.404 ± 0.014	10.035 ± 0.000	13.689 ± 0.005	47.061 ± 0.001	605.728 ± 0.030	40.696 ± 0.026	21.451 ± 0.009	82.304 ± 0.010	14.491 ± 0.001
E1	9230	18.903 ± 0.006	9.259 ± 0.016	16.838 ± 0.000	9.545 ± 0.003	54.365 ± 0.001	582.215 ± 0.021	45.519 ± 0.008	23.060 ± 0.001	104.131 ± 0.016	10.749 ± 0.002
E2	9440	63.240 ± 0.005	37.606 ± 0.027	5.545 ± 0.001	11.290 ± 0.004	56.529 ± 0.002	606.853 ± 0.005	42.524 ± 0.063	14.528 ± 0.007	42.624 ± 0.008	13.462 ± 0.000
E3	9650	30.253 ± 0.006	21.768 ± 0.054	6.701 ± 0.001	11.796 ± 0.001	50.681 ± 0.007	589.797 ± 0.007	42.438 ± 0.075	12.707 ± 0.005	68.129 ± 0.003	11.170 ± 0.001

from being a toxic substance to the environment, it causes catalytic poisoning in the refining column. This baseline data will help in environmental impact assessment during oil exploration and exploitation.

Cobalt concentration ranged from 0.374 to 16.838 ppb, averaging 4.96 ± 4.21 ppb for all the wells (Table 1). This is in excess of concentrations in oils (2.60 ppb) from the Niger delta (Fig. 2). This is as expected since kerogen constitutes the bulk of organic matter in source rocks. It is expected that concentration of metals in kerogen should be more than in the corresponding oil.

Concentration of chromium in the samples ranged from 1.587 to 33.555 ppb, with an average of 12.52 ± 9.98 ppb (Table 1). This averaged concentration is also in excess of 3.92 ppb in oils from the Niger delta (Fig. 2).

Copper and manganese have concentration ranging from 13.963 to 56.529 and 39.620 to 190.191 ppb, with the mean values of 30.57 ± 16.709 and 52.26 ± 38.209 ppb respectively (Table 1). The values are much higher than values obtained for oils (6.82 and 3.51 ppb) respectively (Fig. 2).

Iron ranged in concentration from 283.184 to 667.340 ppb averaging 521.3 ± 140.423 ppb for the wells (Table 1). The oils analysed using the same method have averaged concentration of 83.19 ppb (Fig. 2). Iron had the highest concentrations in both the kerogens and oils. Studies by other workers [19,20] also showed the same distribution pattern. It then indicates that iron is most abundant transition metal in Niger delta organic matter.

Lead concentration ranged from 4.267 to 172.284 ppb with a mean value of 64.878 ± 53.093 ppb (Table 1). This averaged concentration is in excess of an averaged value (40.38 ppb) obtained for Niger delta oils that were determined using the same method of analysis (Fig. 2) [21]. This result is also consistent with the expected trend.

Concentration of nickel and vanadium ranged from 1.367 to 37.801 and 8.228 to 16.829 ppb, with the averaged values of 12.50 ± 9.773 and 11.22 ± 2.384 ppb respectively. These values are less than the averaged concentrations

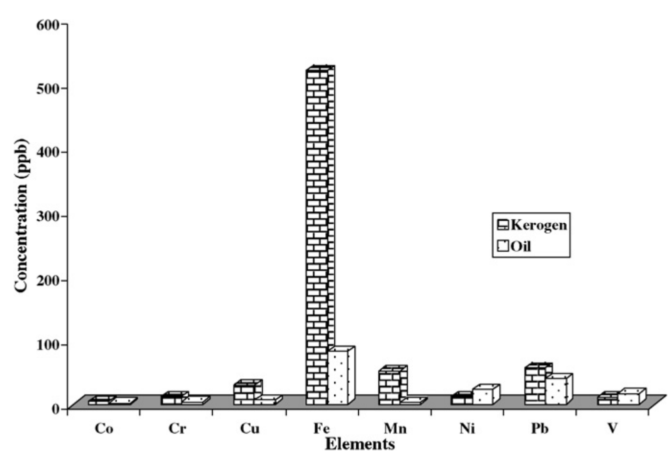

Fig. 2. Comparison of abundance of metal contents of kerogen and oil from the Niger delta.

obtained for Niger delta oils (24.25 and 16.8 ppb respectively) (Fig. 2). It appears that nickel and vanadium enrichment occurs in the oils relative to kerogens. The main source of these two metals in kerogens and crude oils is porphyrin complexes of these metals. If porphyrin metal complexes were the main source, it is then expected that the concentrations of Ni and V should be more in kerogen relative to oil. Higher enrichment in oils relative kerogens here could be a consequence of uptake of these metals during migration of the oils. Lewan and Maynard [22] stated that interstitial waters are the most likely source for enriched concentrations of vanadium and nickel. It then could be as a result of dissolution of these metals in the oils as they encounter interstitial waters during migration, which made the additional enrichment of these metals.

4. Trace metal ratios and bulk geochemical parameters

In the wells, concentrations of the metals decrease with depth (Tables 1 and 2). Highest concentrations of the metals are to be found in low maturity crude oils [16], as well as in biodegraded oils [20]. Thus, since crude oils are derived directly from kerogen, decrease in concentration with depth in the wells suggests increase in maturity of kerogens with depth as T_{max} values support this impression. However, there are anomalies in some wells. The anomalies are due to other factors. For example, irrespective of the depth, samples of higher thermal maturity will have lower metal contents. A typical example is well C where C5 has lower concentration of metals relative to C7 due to its higher thermal maturity of T_{max} of 569 °C. The high T_{max} value and low TOC value of sample C5 seem to be a puzzle. Initial Rock–Eval pyrolysis of this sample indicated T_{max} of 440 °C and TOC of 0.21 wt%, which we presumed was due to contamination. The samples were extracted with organic solvents to remove extractable organic matter including that from oil-based mud. The Rock–Eval pyrolysis of the extracted sample C5 yielded the results presented in Table 2. The issue of T_{max} of sample C5 being an analytical artifact does not arise because of the analytical protocol employed. Although, it has low TOC value but T_{max} (thermal maturity indicator) has a good and expected trend with the concentrations of the metals (Table 2). Since genetic potential of this sample indicates gas prone, this low organic matter concentration may be due to deposition under oxic conditions [23]. Although, this may not account for the high T_{max} value for this sample. Rock–Eval pyrolysis may not fully define the oil proneness of a source rock dominated by terrestrially sourced organic matter [24].

The trace metal contents show a good correlation with total organic carbon (TOC) percentage in whole rock sample from which kerogen was isolated. In samples with high TOC the concentration of most of the elements is low but the relationship is not linear. It seems the effect of thermal maturity predominates in cases where there are high TOC values and low T_{max} values; concentration of the metals is influenced by thermal maturity of the kerogen instead of its TOC.

Hydrogen index (HI) values for these kerogens ranged from 61 to 239 mg HC/g TOC, which are comparable to HI values obtained by other workers in the Niger delta [10,12,13]. These values are typical of type II/III and type III kerogens [10,12,25]. Genetic potential ($S1 + S2$) ranged from 0.50 to 4.48 mg/g. These values indicate that moderate source rocks with potentials for oil and gas [12,26] exist for nine samples especially those in wells B, D and E (Table 2). Other kerogens are more gas prone. Both HI and genetic potential do show any particular trend with the concentrations of the metals. Other Rock–Eval pyrolysis data notwithstanding, thermal maturity has strong influence on the concentrations of the metals.

Co/Ni ratios ranged from 0.104 to 3.857 (Table 2). Apart from sample A4, which has value of 3.857, these values are comparable with those obtained for Niger delta oils

Table 2
Ratios of transition metals and bulk geochemical parameters of kerogens from the Niger delta

Sample	Depth (ft)	Co/Ni	V/Ni	Fe/V	V/V + Ni	TOC	T_{max} (°C)	TTM	$S1 + S2$	HI
A3	8005	0.233	1.078	35.059	0.519	0.96	437	741.178	1.50	128
A4	8390	3.857	7.863	56.655	0.887	2.34	416	720.971	1.83	66
A10	11060	0.104	0.267	30.778	0.211	0.36	435	441.506	0.82	106
B1	10190	0.392	1.672	30.814	0.626	0.62	434	389.384	2.97	82
B2	10390	0.288	1.742	46.035	0.635	0.51	427	693.386	1.88	61
B4	10590	0.335	1.76	32.406	0.638	0.46	436	380.933	2.38	74
C4	10128	0.359	0.508	72.129	0.337	0.52	438	844.34	0.93	106
C5	10199	0.187	3.317	31.239	0.768	0.12	569	370.065	0.50	142
C7	10249	0.147	3.225	68.341	0.763	0.59	438	640.66	3.34	95
D4	9680	0.285	1.046	63.68	0.511	0.92	438	734.087	2.17	210
D5	10100	0.640	1.297	47.715	0.565	1.69	436	893.615	3.69	201
D8	11580	0.468	0.676	41.8	0.403	1.05	440	764.555	2.75	239
E1	9230	0.730	0.466	54.164	0.318	1.01	437	751.55	3.10	231
E2	9440	0.382	0.927	45.079	0.481	1.74	438	788.337	4.00	180
E3	9650	0.527	0.879	52.802	0.468	2.02	434	747.058	4.48	168

Note: TTM – total transition metals, TOC – total organic carbon, T_{max} – temperature of maximum hydrocarbon generation, HI – hydrogen index (mg HC/g TOC).

(0.023–0.420) of Akinlua and Torto [21]; 0.01–0.41 of Udo et al. [18] and 0.09–0.53 of Nwachukwu et al. [20]. The T_{max} values of these kerogens, which are mostly greater than 430 °C indicates that the kerogen samples are mature except sample A4. It then suggests that Co/Ni ratio decreases with thermal maturity. Co/Ni ratios are generally less than 1 for the matured kerogens (Table 2). Fe/V ratio is much greater than 1 (30.778–72.129) in all the wells (Table 2). The values are in a good agreement with those obtained for oils from the Niger delta [19–21]. V/Ni ratios ranged from 0.267 to 7.863 (Table 2).V/Ni ratio increases with decrease in thermal maturity (Table 2) [18]. However, it seems that the TOC also has influence on this ratio. The high values in these samples are either as a result of low maturity or low TOC. For example, sample A4 has low T_{max} of 416 °C (low maturity) and high V/Ni value of 7.863, C5 has low TOC value of 0.12 and high V/Ni value of 3.317. This suggests that V/Ni increases with decrease in maturity and low organic richness. V/V + Ni ratios in the kerogens varied from 0.211 to 0.887 (Table 2). These low values are in consonant with low V/V + Ni values obtained for the Niger delta oils [19–21]. These values are generally less than 1, which is consistent with the values for source rocks derived from terrestrial origin [27], which is characteristic of the Niger delta.

The relative distribution of the metals in the kerogens in each well is similar especially in wells B, C and E. (Figs. 3a–3e). These fingerprints of the elements in the kerogen from a well are quite distinct from the fingerprints from another well. Metal contents of kerogens can be used to distinguish kerogens of different geographic origins. Though, the organic matter in the Niger delta and in the Cambay basin, India are similar (i.e. type III and type II/III kerogens) except that Cambay basin has two petroleum systems. The organic matter from these similar basins can be distinguished by the fingerprints of metals in their kerogens. The fingerprints of the metals in kerogens from Niger delta (Fig. 4) are quite different from the fingerprints of the metals in kerogens from North Cambay basin, India [28] (Fig. 5). Iron is the most abundant element in the Niger delta kerogen while chromium is most abundant element in the North Cambay, India kerogen. This indicates that the distribution of the trace metals in kerogen can be used to distinguish kerogens from different geographic origins.

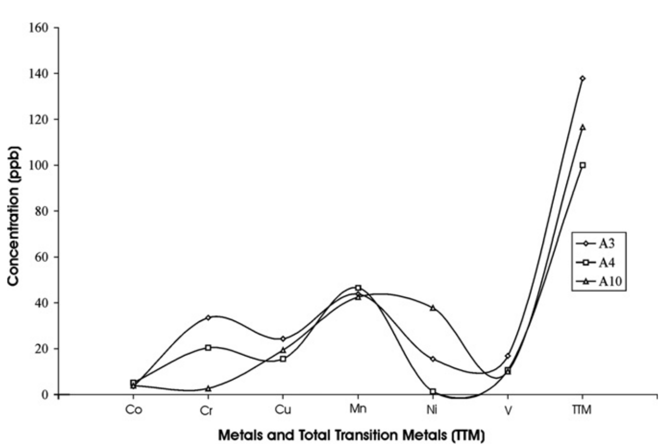

Fig. 3a. Trace metal distribution patterns in well A.

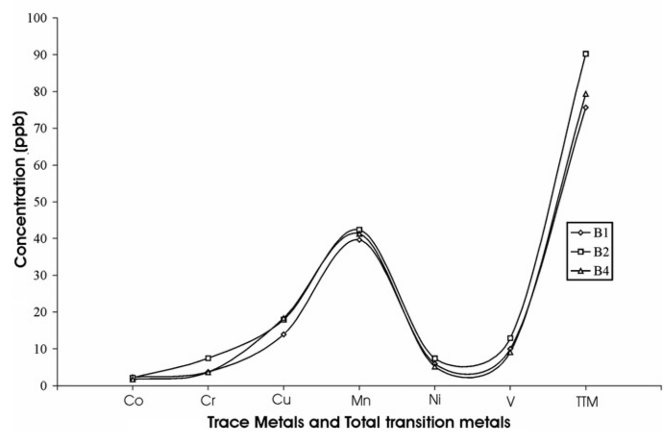

Fig. 3b. Trace metal distribution patterns in well B.

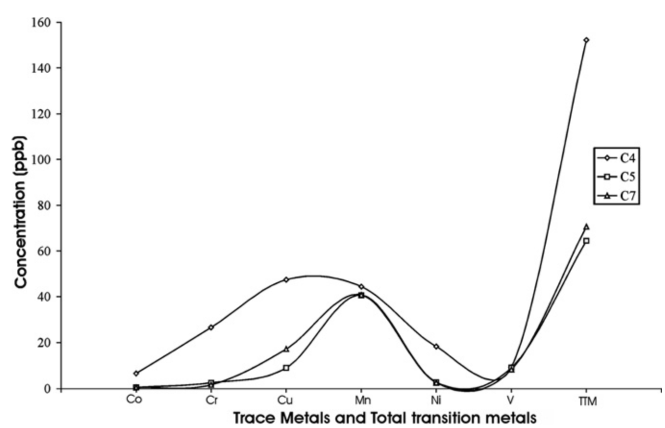

Fig. 3c. Trace metal distribution patterns in well C.

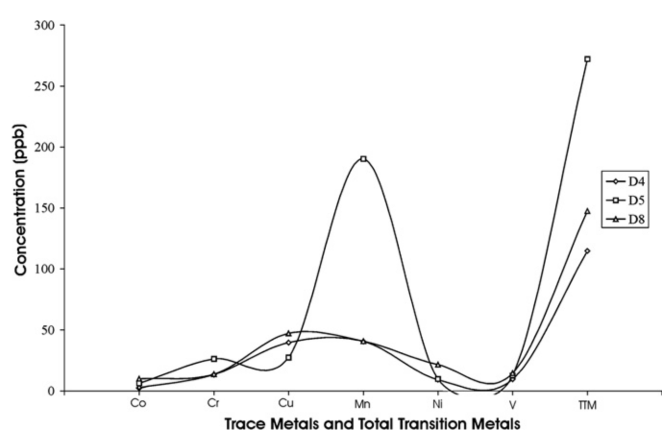

Fig. 3d. Trace metal distribution patterns in well D.

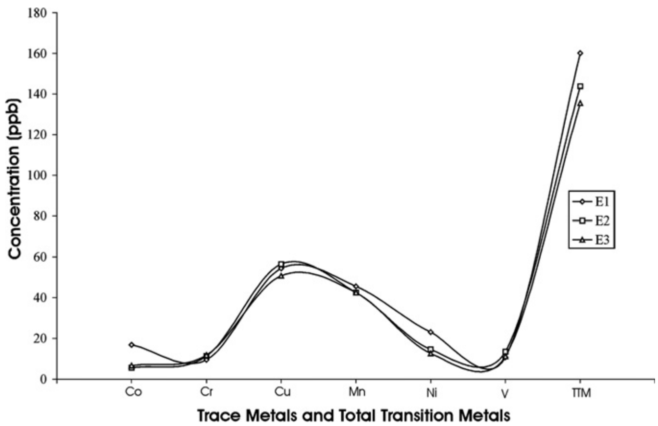

Fig. 3e. Trace metal distribution patterns in well E.

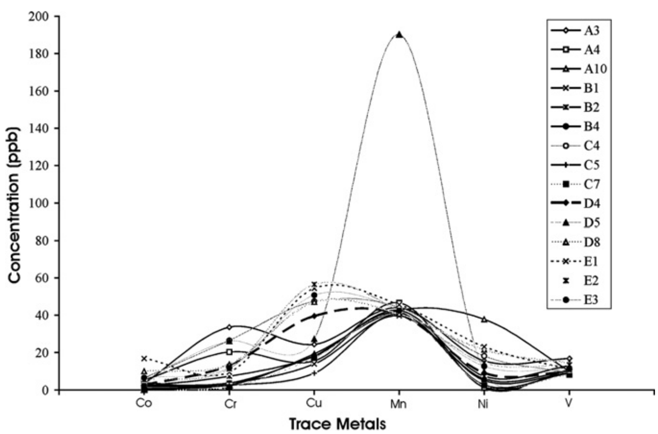

Fig. 4. Trace metals fingerprints of kerogens from the Niger delta.

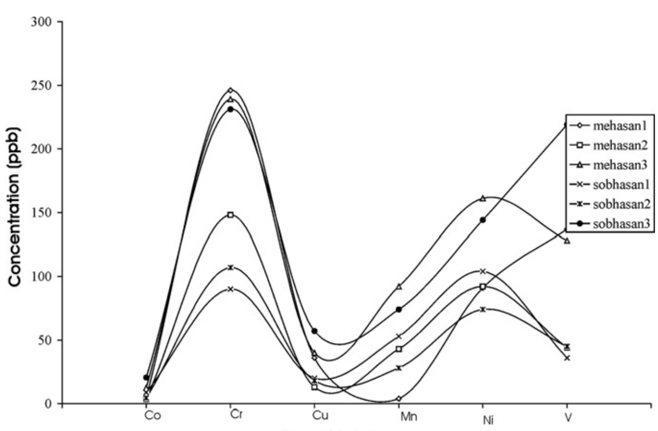

Fig. 5. Trace metals fingerprints of kerogens from the North Cambay, India (Data from Dekawar and Sharma, 2000).

5. Conclusions

The determination of some trace metals in kerogen samples from five wells from the Niger delta by graphite furnace atomic absorption spectrometry shows that the concentrations of the metals are relatively low. The low concentration values are known to be characteristic feature of organic matter of strong terrestrial input. The concentrations of the metals in the kerogens are in excess of those obtained for the Niger delta oils, which is in a good agreement with the expected trend.

Concentrations of the metals decrease with depth. Trace metals concentrations also decrease with increase thermal maturity. However, this trend could be altered in horizons with low organic richness. Non-linear correlation exists between the TOC and the concentration of the metals. The ratios of the metals are comparable with ratios obtained for the Niger delta oils. The fingerprints of the metals can be used to distinguish one well from another and kerogen from sedimentary basin from another.

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