Physico-Chemical Analysis of Some Pakistani Crude Oils

[1]S.M.S.R. NAQVI*, [1]HILAL A. RAZA, [1]S.N.SARWAR, [2]T.M. ANSARI AND [2]A.RAUF
[1]*Hydrocarbon Development Institute of Pakistan*
[2]*Department of Chemistry, Bahauddin Zakariya University, Multan 60800, Pakistan*

(Received 26th July, 1995, revised 28th December, 1995)

Summary: Physico-chemical characteristics such as API gravity, Specific gravity, Pour point, Calorific value, Kinematic viscosity, Flash point, Reid vapour pressure, Copper corrosion, Conradson carbon, Water and sediments, Total sulphur, salt contents, Distillation range, I.B.P, F.B.P,. total recovery, residue and metallic contents of some Pakistani crude oils collected from different oil fields of the Punjab and Sindh provinces have been evaluated using standard ASTM/IP procedures. Atomic emission spectrometry has been employed to estimate the amounts of metallic elements, Al, Ca, Cr, Fe, Pb, Mg, Ni, Si, Na and K and V. Results have been compared with other international crude oils to assess the quality of Pakistani crude oils.

Introduction

Crude oils are organic in nature and consist of compounds of carbon and hydrogen with lesser amounts of sulphur, nitrogen, oxygen and trace metals. Compounds of carbon and hydrogen are complex but mainly paraffinic, naphthenic and aromatic. Crude oils contain all normal alkanes from C_1 to C_{40} and a few beyond C_{40}. On average 15 to 20% of such compounds are usually found. However this percentage rises to 35% in highly paraffinic and decreases to zero in highly biodegraded oils. Methane is the predominant component of natural gas and alkanes ranging from pentane to pentadecane are the chief constituents of straight run (uncracked) gasoline or petrol. Above C_{17}, the alkanes are solid wax like substances and crude oils which contain high concentrations of parafin wax will be viscous and have high cloud and pour points. These paraffins may also contain isoalkanes, anti isoalkanes and methyl cycloalkanes.

Most commonly found naphthenes are five and six membered rings and occasionally a few rings with seven carbon atoms. Among these methyl derivatives are the most abundant compounds as compared with the parent dicyclic compounds. Crude oils contains upto 50 % of such naphthenes Aromatic compounds rarely amount to more than 15% of the crude oils. These are concentrated in heavy fractions such as gas oil, lubricating oils and the residuum. The alkyl derivatives of the benzene namely roluene and xylene are the most common aromatic compounds in petroleum. The other derivatives of benzene include fused compounds, the di-aromatics (naphthalenes) and tri-aromatics (phenanthrene or anthracene). Naphtheno-aromatic compounds have also been identified in crude oils. These compounds are abundant in shallow and immature oils. Many of these compounds can be related to steroid and triterpenoid structures.

*To whom all correspondence should be addressed.

Sulphur compounds like thiols, sulphides and thiophenes also occur in crude oils. Sulphides are fairly evenly distributed over medium and heavy fractions of crude oils. Compounds of nitrogen in crude oils are unwelcomed because of catalyst poisoning and formation of gum in fuel oils. Nitrogen compounds which can easily separated include pyridines, quinolines, indoles, pyroles and carazoles. Oxygen compounds in the form of organic acids occur in young and immature crude oils. These organic acids range in size from C_1 to C_{30} and have isoprenoid structures with members such as carboxylic acids, phenols, cresol anhydride etc.

Most of the crude oils contains metals normally in prophyrin complexes derived from chlorophyll and haemoglobin. The commonest metals are vanadium, nickel, iron, aluminium, chromium, copper, silicon, sodium, potassium, calcium, magnesium and lead. Metallic elements may play important role. These can cause serious refining problems and lead to deterimental properties in the finished commercial products. Their presence also lead to the poisoning of catalysts used in cracking and desulphorization. Nickel and vanadium are the most abundant metals in petroleum. Ratio of nickel/vanadium is a useful classification parameter. Metallic contents of crude oil provide useful insight into the source of a petroleum accumulation, especially when combined with classification parameters derived from molecular, isotopic and bulk analysis.

Various physico-chemical parameters which are commonly determined to assess the quality of crude oils are given below:

API gravity:- This parameter (API stands for American Petroleum Institute) expressed in "degrees" is mathematically related to specific gravity. API gravity usually, although not infallibly, indicates the gasoline and kerosine contents of the crude.

Specific gravity:- Gravity is a term used to denote the density of oil and is useful as a means of identification. Specific gravity is the ratio of the mass of a given volume of oil at a temperature of 60 °F to the mass of an equal volume of water at the same temperature.

Pour point:- Lowest temperature at which the material will pour. It is function of the oil interms of waxiness and bitumen content.

Calorific value - It is a mean for direct measurement of fuel energy content

Kinematic viscosity - It is determined by measuring the time for the liquid to flow under gravity through a glass viscometer.

Flash point Flash point of a liquid is the lowest temperature at which application of a flame causes the vapour above the sample to ignite. It is an indicative of potential fire hazard.

Reid vapour pressure:- It is a measure of tendency of more volatile oil components.

Copper corrosion It is a qualitative test and is used to ascertain whether oils are free of a tendency to corrode copper fuel lines and brass or bronze parts used in the bumer assemblies.

Conradson carbon-: Carbon residue is a measure of carbonaceous material left in an oil after all the volatile components are vapourised in the absence of air.

Sediments and Water:- These are measures of dirt and other foreign matter as well as water.

Sulphur contents:- The amount of sulphur in crude is important in terms of handling the crude within the refinery and the undesirable effects of sulphur in finished products.

Salt contents:- It is not confined to sodium chloride but usually is interpreted in terms of NaCl. Salt is undesirable because of the tendency to obstruct fluid flow, to accumulate as an undesirable constituent of residual oils and asphalts, and a tendency of certain salt compounds to decompose when heated causing corrosion of refinery equipments.

Mettalic contents:- Heavy metals such as Vanadium, Nickel, Iron etc. tend to accommodate in the heavier gas oil and residuum fractions where metals may interfere with refining operations particularly by poisoning catalysts. The heavy

metals also contribute to the formation of deposits on heated surfaces in furnaces and boiler fire boxes leading to permanent failure of equipments. Further they interfere with heat transfer efficiency and increased maintenance.

Distillation ranges:- These indicate what fractions and how much of each fraction is present temperature of the distilled vapours are recorded at the initial boiling point and at the different volume percentage fractions of the charge in the receiver and at the end point.

Light Hydrocarbon Analysis:- Analysis of light hydrocarbons dissolved in the crude oil usually ethane through pentane or some time hexane.

Characterization Factor This factor is used to classify crude oils into various groups to evaluate their quality and commercial value [1,2].

Pakistan is one of the oil producing country in the world. Its annual crude oil production is 21, 895, 398 barrels [3]. To our knowledge, quite a few studies on Pakistani crude oils have been reported in the literature M.A Quddus,. *et al.* [4] classified some of the Pakistani crude oils using modified formula of characterization factor. S.N. Sarwar *et al* [5] determined salt setting tendency in paraffinic crude from Sindh province. W. Ahmad and S. Alam [6] reported organic geochemistry of crude oils from Potwhar-Kohat region. A. Jamil *et al* [7] estimated some metallic elements in some crude oils using mixed solvent system and dry ashing procedures. Recently, M.A. Quddus *et al.* [8] have reported comparison of some physical parameters of imported crude oils with indigenous crude oils. We thought is worthwhile to investigate thoroughly the physio-chemical parameters of some of Pakistani crude oils to assess their quality and commercial value.

Analytical methods

A.R. Grade chemicals and deionised water was used. Calibrated Pyrex glasswares and equipments such as Viscometer Baths VHC-220 (Gallenkamp, England). Flash point tester Cleveland-DIN-51376 (Lauda, Germany). Muffle fumace FSE-621 (Gallenkamp, England) and Atomic Emission spectrometer F-500 (Labsoft, Germany) were used throughout this work.

Crude oil (A-L) as detailed in Table-1 were sampled using standard sampling procedure (ASTM D-270) from different oil fields in different stratographic locations of Pakistan. Physio-chemical characteristics such as API gravity, specific gravity, pour point, calorific value, kinematic viscosity, flash point reid vapour pressure, copper corrosion, conradson carbon, water and sediments, total sulphur, salt contents

Table-1: Crude oils and well locations

Crude oil	Well location
A	Composite Tool Crude Oil, Punjab, Pakistan
B	Tobra Crude Oil Adhi-), Punjab, Paksitan
C	Bhalsaydan Crude Oil Well # 1, Punjab, Pakistan
D	Missa Keswal Crude Oil Well # 3, Punjab, Pakistan
E	Ratana # 2 Condensate, Punjab, Pakistan.
F	Sadkal Crude Oil Well # 3, Punjab, Pakistan.
G	Tajedi Crude Oil Well # 1, Sindh, Pakistan
H	Mazari Crude Oil South # 1, Sindh, Pakistan
I	South Mazari Deep Well # 1, Sindh, Pakistan.
J	Tando Alam Crude Oil Well # 8, Sindh, Pakistan
K	Buzdar Well # 1, Sindh, Pakistan
L	Meyun Ismail Well # 1, Sindh, Pakistan

Table-2: Instrument and Instrumental Conditions

Instrument	Atomic Emission Spectrometer, F-500 (Labsoft, W. Germany)
Excitation Source	Electric arc (Graphite Disc electrodes)
Wavelenght (Å)	
Fe	2599
Si	2516
Ni	3414
Mg	2803
Al	3082
Cr	4254
Na	5895
V	4379
Pb	2833
Ca	4227
K	7665
Calibration range (ppm)	0-100
Background Corrector	Mercury lamp
Detector	Photomultiplier tubes
Readout Device	i-Optional automatic printer ii-Visual seven segment LED indicator

and distillation ranges were determined following standard ASTM/IP methods, D-1298, D-97, D-240, D-445, IP-170, D-323, D-130, D-130, D-96, IP-63, IP-77 and D-86 respectively [2]. Trace metals viz. Al, Ca, Cr, Fe, Pb, Mg, Ni, Si, Na, K and V in crude oils were analysed directly using atomic emission spectrometry. Instrumental conditions for metals analysis are given in Table-2.

Results and Discussion

In this study, twelve local crude oil samples collected from different oil fields of Punjab and Sindh provinces of Pakistan have been analysed for the evaluation of various physico-chemical parameters, *i.e.* API gravity, specific gravity, pour point, calorific value, kinematic viscosity, flash point, reid vapour pressure, copper corrosion, conradson carbon, water and sediments, total sulphur, salt contents, distillation ranges, I.B.P, F.B.P. Total recovery, residue and trace metal contents using standard ASTM/IP procedures. Well locations of these crude oils have been listed in Table-1. Out of the twelve crudes, six samples each have been collected from the oil fields of the Punjab and the Sindh provinces of Pakistan Table-3 shows general physico-chemical characteristics of these oils. Comparison of Pakistani crude oils with international crudes have been given in Table-4.

Characterization factor (K) values of Pakistani crude oils have been determined

Table-3: General Physico-Chemical Characteristics of Pakistani Crude Oils

Characteristics	Test Method (ASTM/IP	Crude Oil											
		A	B	C	D	E	F	G	H	I	J	K	L
API Gravity @ 60°F	D-1298	40.00	48.40	41.40	42.14	42.86	41.73	42.60	42.93	39.40	41.46	44.18	44.60
Specific Gravity @ 60/60 °F	D-1298	0.8253	0 7863	0.8184	0.814	0.8115	0.8098	0.8128	0.8112	0.8278	0.8181	0.8054	0.8035
Pour Point °F	D-97	-22	-5.8	-16.6	-22	5.0	-5.8	75.2	53.6	69.8	69.8	75.2	75.2
Calorific values Btu/lbe Gross	D-240	19420	18220	18900	19120	19290	18960	18915	19570	18500	18736	18921	18960
Kinematic Viscosity	D-445												
at 100 °F cst		2.33	1.54	1.41	1.59	1.25	1.46	3.8	2.93	2.47	2.13	1.64	2.05
at 122 °F cst		1.91	1.34	1.74	1.66	1.46	1.57	3.05	2.40	3.05	2.43	2.05	2.42
Reid Vapour Pressure @ 37.7 °C	D-323	1.5	7.0	7.2	4.9	7.8	4.8	2.0	4.6	3.8	3.5	4.3	5.8
Flash Point Abel °F	IP-170	-	-	<14	<14	-	<14	-	-	-	<5	<14	-
Copper Corrosion 122 °F	D-130	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a
Conradson Carbon % wt	D-189	0.74	0.003	0.02	0.34	0.01	0.06	0.80	0.49	1.01	0.38	0.24	0.3
Water & Sediments (B.S. & W) % vol	D-96	0.05	traces	0.05	0.05	0.05	0.05	0.1	0.05	0.05	0.05	0.05	0.05
Total Sulphur % wt	IP-63	0.15	0.2	0.25	0.1	0.12	0.18	0.05	0.02	0.05	0.05	0.05	0.06
Salt Content lbs/1000 bbl	IP-77	0.05	0.05	1.0	1.0	1.0	1.0	2.0	1.0	1.0	1.0	1.0	4.6
Distillation	P-86												
I.B.P		161.6	114.8	113	105.8	141.8	127.4	235.4	140	136.4	138.2	104	140
10 % recovery at (°F)		235.4	174.2	154.4	206.6	233.6	203	320	253.4	246.2	222.8	204.8	228.2
30 % ""		329	244.4	275	305.6	303.8	284	446	401	365	325.4	302	300.2
50 % ""		447.8	338	413.6	437	401	390.2	555.8	518	507.2	467.6	428	392
70% ""		593.6	434	-	-	527	509	660.2	651.2	644	-	-	518
90 % ""		687.2	656.6	-	-	-	-	732.2	752	734	-	-	-
F.B.P		692.6	698	-	-	-	-	-	-	-	-	-	-
Total recovery at 572 °F vol %		95	95	70	73	77	80	92	96	90	66	73	75
Residue vol %		4	4.5	-	-	-	-	7.5	3.5	9.5	-	-	-
Lear vol %		1	0.5	-	-	-	-	0.5	0.5	0.5	-	-	-
Characterization* Factor		10.71	10.90	10.70	10.81	10.75	10.74	11.18	11.09	10.84	10.86	10.91	10.74

*[4]

Table-4: Comparative Evaluation of Pakistani Crude Oils.

Characteristics	Texas Gulf+ Coast Mix	Nigerian+ (Bonney)	Canada+ (Red water)	Venezuela+ (Lagemar)	Pakistani* (min	max)
API Graveity @ 60 °F	36.5	38.1	34.9	30.7	39.4	48.4
Pour Point °F	5.0	-35.0	10.0	10.0	-22.0	75.2
Viscosity SUS at 77 °F	41.0	38.4	47.8	107.0	–	–
100°F	37.3	35.7	41.7	64.3	1.25	3.8
Sulphur wt %	0.16	0.14	0.56	1.48	0.05	0.20
Salt Contents lbs/1000 bbl	7.0	<2.0	3.0	<2.0	0.5	46.0
Flash Point °F	<40.0	<40.0	<40.0	<40.0	<5.0	<14.0
Water & Sediments % vol	0.1	trace	trace	trace	trace	0.1
Reid Vapour Pressure at 100 °F	3.2	6.9	8.4	2.5	1.5	7.8
Iron (ppm)	8.0	7.0	5.0	10.0	0.2	12.0
Nickel (ppm)	0.9	5.0	12.0	17.0	<0.1	1.9
Vanadium (ppm)	0.7	0.3	3.0	175.0	<0.1	0.5
Copper (ppm)	0.0	0.0	0.0	0.0	–	–
Distillation						
I.B.P. °F	<50	<50	<50	<50	104	235.4
10% recovery at (°F)	245	220	230	269	154.4	320
30% recovery (°F)	398	375	382	422	244.4	446
50% recovery (°F)	513	518	573	677	338	555.8
70% recovery at (°F)	654	684	792	907	464	660.2
90% recovery (°F)	884	897	1032	–	656.6	752
F.B.P. °F	1033	1045	1050	1083	692.6	752
Total recovery vol %	96	96	92	84	66	96
Residue vol %	4	4	8	16	–	3.5
Loss vol %	0	0	0	0	–	0.5

* Data bored on twelve crude oil samples collected from different oil fields of Pakistan.
+ [2]

Table-5: Concentration of Trace Elements in Pakistani Crude Oils.

Element	Concentration* (ppm)											
Crude oil	A	B	C	D	E	F	G	H	I	J	K	L
Aluminium	0.4 ± 0.1	0.8 ± 0.1	1.0 ± 0.2	0.9 ± 0.4	1.8 ± 0.0	0.9 ± 0.2	0.4 ± 0.2	2.4 ± 0.0	1.0 ± 0.1	0.7 ± 0.1	1.1 ± 0.1	1.0 ± 0.1
Calcium	0.7 ± 0.2	1.3 ± 0.0	1.5 ± 0.0	0.6 ± 0.1	0.9 ± 0.3	< 0.1	1.0 ± 0.2	>12.0	8.3 ± 1.5	3.1 ± 0.1	1.8 ± 0.2	2.3 ± 0.6
Chromium	<0.1	0.3 ± 0.1	0.2 ±0.1	<0.1	0.5 ± 0.1	0.3 ± 0.2	< 0.1	0.2 ± 0.1	0.2 ±0.1	< 0.1	0.2 ± 0.1	<0.1
Iron	1.2 ± 1.1	0.3 ± 0.2	6.5 ± 0.4	2.3 ±0.4	1.1 ± 0.2	0.2 ± 0.1	0.3 ± 0.2	> 12.0	0.5 ± 0.2	1.1 ± 0.1	1.0 ±0.2	0.9 ±0.1
Lead	2.2 ± 0.4	2.0 ±0.0	2.8 ± 0.1	3.3 ±0.1	3.5 ± 0.2	3.2 ± 0.2	3.1 ±0.5	4.8 ± 0.1	2.7 ± 0.1	4.3 ± 0.8	4.1 ± 0.3	2.7 ± 0.1
Magnesium	<0.1	0.2 ± 0.1	0.2 ± 0.1	< 0.1	0.2 ± 0.1	< 0.1	0.2 ± 0.1	2.4 ± 0.5	0.2 ± 0.1	< 0.1	< 0.1	< 0.1
Nickel	1.0 ± 0.0	< 0.1	0.2 ± 0.1	< 0.1	0.2 ± 0.1	< 0.1	0.7 ± 0.2	0.7 ± 0.2	1.0 ± 0.1	1.9 ± 0.2	0.4 ±0.0	< 0.1
Silicon	3.4 ± 0.2	9.7 ± 0.2	0.3 ± 0.1	< 0.1	0.4 ± 0.1	< 0.1	0.3 ± 0.2	9.8 ± 1.7	< 0.1	0.4 ± 0.1	0.4 ±0.2	< 0.1
Sodium	3.1 ±0.0	0.2 ± 0.0	0.7 ± 0.1	0.7 ± 0.1	1.4 ± 0.4	0.2 ± 0.0	1.5 ± 0.2	8.5 ± 0.8	> 12.,0	2.7 ± 0.1	1.7 ±0.1	3.6 ± 0.2
Vanadium	0.5 ± 0.1	< 0.1	< 0.1	< 0.1	0.2 ± 0.2	< 0.1	0.2 ± 0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Potassium	+	+	+	+	+	+	+	+	+	+	+	+

* Mean of duplicate measurements ± one standard de iation; + present

following the modified formula proposed by M.A Quddus. *et al.* [4]. Calculated K values lie in the range of 10.70 and 11.18 indicating that all are naphthenic bases. Results show that these crudes contain traces of sediments and water. Total sulphur and salt contents have been found to be in the ranges of 0.05 - 0.20 (wt %) and 0.5 - 2.0 lbs/1000 bbl (except sample L which contains high amount of salt on the order of 4.6 lbs/1000 bbl) respectively which are quite comparable to international crudes. Crude oils collected from the Sindh province show higher salt contents as compared to those collected from the Punjab province of Pakistan which may be due to soil composition of different stratographic regions.

Specific and API gravities of the crudes lie in the ranges 0.7863 - 0.8278 and 39.4 - 48.4 respectively which indicate good oil quality when compared with international crudes. Calculated

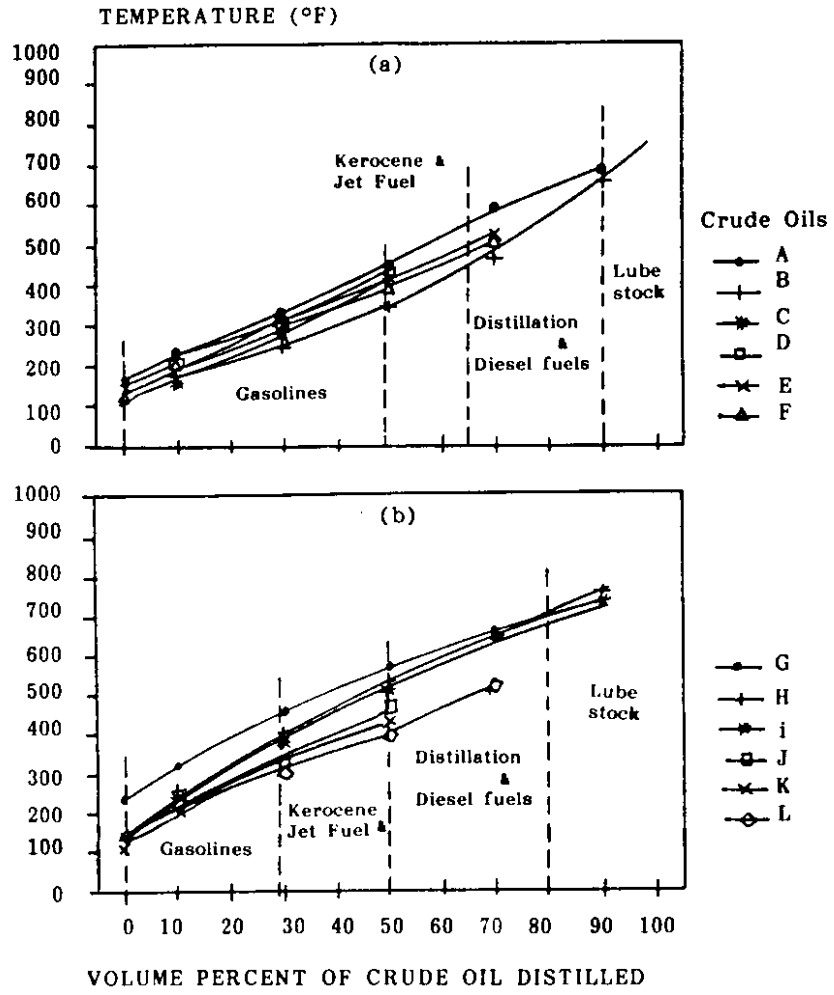

Fig. 1: True boiling point distillation curves of Pakistani crude oils (a Punjab, b Sindh).

kinematic viscosities of these crudes at two different temperatures, i.e. 100 and 122 °F are in the ranges 1.25 - 3.8 and 1.34 - 3.05 respectively. Low kinematic viscosity values are characteristic of better crudes. Pour points of Pakistani crude oils lie in the range between 22-75.2°F. High values in crude oils indicate the presence of more waxes and bitumen contents in samples collected from Sindh provinces. Flash points have also been found to be in the range < 4 - < 14 F°. All the crudes show copper corrosion and conradson carbon values as 1a and 0.003 - 1.01 % respectively Copper corrosion value of 1a indicates that all samples are neutral in nature. Most of the crude oil samples leave minute amounts of carbonaceous material on complete vaporization of all the volatile components in the absence of air.

Calorific values of Pakistani crudes are in the range 18220 - 19570 Btu/lbs which are indicative of sufficient fuel energy. Calorific data suggest that these crudes can be recommended for power generation purposes. Reid vapour pressure values (1.5 - 7.8 psi) indicate the presence of volatile components in crude oils. Lower values have been calculated in crudes collected from Sindh province as compared to those collected from the Punjab province of Pakistan.

Distillation ranges of Pakistani crude oils have been given in Table-3. Figure 1 represents various distillation fractions of these crude oils. It has been noted that on distillation, crude oils collected from the Punjab (Fig. 1a) have comparatively larger gasoline fraction range than

those collected from the Sindh whereas large distillation fractions of kersoine oil, jet fuel, diesel fuel and lube stock have been observed in crude oils collected from Sindh province (Fig. 1b). These results thus show that the quality and commercial value of oils from Punjab are comparatively better.

Metallic elements such as Al, Ca, Cr, Fe, Pb, Mg, Ni, Si, Na, K and V have been estimated quantitatively using atomic emission spectrometry. It has been found that Pakistani crude contain variable amounts of metallic elements. Elemental concentrations have been given in Table-5. Results show that comparatively higher amounts of Ca, Fe, Pb, Si and Na, moderate amounts of Al and lower quantities of Cr, Mg, Ni and V are present. Concentrations of Ni, V and Fe in Pakistani crude oils are considerably lower than the reported values on international crudes.

On the basis of the results presented in this paper, it can be concluded that Pakistani crude oils are of comparable quality to those of international crudes.

References

1. D.M. Considine, "Van Nostrands Scientific Encyclopedia", Fifth Edition, Van Nostrand Reionhold Company International, New York, U.S.A, p. 1736 (1968).
2. K. Boldt and B.R. Hall, "Significance of Tests for Petroleum Products, American Society for Testing and Materials", Philadelphia, U.S.A., p. 3 (1973).
3. Pakistan Energy Year Book, HDIP, Ministry of Petroleum and Natural Resources, Government of Pakistan p. 13 (1993).
4. M.A. Quddus, S.S. Anwar, S.N. Sarwar and A.H. Chotani, *Proc. Pakistan Acad. Sci.*, **24**(2), 137 (1987).
5. S.N. Sarwar, S.S. Anwar, S.N.R. Naqvi and H. Rehman, *Pak. J. Hydrocarbon Res.*, **1**(2), 71 (1989).
6. W. Ahmad and S. Alam, *Pak. J. Hydrocarbon Res.*, **2**(1), 1 (1990).
7. J. Anwar, F. Nahid and Z.U. Kirmani, *J. Chem. Soc. Pak.*, **12**(3), 249 (1990).
8. M.A. Quddus, M.H. Rehman and S.N. Sarwar, Pak. *J. Hydrocarbon Res.*, **7**(1), 91 (1995).