Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 180, No. 2 (1994) 285–294

A COMPARISON OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS AND INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY FOR TRACE ELEMENT DETERMINATION IN PETROLEUM GEOCHEMISTRY

R. H. FILBY,* S. D. OLSEN**

**Department of Chemistry and Nuclear Radiation Center, Washington State University, Pullman, WA 99164 (USA)*
***Rogaland Research Institute, P.O. Box 2503, 4004 Stavanger (Norway)*

(Received January 4, 1994)

INAA and ICP-MS methods for determining trace elements in crude oils, oil fractions and sourcerock bitumens are compared. Results for a wide variety of crude oil types show good agreement for many elements for which the two techniques are suited and which are geochemically important (e.g., Ni, V, Fe, Se, As, etc.). For some other elements, the two techniques are complementary (e.g., B, Be, Cd, Br). The advantages and disadvantages of INAA and ICP-MS in geochemical exploration programs are reviewed and practical examples presented.

Trace elements are minor constituents of virtually all crude oils and their geochemical significance has been the subject of considerable study.[1,2] For most crude oils, Ni and V are the most abundant elements and occur primarily as metalloporphyrins, predominantly etio or deoxophylloerythroetio (DPEP) porphyrins with small amounts of other structural types, e.g., benzo, tetrahydrobenzo.[1,2] The Ni and V porphyrins have been used extensively as biomarkers in maturation, depositional environment, and correlation studies.[1,3-6] In common with other biomarker methods, the use of metalloporphyrins for oil-oil and oil-source rock correlation studies is time-consuming and expensive. Several studies have reported the use of trace element abundances (or elemental ratios) to correlate oil families and oils to source rocks, even though, except for Ni and V, the molecular species of the trace elements are not known.[2,7-10] The principle involved is that the bitumen generated from kerogen catagenesis in a source rock inherits a trace element distribution pattern from the parent kerogen or from mineral-kerogen interactions during catagenesis. Subsequent migration of the bitumen from the source rock to a trap or reservoir preserves this fingerprint and makes oil-oil and oil-source rock correlations feasible.

Instrumental neutron activation analysis has been used in several correlation studies using trace elements[7,8,11-12] primarily because the method is non-destructive and has adequate sensitivity for a range of geochemically important elements, e.g., Ni, V, Se, Br and Fe.[10] An alternative technique, ICP-MS,[13] has the potential to determine more elements with lower detection limits than INAA. The work reported here compares INAA and ICP-MS for analysis of crude oils and related geochemical materials.

Experimental

Sample Selection: For the intercomparison study, six crude oils were chosen to represent a range of compositions from light oils with low trace element contents and high API gravities to heavy, low API gravity, oils with high Ni and V contents. These oils were supplied by Conoco, Inc., Ponca City, OK. The oils were analyzed by INAA and ICP-MS without further treatment. SRM 1634b Fuel Oil (NIST) was also analyzed by ICP-MS. A source rock bitumen from the New Albany shale (Indiana) was also analyzed.

Elsevier Science S. A., Lausanne
Akadémiai Kiadó, Budapest

Neutron Activation Analysis: The INAA method used was similar to that of JACOBS and FILBY.[14] Samples (0.1-0.3 g) were weighed into 2/5 dram polyethylene irradiation vials which were sealed and then doubly encapsulated in 2 dram polyvials. Irradiation conditions and nuclides used are shown in Table 1.

Table 1
Irradiation conditions and nuclides measured by INAA

Nuclide measured	Irradiation time at 5x10^{12} n/cm^2/sec	Ge(Li) spectroscopy aquisition time
^{28}Al, ^{27}Mg, ^{51}Ti ^{52}V	5 min	180s
^{38}Cl, ^{56}Mn	5 min	1000s
^{76}As, ^{82}Br, ^{72}Ga, ^{42}K ^{140}La, 99mTc (for Mo), ^{24}Na, ^{153}Sm	8 hr	4000s
^{131}Ba, ^{141}Ce, ^{60}Co, ^{51}Cr, ^{152}Eu, ^{59}Fe, ^{181}Hf, ^{58}Co (for Ni), ^{86}Rb, ^{124}Sb, ^{46}Sc, ^{75}Se, ^{85}Sr, ^{233}Pa (for Th), ^{65}Zn	8 hr	40,000s

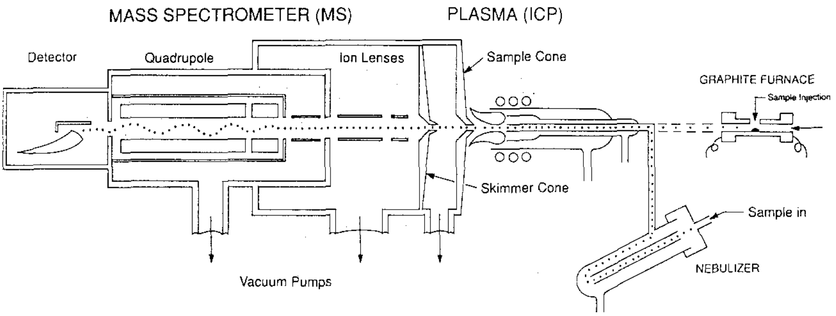

Figure 1.
Schematic diagram of ICP-MS spectrometer.

Standards used were NIST SRM 1632a (Coal), SRM 1633a (Fly Ash), SRM 1571 (Orchard Leaves). Gamma-ray spectra were accumulated on a Ge(Li)-ND6700 spectrometer system, and data reduction was performed on a MicroVAX computer.

ICP-MS Analysis: Approximately 1.5g of oil was accurately weighed in a polyethylene container and 50 µL of a 15 µg/g In internal standard (in xylene) added. Ultrapure xylene (Merck AR) was added to give a total weight of 15.0g. The xylene solution was mixed thoroughly and stored in a closed polyethylene bottle. A VG Plasma Quad PQ2+ ICP-MS system was used and Ar (99.998%) was used as

Table 2
Instrument conditions for ICP-MS analysis

Variable	Value	Variable	Value
Plasma RF power	1.8 kW	Nebulizer oxygen flow	0.11 L/min
Reflected power	25 watts	Spray chamber	double pass
ID of torch injector	1.5 mm	Spray chamber temperature	-15°C
Coolant argon flow	17 L/min	Sample uptake rate	0.5 ml/min
Auxiliary argon flow	1.2 L/min	Pt sampling cone orifice	0.75 mm
Nebulizer argon flow	0.85 L/min	Pt skimmer cone orifice	1.0 mm
Upgraded interface		Resolution	0.7 amu

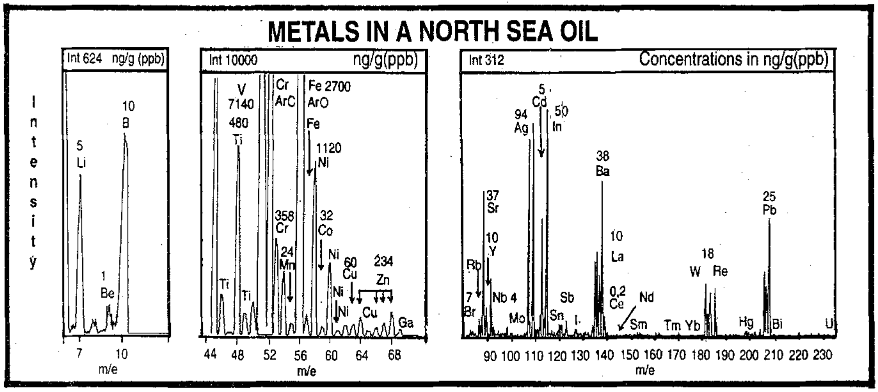

Figure 2.
Mass spectrum of a North Sea oil (concentrations in ng/g listed above element symbol)

the plasma gas. Because the xylene solution was nebulized directly into the plasma, oxygen (99.998%) was added to reduce carbon build-up on the outer Pt cone inlet to the mass spectrometer. A schematic diagram of the ICP-MS system is shown in Figure 1 and instrument conditions are shown in Table 2. Standard curves for each element were established using CONOSTAN (Conoco Oil Co.) elemental standards (organic-solvent based). Figure 2 shows a mass spectrum of a North Sea oil.

Results and Discussion

Table 3 compares concentrations of Ni and V determined by ICP-MS and INAA in six crude oils and an asphaltene-rich bitumen extracted from the New Albany shale.[5] Also shown in Table 3 are Ni and V data obtained by ICP-MS for the NIST SRM 1634b, Fuel Oil standard.

Agreement between the INAA and the ICP-MS data is generally good over a wide range of Ni and V concentrations and no systematic bias between the methods can be recognized. Data for a heavy and a light oil for elements other than Ni and V are shown in Table 4.

Table 3
Ni and V concentrations (μg/g) in petroleum samples determined by INAA and ICP-MS.

Sample	Nickel Concentration (μg/g)[1]			Vanadium Concentration (μg/g)[1]		
	INAA	ICP-MS	Ref. Value[2]	INAA	ICP-MS	Ref. Value[2]
Crude Oils						
171-4	99.2±5.1	76±12	120	381±23	314±56	398
171-8	126±7	107±13	137	387±26	396±34	384
28-2	5.80±0.91	4.8±0.1	5.8	1.46±0.11	2.03±0.04	6.2
28-4	2.70±0.71	1.92±0.15	3.5	0.832±0.060	0.893±0.08	1.8
28-6	23.5±1.6	25.5±0.4	24.9	5.74±0.41	5.97±0.85	6.7
28-8	10.2±1.1	9.25±0.1	11.5	1.76±0.13	2.41±0.6	2.5
New Albany bitumen						
	1900±110	2150±260		2030±150	1700±200	
NIST SRM 1634b						
		29.7±2.7	28±2		58.1±6.2	55.4±1.1

1. Mean ± standard deviation.
2. Conoco, Inc. values for Conoco oils; precision ± 5% RsD. Certified values for NIST SRM 1634b.

Table 4 indicates good agreement between ICP-MS and INAA, except for Cr and La in crude oil 171-4. The Cr value by ICP-MS may be high because of the difficulty of correcting the $^{53}Cr^+$ intensity for $ArCH^+$ (53). The discrepancy in La values is currently unresolved. Table 4 also shows that several elements are determined by ICP-MS that cannot normally be determined by INAA in crude oils, e.g., B, Cd, Cu, Li, Pb, Sn, and Ti. Thus ICP-MS complements the suite of elements normally determined by INAA.

A comparison of detection limits for nebulization ICP-MS and INAA is shown in Table 5. For ICP-MS, detection limits are given for xylene which represent practical detection limits in mixed element standards. The determination limits in xylene represent five times the detection limit or a higher value based on apparent concentrations found when running different API gravity oils and where varying amounts of interferences from matrix ions such as $^{40}Ar^{12}C^{1}H^+$ occur. For INAA, detection limits vary with sample composition because radionuclides from elements other than that of interest constitute the Compton background on which the peak of interest is located. Values given are those for a typical intermediate API crude oil, uncontaminated by clay minerals and are calculated assuming a 1g sample irradiated in a 5 x 10^{12} n/cm^{2}sec neutron flux for 8.0 hr irradiation and 40,000 sec count on a 20% efficient Ge(Li) detector. For both ICP-MS and INAA the determination limits do not represent the ultimate detection limits which can often be approached by optimizing experimental conditions (i.e., irradiation time, count time) but do provide practical limits for routine analyses of crude oils. The use of single-ion monitoring using the graphite furnace (ETV-see Fig. 1) attachement to ICP-MS increases the sensitivity 100 fold.

It can be seen from Table 5 that ICP-MS gives lower detection limits than INAA for many elements, e.g., Ag, Mo, Cd, Ba, Hg, In, Sn, Sr, and Zn and, more importantly, it is sensitive for a number of elements than cannot normally be determined by INAA, i.e., B, Be, Li, and Pb. For the geochemically

Table 4
Comparison of INAA and ICP-MS data for trace elements in light (28-2) and heavy crude oils (171-4)

Element	Concentration (ng/g) or µg/g)[1,2]			
	Crude Oil 171-4		Crude Oil 28-2	
	ICP-MS	INAA	ICP-MS	INAA
Ag	<13	ND	<13	ND
As	17.7±2.6	19.5±3	<17	<12
B	7900±660	ND	<395	ND
Ba	44±18	ND	61±38	ND
Be	<1	ND	<1	ND
Br	<110	145±10	<110	164±14
Cd	11±3.6	ND	<8	ND
Co	168±4	162±10	64±1.7	61±8.4
Cr	3170±320	1120±70	<108	<100
Cu	42±2.9	ND	9.2±2.5	ND
Fe#	2.6±0.15	<5.3	0.69±0.04	<8.9
Ga	1150±50	1250±60	<7	<18
Hg	<47	<50	<27	22±26
K#	ND	0.506±0.233	ND	2.62±0.46
La	4.6±0.9	36.2±3.3	<3	<10
Li	<1	ND	1.6±0.95	ND
Mn	<2	ND	<2	ND
Mo	2560±50	2340±170	<22	<440
Na#	ND	3.02±0.15	ND	8.14±0.4
Pb	<4	ND	<4	ND
Sb	<12	<15	<10	<28
Sc	ND	1.18±0.23	ND	<0.87
Se	415±52	276±38	<38	120±31
Sm	<5.2	0.94±0.39	<5.2	<1.6
Sn	123±8.5	ND	2540±29	ND
Sr	<9	ND	<13	ND
Ti#	7±4.7	<81	0.28±0.01	6.84±3.29
U	<3.4	<22	<3.4	<28
Zn	163±8.4	<94	97±4.5	<170

[1] Concentration: Mean ± standard deviation concentrations in ng/g except elements marked # in µg/g.
[2] < Values: Less than blank value for ICP-MS or 2 standard deviations of background of photo peak energy. ND--not determined/detected.

Table 5
Detection Limits for ICP-MS and INAA for trace elements in oils.

Element	ICP-MS[1]		INAA[2]
	Detection Limit (ng/g)	Determination Limit (ng/g)	Determination Limit (ng/g)
Ag	0.7	3.4	1000
As	3.1	15	5
Ba	0.4	10	5000
Be	0.3	1.3	ND
B 10	25	ND	ND
Br	110	550	10
Cd	3.0	15	2000
Co	0.1	0.5	0.5
Cr 53	150	3000	20
Cu 63	9.2	46	500
Cu 65	8.6	43	-
Fe 57	113	570	50
Hg 202	2.0	10	50
In	0.1	0.5	100
La	0.2	0.8	5
Li	28	140	ND
Mn	7.9	40	1.0
Mo	1.4	7.0	100
Ni 58	3.0	15	100
Ni 60	10	50	-
Pb	0.4	2.0	ND
Sb	0.7	3.5	1.0
Sc	ND	3500	0.05
Se 82	18	42	10
Sn	0.9	4.3	50,000
Sr	0.3	1.5	5000
Ti 47	20	98	100
Ti 48	5.6	28	-
U	ND	ND	100
V	11	53	50
W	0.5	2.5	500
Y	0.2	1.0	ND
Zn 66	1.4	7.0	25

Notes: [1]ICP-MS detection limits for mixtures of elemental standards; determination limits take account background ions from oil type matrix. Data corrected for solvent dilution (xylene). ND - not determined.

[2]INAA detection limits based on intermediate API oil; $\phi = 5\text{x}10^{12}$ n/cm^{2}sec; 8 hr (max) irradiation.

important trace elements in crude oils, Ni, V, and Fe, the two techniques are comparable in detection limits.

Both INAA ICP-MS are subject to interferences and other sources of systematic error. In the case of INAA the crude oil matrix, predominantly hydrocarbons and heteroatom-containing organic species, causes little attenuation of the neutron flux during irradiation. However, long irradiations (e.g., more than 30 mins) of light oils result in some sample loss by radiolysis/volatilization. Metal ions are associated with either the metalloporphyrins or with the high molecular weight involatile asphaltenes in the oil, hence negligible loss of metal species occurs as a result of hydrocarbon radiolysis. For such oils, irradiation in sealed polyethylene does not result in excessive pressure build-up because light gases resulting from radiolysis, CH_4, C_2H_6, H_2, O_2, etc. diffuse rapidly through the polyethylene wall. The potential sources of error in INAA are interfering reactions producing the nuclide of interest, or overlapping γ-rays. Table 6 lists potential interfering reactions for a crude oil matrix.

Table 6
Interfering reactions in INAA

Analytical reaction	Interfering reaction	Correction
$^{51}V(n,\gamma)^{52}V$	$^{52}Cr(n,p)^{52}V$	None needed for typical oils where [V]>[Cr]
$^{58}Ni(n,p)^{58}Co$	$^{59}Co(n,2n)^{58}Co$	Negligible cross section for thermalized neutron flux
$^{58}Fe(n,\gamma)^{59}Fe$	$^{59}Co(n,p)^{59}F$ $^{62}Ni(n,\alpha)^{59}Fe$	Negligible in crude oils, except for very high Ni content
$^{50}Ti(n,\gamma)^{51}Ti$	$^{51}V(n,p)^{51}Ti$	Corrections needed for high V oils
$^{75}As(n,\gamma)^{76}As$	$^{76}Se(n,p)^{76}As$	Correction needed only for [Se] >> [As]

In ICP-MS the principal sources of interference are isobaric ions and plasma gas ions of coincident mass. High concentrations of low ionization energy elements (e.g., Na in sea water) in the sample may also depress plasma temperature but this is not a problem in petroleum analysis. Atomization of organic (xylene) solutions of crude oils into the plasma, however, requires the addition of O_2 to the gas stream to oxidize carbon to CO/CO_2 to prevent soot build-up on the mass spectrometer inlet cone. This causes some plasma instability and also results in additional interfering gaseous ions, e.g., ArO^+ (56), CO_2H^+ (45), ArC^+ (52). The major interfering gaseous ions are shown in Table 7. In general, isobaric ions of other elements (e.g., ^{82}Se - ^{82}Kr) are corrected for using known isotopic ratios of the analyte element and the interfering element.

Table 8 is an attempt to summarize the major advantages and disadvantages of NAA and ICP-MS as applied to petroleum geochemistry. The high sensitivity of ICP-MS for many elements is probably the most important advantage of ICP-MS for multi-element measurement in oil-oil and oil source rock correlations, and relative to other non-nuclear analytical methods (e.g., AAS, XRF), the method suffers from few sources of interference. For very light oils, and refined products which contain sub-ppm levels of most metals, ICP-MS is the method of choice. On the other hand, for kerogens, source rocks, and many bitumens and asphalts, the insolubility of these complex matrixes in organic solvents or typical aqueous acids and bases requires a difficult dissolution step and increases the blank value in ICP-MS.

Table 7
Interfering gas ions in ICP-MS

Isotope of Interest	Interfering Gas Ion	Correction
^{10}B	$^{12}C^+$ very intense line overlap	ETV-ICP-MS; matrix removed by ashing
^{24}Mg	$^{12}C_2{}^+$	Use ^{25}Mg
^{28}Si	$^{12}C^{16}O^+$; $^{14}N_2{}^+$	
^{40}Ca	$^{40}Ar^+$	Use ^{43}Ca(0.14%)
^{44}Ca	$^{12}C^{16}O_2{}^+$	Use ^{42}Ca
^{45}Sc	$^{12}C^{16}O_2H^+$	Small interference
^{48}Ti	$^{32}S^{16}O^+$	Use ^{47}Ti and ^{48}Ti corrected for S content using $^{40}Ar^{32}S^+$
^{51}V	$^{35}Cl^{16}O^+$	Small interference in oils (monitor 51/53 mass ratio)
^{52}Cr	$^{40}Ar^{12}C^+$	Use ^{53}Cr
^{53}Cr	$^{40}Ar^{13}C^+$; $^{37}Cl^{16}O$	Small interference in oils (monitor 51/53 mass ratio)
^{56}Fe	$^{40}Ar^{16}O^+$	Use ^{57}Fe
^{57}Fe	$^{40}Ar^{16}O^1H^+$	
^{75}As	$^{40}As^{35}Cl^+$	Small interference in oils (monitor 75/77 mass ratio)

For these materials the non-destructive INAA technique is superior. ICP-MS is capable of high sample throughput compared to INAA; however, the technique is more labor intensive which partially offsets this advantage.

ICP-MS is a complementary technique to INAA in a geochemical exploration program. Elements such as Pb, Tl, Bi, B, Be, Cd cannot be routinely determined by INAA and are best determined by ICP-MS. Elements of geochemical significance such as Ni, V, Fe, Co and other transition metals can be readily determined by both INAA and ICP-MS. In a typical geochemical correlation study in which oils, bitumens and kerogens, and source rocks are analyzed, the versatility and non-destructive nature of INAA is a major advantage--however, the combination of the two techniques provides the most powerful analytical tools for trace element determination in such a program.

Conclusions

ICP-MS and INAA are both extremely powerful methods for trace element determination in petroleum geochemistry. ICP-MS has the capacity to measure a large number of elements with high sensitivity and relatively few interferences. INAA lacks sensitivity for some elements but has sufficient sensitivity for the geochemically significant elements V, Ni, Fe, Sc, Br, etc. Light oils are particularly suited to the ICP-MS technique whereas complex matrices such as kerogens, shales, asphalts are more suitably analyzed by INAA. Together, the two techniques offer the geochemist the most comprehensive suite of methods for trace element analysis available.

Table 8
Advantages and disadvantages of ICP-MS and
INAA for geochemical analysis

INAA	ICP-MS
	Advantages
High sensitivity for many elements (sub ng to μg)	High sensitivity for many elements - sensitivities similar over large mass range (sub ng to μg)
No or minimal matrix effects	Many elements determined which are not routine by INAA, e.g., Cd, Tl, Bi, Be, I, Li, Pb, Pd, Pt, Sn
Minimal sample preparation for a wide variety of matrixes, e.g., kerogens, bitumens, heavy-light oils	Isotope ratios of elements can be determined if significant variation present, e.g., Pb isotopes
Few interferences on elements of interest; corrections possible where necessary	High sample throughput (e.g., 20 samples per day)
Good accuracy and precision demonstrated for many matrices	On-line analyses of molecular sub-fractions separated by HPLC or SFC can be done
Standards may be of different matrix to sample	Laser ablation can be used for solid samples
	Disadvantages
Several important elements cannot be routinely determined, e.g., Pb, Cd, B, Be	Light elements may have poor sensitivity because of interferences, e.g., ${}^{10}B$, $({}^{12}C)$ ${}^{24}Mg({}^{12}C^{12}C)$, ${}^{28}Si({}^{12}C^{16}O)$
Long analysis time because of decay periods	Organic or aqueous solution required for nebulization ICP-MS
Reactor and radioactivity handling required	Complex solids, e.g., kerogens, shales, must be in solution for nebulization ICP-MS
Very light oils undergo significant radiolysis	Pre-analysis treatment introduces blank values and sources of contamination/loss

*

The authors acknowledge the assistance of Eric Michael of Conoco, Inc., Ponca City, OK for supplying the crude oils and analytical data. The authors also are grateful to G. E. Mercer and Cathy Grimm of the Nuclear Radiation Center, Washington State University, for assistance in the INAA analyses.

References

1. R. H. FILBY, G. J. VAN BERKEL, in: Metal Complexes in Fossil Fuels, R. H. FILBY, J. F. BRANTHAVER, (Eds), ACS Symposium Ser. No. 344, Washington, DC, 1987, p. 2.
2. J. F. BRANTHAVER, R. H. FILBY, in: Metal Complexes in Fossil Fuels, R. H. FILBY, J. F. BRANTHAVER, (Eds), ACS Symposium Ser. No. 344, Washington, DC, 1987, p. 84.
3. E. W. BAKER, J. W. LOUDA, in: Biological Markers in the Sedimentary Record, R. B. JOHNS, (Ed.), Elsevier, Amsterdam, 1986, p. 125.
4. A. S. MACKENZIE, J. M. E. QUIRKE, J. R. MAXWELL, in: Advances in Organic Geochemistry, 1979, J. R. MAXWELL, A. G. DOUGLAS (Eds), Pergamon Press, Oxford, 1980, p. 239.
5. G. J. VAN BERKEL, J. M. E. QUIRKE, R. H. FILBY, Org. Geochem., 14 (1989) 119.
6. J. H. CHEN, R. P. PHILP, Chem. Geol., 91 (1991) 139.
7. B. HITCHON, R. H. FILBY, K. R. SHAH, Prepr. ACS Div. Petrol. Chem., 18 (1973) 623.
8. A. V. HIRNER, in: Metal Complexes in Fossil Fuels, R. H. FILBY, J. F. BRANTHAVER, (Eds), ACS Symposium Ser. No. 344, Washington, DC, 1987, p. 146.
9. J. A. CURIALE, in: Metal Complexes in Fossil Fuels, R. H. FILBY, J. F. BRANTHAVER, (Eds), ACS Symposium Ser. No. 344, Washington, DC, 1987, p. 135.
10. J. R. ODERMATT, S. A. CURIALE, Chem., Geol., 91 (1991) 99.
11. B. HITCHON, R. H. FILBY, AAPG Bull., 68 (1984) 838.
12. J. ELLRICH, A. V. HIRNER, H. STARK, Chem. Geol., 48 (1985) 313.
13. M. I. CHICARELLI, C. B. ECKARDT, C. R. OWEN, J. R. MAXWELL, G. EGLINTON, R. C. HUTTON, A. N. EATON, Org. Geochem., 15 (1990) 267.
14. F. S. JACOBS, R. H. FILBY, Anal. Chem., 55 (1983) 74.