

3. RESULTS AND DISCUSSION

3.1. Oil-Field Waters Studied

Seven oil-field water samples were collected from individual wells of six oil-fields lying in three different regions of Egypt, namely, Sinai, Gulf of Suez and Western Desert of Egypt. These oil-fields are Ashrafi, Belayim Land, Meleiha, Ramadan, Razzak and Zeit Bay. Their locations are shown in Fig. 1.

The geological data of the oil productive zones in the wells of the oil-fields, from which the studied water samples were produced with the oil, are given in Table 1.

These data indicate that the depths of the average intervals of the productive zones in these wells vary from about 4800 to 11400 ft.

The lithology is mainly composed of sandstone, shale, limestone, dolomite, and granite. This constitutes, from lower to upper, the Basement, Nubia, Alamein Dolomite, Baharia, Kareem Carbonate and South Gharib Formations. The geological ages of these Formations are Pre-Cambrian, Carboniferous, Lower and Upper Cretaceous, as well as Lower and Middle Miocene.

The pressures of the oil reservoirs vary from about 400 to 4300 psi, while their temperatures are in the range of 120 to 280°F (50 to 140°C).

3.2. Methods Used for the Analysis of the Oil-Field Waters

The studied oil-field water samples have been analyzed according to ASTM [1] and/or APHA [2] standard methods for water analysis, unless otherwise indicated.

These methods have included acid-base potentiometric and complexometric titration as well as gravimetric analysis. They also involve the use of pH-meter and electrical conductivity-meter.

Methods applying ultraviolet, visible and infrared absorption spectrometry, as well as inductively coupled plasma-atomic emission spectrometry are carried out. Chromatographic procedures comprise liquid column, gas-liquid, ion and high performance liquid chromatography.

Generally, the results of these analyses have been reported to at least three significant digits.

3.3. General Physico-Chemical Properties of the Oil-Field Waters

General physico-chemical properties, including pH, density, specific gravity, electrical conductivity, resistivity, total dissolved solids, salinity, acidity, alkalinity and hardness, have been determined for the oil-field waters under study. The obtained results are given in Table 2.

Table 1. Geological Data of the Productive Zones in the Wells of the Oil-Field Waters

Geological Data	Water Sample No.						
	1	2	3	4	5	6	7
Oil-Field	Belayim Land	Ashrafi	Zeit Bay	Zeit Bay	Ramadan	Meleiha	Razzak
Well No. (Zone No.)	113-46 (I-B)	SW2	ZB-B2	ZB-L10A	R6-43	M-12	RZK-2
Location	Sinai	Gulf of Suez	Gulf of Suez	Gulf of Suez	Gulf of Suez	West Desert	West Desert
Oil Productive Zone:							
- Depth, ft.	6227	5650	4768	5566	11400	5960	7500
- Lithology	Interbedded sandstone and shale	Granite	Dolomitic limestone	Dolomitic limestone	Sandstone	Sandstone and shale	Dolomite and limestone
- Formation	South Gharib	Basement	Kareem Carbonate	Kareem Carbonate	Nubia	Baharia	Alamein Dolomite
- Age	Middle Miocene	Pre-Cambrian	Lower Miocene	Lower Miocene	Carboniferous	Cenom., U. Cret.	Aptian, L.Cret.
- Pressure, psi.	2615	420	1550	1550	4300	750	3200
- Temperature, °F	170	147	158	158	284	120	225
- Temperature, °C	77	64	70	70	140	50	107
Producing Co.	PETROBEL	AGIBA	SUCO	SUCO	GUPCO	AGIBA	GUPCO

L. and U. Cret. : Lower and Upper Cretaceous.

AGIBA, GUPCO, PETROBEL and SUCO: Agiba Petroleum, Gulf of Suez Petroleum, Belayim Petroleum and Suez Oil Company, respectively.

Table 2. General Physico-Chemical Properties of the Oil-Field Waters

Physico-Chemical Properties	Water Sample No.						
	1	2	3	4	5	6	7
pH at 25°C	5.11	4.78	5.50	5.40	3.80	7.31	6.85
Density at 15°C, g/mL	1.2224	1.2120	1.1818	1.1812	1.1434	1.0762	1.1116
Specific gravity at 60/60°F	1.2233	1.2128	1.1826	1.1820	1.1442	1.0769	1.1124
Conductivity at 25°C, mS/cm	204	245	232	232	196	142	187
Resistivity at 25°C, ohm m	0.0490	0.0408	0.0431	0.0431	0.0511	0.0706	0.0535
Total dissolved solids, mg/L:							
- at 105°C	456420	338760	296240	294580	237980	114140	173900
- at 180°C	318660	315260	271280	262560	197800	108000	160980
- at 550°C	263740	309940	257920	255020	183780	105630	157030
Salinity, as NaCl, mg/L	339232	312509	274122	261248	199000	103849	157102
Acidity to pH 8.3, as CaCO ₃ , mg/L	1100	902	0	0	1871	0	0
Alkalinity to pH 4.5, as CaCO ₃ , mg/L	0	0	64.4	27.0	0	248	141
Hardness, as CaCO ₃ , mg/L:							
- Ca	48801	34868	21557	19287	66448	8153	16642
- Mg	114509	9891	24539	24543	28587	3401	5596
- Total	163310	44759	46096	43830	95035	11554	22238

3.3.1. pH

The pH has been measured by the electrometric method [1-3]. The pH values at 25°C of the examined oil-field waters vary from 3.8 to 7.3, which indicate that five of them are moderately acidic (pH = 3.8 - 5.5), while the other two are nearly neutral (pH = 6.8 and 7.3).

3.3.2. Density and specific gravity

The specific gravity has been determined by the pyknometer method [1, 3], then the density has been estimated from it. The density at 15°C of the studied waters is in the range of 1.08 to 1.22 g/mL. Thus, their specific gravity at 60/60°F has more or less the same values.

3.3.3. Electrical conductivity and resistivity

The electrical conductivity has been measured using the instrumental method [1-3], and the resistivity has been calculated from it. The conductivity of the studied oil-field waters varies from 142 to 245 mS/cm at 25°C. Thus, the corresponding resistivity values are in the range of 0.071 to 0.041ohm m.

3.3.4. Total dissolved solids

Total dissolved solids have been determined by the heating method [1, 2]. In the examined oil-field waters, the total dissolved solids measured at 105, 180 and 550°C are in the range of 114000 to 456000, 108000 to 319000, and 106000 to 264000 mg/L respectively.

3.3.5. Salinity

The salinity has been calculated from the determined chloride ion to give "salinity as sodium chloride". In the waters under study, the salinity has the range of 104000 to 339000 mg/L. These values are nearly equal to the total dissolved solids determined at 180°C, rather than at 550°C which have generally lower results.

3.3.6. Acidity and alkalinity

The acidity and alkalinity of the investigated oil-field waters have been carried out by the potentiometric titration methods [1-3].

The acidity is found only in three water samples, being about 900, 1100 and 1870 as mg/L CaCO₃ in the sample Nos. 2, 1 and 5, respectively.

On the other hand, the bicarbonate alkalinity is found in the remaining four water samples, having the values of 27, 64, 141 and 148 as mg/L CaCO₃ in the water Nos. 4, 3, 7 and 6 respectively. Both the alkalinity of carbonate and hydroxide are not present in these water samples, as their pH values vary only from 5.4 to 7.3.

3.3.7. Hardness

The hardness [1, 2] has been estimated from the calcium and magnesium concentrations determined by the ICP-AES with the standard additions method [1, 2]. The calcium, magnesium and total hardness of the studied water samples are in the order of 8000 to 66000, 3000 to 114000 and 12000 to 163000 as mg/L CaCO₃ respectively. The water sample No. 6 has the lowest values in the three types of hardness, while the sample No. 5 has the highest value in the Ca hardness, and sample No. 1 has the largest concentrations in both the Mg and total hardness.

3.4. Determination of Alkali and Alkaline Earth cations in the Oil-Field Waters

The alkali and alkaline earth cations, including lithium, sodium, potassium, magnesium, calcium, strontium and barium, have been determined in the water samples under investigation using three analytical techniques. These include the inductively coupled plasma-atomic emission spectrometry (ICP-AES), ion chromatography (IC) and EDTA complexometric titration (EDTA). The obtained results of these analyses are given in Table 3. Ion chromatograms of cations in the studied water samples are shown in Fig. 7.

Lithium, sodium and potassium have been determined by both the ICP-AES and IC methods. However, results of lithium determined by either the ICP or IC are not reliable at all, so they are not given, but they are more reliable for other alkali and alkaline earth cations.

Sodium concentrations in the studied water samples vary from nearly 33000 to 102000 and 31800 to 97300 mg/L as carried out by the ICP-AES and IC procedures, respectively. Their results are very strongly correlated as the correlation coefficient is nearly equal one ($r = 0.998$) as shown in Fig. 8.

On the other hand, potassium concentrations are in the range of about 470 to 5010 and 360 to 4660 mg/L as determined by the ICP-AES and IC methods, respectively. Their results are also very strongly associated with a correlation coefficient of about one ($r = 0.980$) as shown in Fig. 9.

Both magnesium and calcium cations have been determined by the three techniques, i.e. ICP-AES, IC and EDTA. Concentrations of magnesium are in the range of about 930 to 29000, 1080 to 27200 and 810 to 30600 mg/L as determined by these three techniques, respectively. Also, those of calcium vary from nearly 3570 to 29600, 2960 to 26300 and 3290 to 26100 mg/L as carried out by three techniques, respectively.

The results of both magnesium and calcium, as determined by the ICP, IC and EDTA techniques, are very strongly correlated ($r = 0.996$ to 0.999) as shown in Figs. 10 to 13.

Strontium and barium cations have been only determined by the ICP-AES method, being in the range of about 100 to 660 and 1 to 6 mg/L, respectively.

Table 3. Alkali and Alkaline Earth Cations in the Oil-Field Waters Using Different Analytical Techniques

Concentration, mg/L	Water Sample No.						
	1	2	3	4	5	6	7
ICP-AES :							
- Sodium, Na ⁺	53640	101975	87790	87442	33031	36109	55076
- Potassium, K ⁺	2143	5010	1880	2014	2450	470	1108
- Magnesium, Mg ²⁺	29008	2562	6128	6574	7584	930	1743
- Calcium, Ca ²⁺	20556	15199	8705	8130	29620	3570	7655
- Strontium, Sr ²⁺	659	362	265	238	631	97.0	231
- Barium, Ba ²⁺	6.07	4.67	1.16	0.902	5.36	1.00	1.62
Ion chromatography							
- Sodium, Na ⁺	55048	97292	83526	81510	31798	34736	52753
- Potassium, K ⁺	1897	4661	2130	1390	2150	360	1169
- Magnesium, Mg ²⁺	27250	3629	6589	6088	9258	1075	1927
- Calcium, Ca ²⁺	18666	13600	8665	6185	26267	2957	6571
EDTA titration							
- Magnesium, Mg ²⁺	30624	3160	5590	6198	7656	814	1750
- Calcium, Ca ²⁺	18437	14028	8216	7214	26052	3287	7695

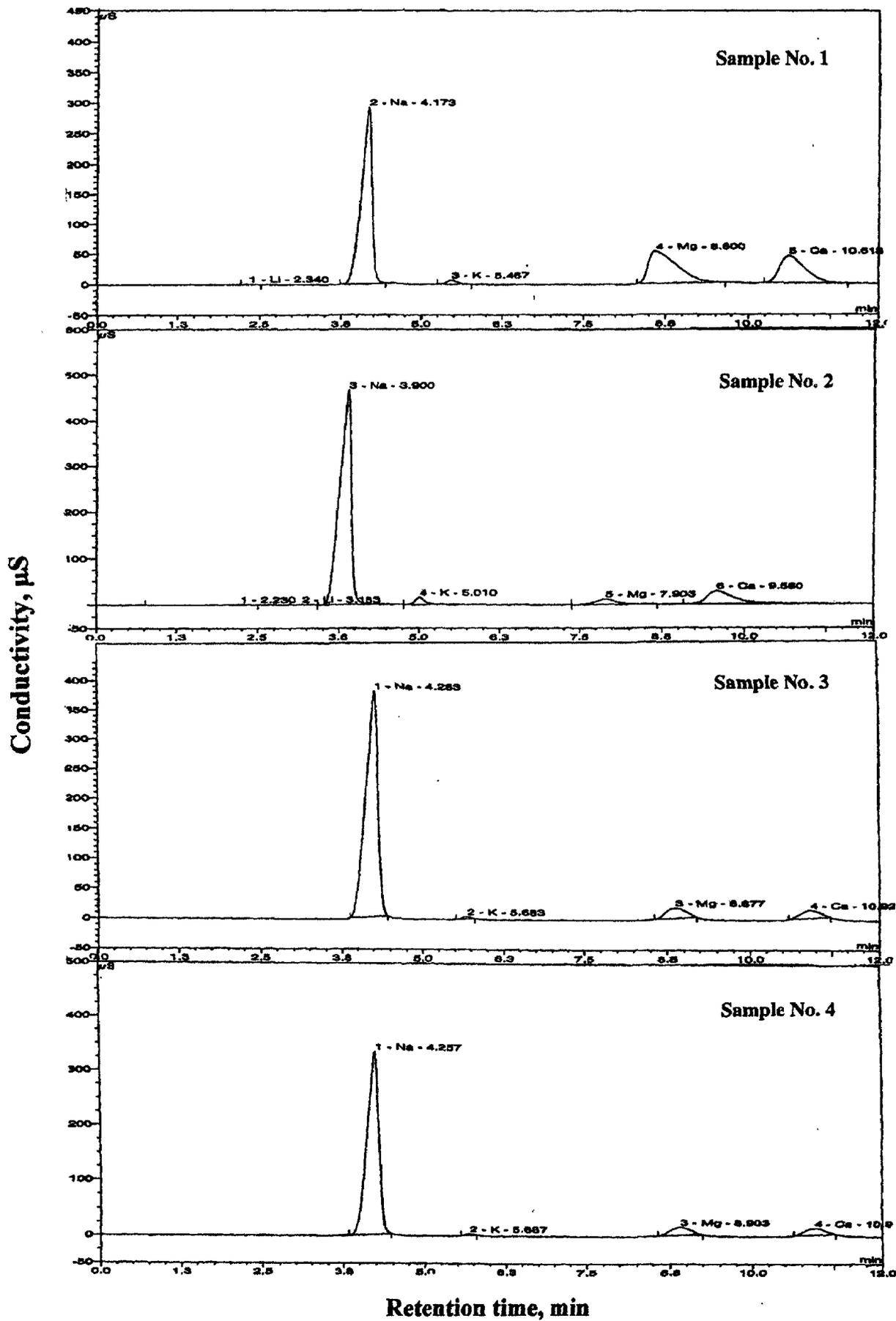


Fig. 7. Ion chromatograms of the cations in the oil-field waters.

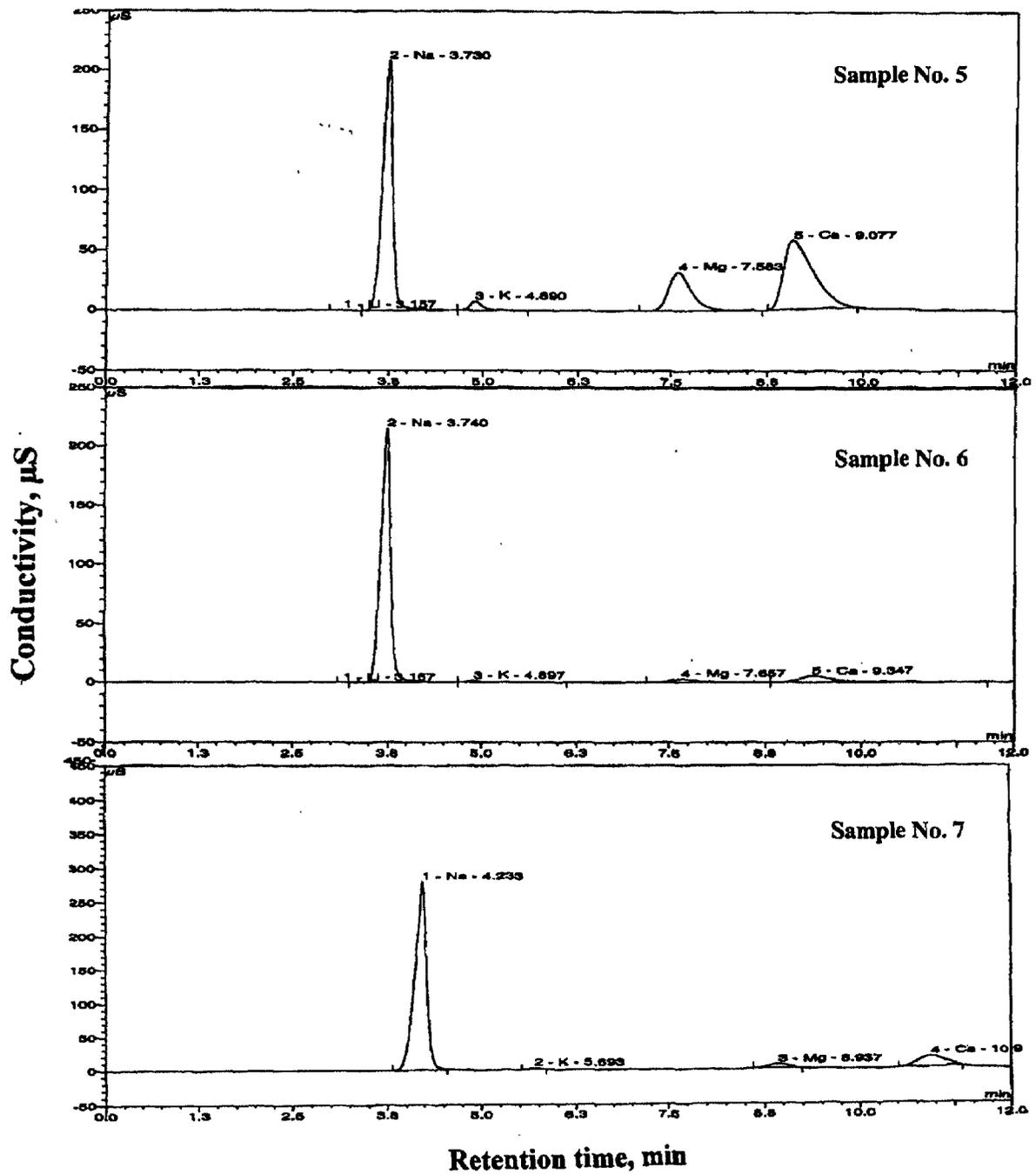


Fig. 7. Continued.

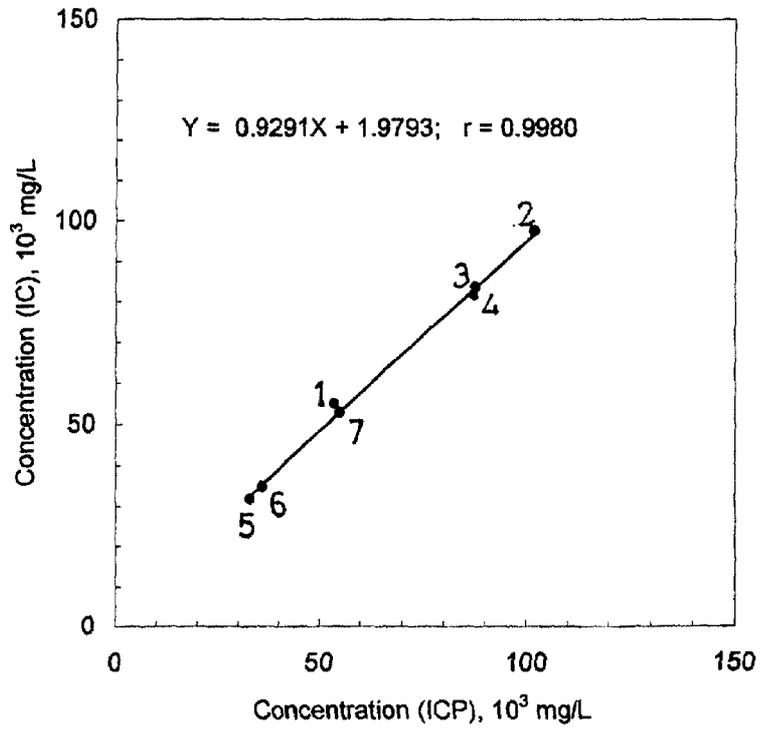


Fig. 8 Correlation between the ICP and IC methods for determination of sodium in the oil-field waters.

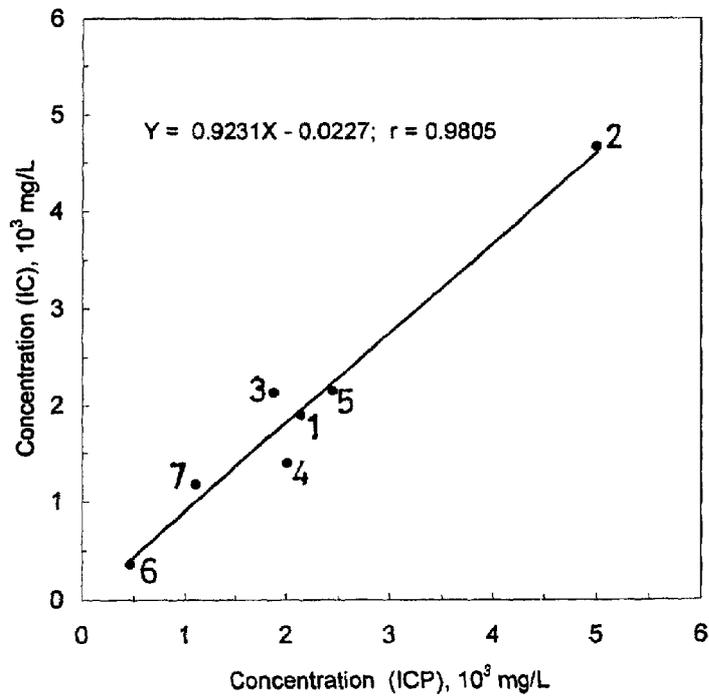


Fig. 9. Correlation between the ICP and IC methods for determination of potassium in the oil-field waters.

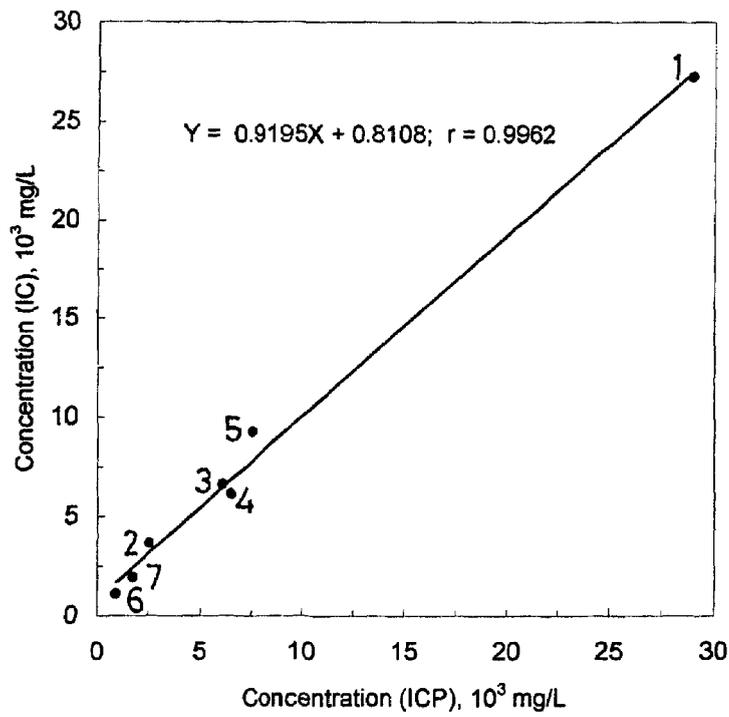


Fig. 10. Correlation between the ICP and IC methods for determination of magnesium in the oil-field waters.

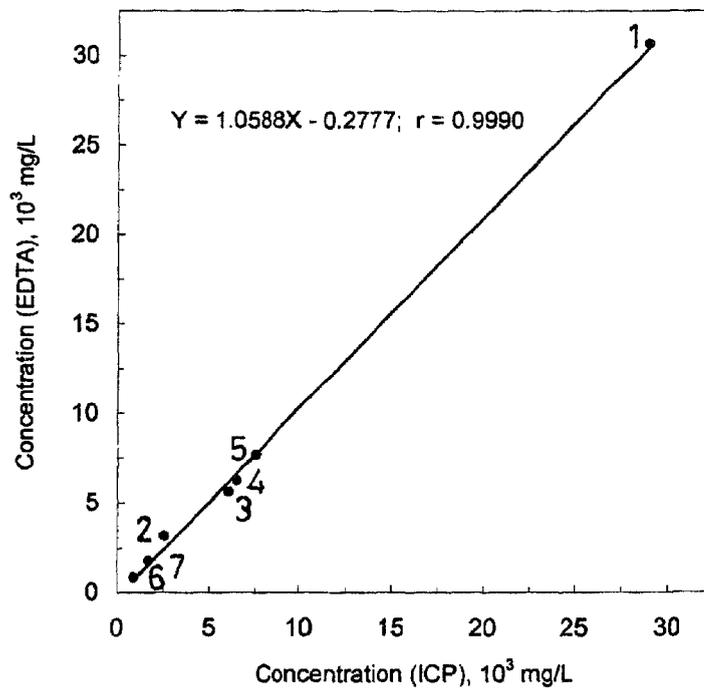


Fig. 11. Correlation between the ICP and EDTA methods for determination of magnesium in the oil-field waters.

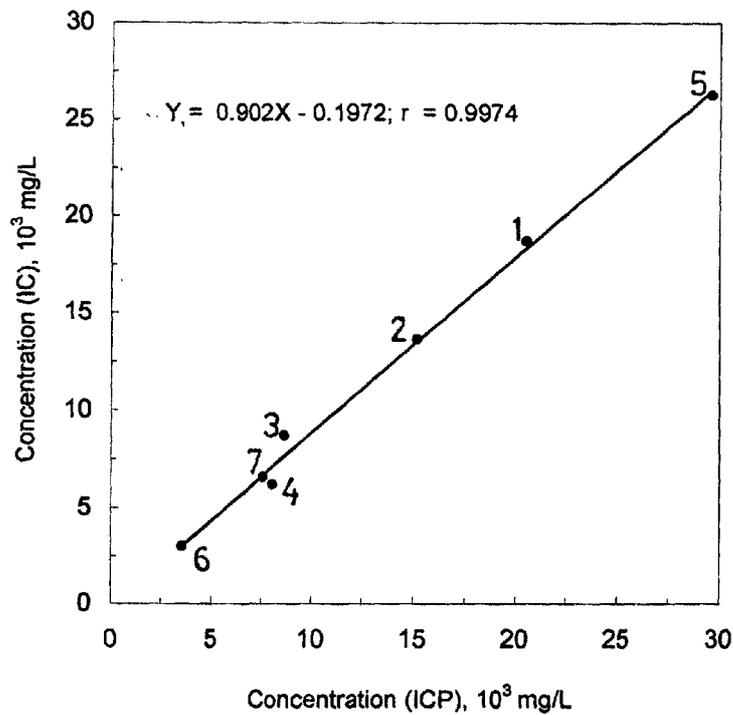


Fig. 12. Correlation between the ICP and IC methods for determination of calcium in the oil-field waters.

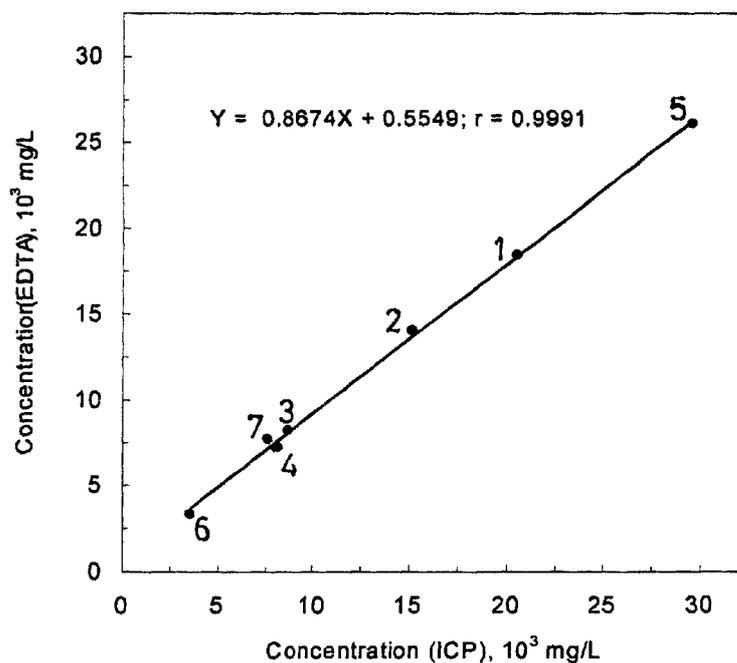


Fig. 13. Correlation between the ICP and EDTA methods for determination of calcium in the oil-field waters.

To overcome the slight discrepancies or lack of agreement between the results given by the three analytical techniques applied for the determination of sodium, potassium, magnesium and calcium cations, the ICP-AES with the method of standard additions (to get rid of matrix interference) has been applied, and the results are given in Table 4. These results are compared with those of the ICP direct method, which indicate very strong correlation ($r = 0.991$ to 1.000), but with very slight association as shown in Figs. 14 to 17.

It is noticed that lithium cation is about 30, 60, 150 and 160 mg/L in the water samples 6 and 7, 1, 3 and 4, 5 and 2, respectively. Potassium and sodium cations vary from nearly 360 to 4730 and 31600 to 98900 mg/L, respectively. For the alkaline earth cations, their concentrations (mg/L) are in the range of about 830 to 5960 (except the sample No.1, being 27800) for magnesium, 3260 to 8630 (except the sample Nos. 2, 1 and 5, being 14000, 19500 and 26600 respectively) for calcium, 85 to 690 for strontium, and 1 to 9 for barium. Thus, concentrations of total cations in the studied water samples vary from nearly 40000 to 121000 mg/L.

3.5. Determination of Boron, Iron, and Manganese in the Oil-Field Waters

Boron, iron, and manganese have been determined in the examined oil-field waters using different procedures. Their concentrations are presented in Table 5.

Boron has been determined by the mannitol titration method [1, 3] to give total, inorganic and organic boron, and by the carminic acid colourimetric method [1, 2] to give only total boron. Results given by both techniques are very strongly correlated ($r = 1.000$) as shown in Fig. 18.

In the studied formation waters, the total boron concentrations range from approximately 16 to 65 mg/L in the sample Nos. 2-7. However, the sample No.1 has a high value, being about 330 mg/L. The inorganic boron is the main constituent of the total boron, and the organic boron is present in very low concentrations, from nearly zero up to 4 mg/L.

Iron has been determined by the spectrophotometric *o*-phenanthroline method [1, 2], as well as the inductively coupled plasma-atomic emission spectrometric method [1, 2]. Results obtained by both methods are very strongly correlated ($r = 1.000$) as shown in Fig. 19.

In the investigated waters, iron concentrations are in the order of 0.1 to 0.3 mg/L in the water Nos. 3, 4, 6 and 7. However, they are about 6, 60 and 550 mg/L in the water Nos. 1, 2 and 5, respectively. This may be explained by the fact that these waters are acidic, having pH 5.1, 4.3, and 3.8 (Table 2) as well as acidity of about 1100, 900 and 1870 mg/L as CaCO_3 , respectively.

Manganese has been carried out by the inductively coupled plasma-atomic emission spectrometric method [1, 2]. Its concentrations in the examined oil-field waters are in the range of 1 to 17 mg/L in the sample Nos. 3, 4, 6, and 7. It has higher values in the other three samples, being 52, 65 and 181 mg/L in the water Nos.1, 2 and 5 respectively.

Table 4. Alkali and Alkaline Earth Cations in the Oil-Field Waters Determined by the ICP-AES with Standard Additions Method.

Concentration, mg/L	Water Sample No.						
	1	2	3	4	5	6	7
Lithium, Li ⁺							
- St. 1	57.9	156	56.4	56.1	152	29.9	31.8
- St. 2	60.0	156	57.0	58.4	149	29.7	32.4
- Av.	59.0	156	56.7	57.3	151	29.8	32.1
Sodium, Na ⁺							
- St. 1	59880	99188	85898	79975	32181	35033	50593
- St. 2	58592	98571	88104	82159	31034	35523	52387
- Av.	59236	98880	87001	81067	31608	35278	51490
Potassium, K ⁺							
- St. 1	1959	4726	1807	1774	2382	365	1186
- St. 2	1924	4728	1775	1734	2302	357	1147
- Av.	1942	4727	1791	1754	2342	361	1167
Magnesium, Mg ²⁺							
- St. 1	27633	2377	5435	5994	7021	833	1342
- St. 2	27981	2427	5755	5925	6862	818	1376
- Av.	27807	2402	5595	5960	6942	826	1359
Calcium, Ca ²⁺							
- St. 1	19410	14018	8555	7674	27119	3235	6581
- St. 2	19678	13909	8710	7773	26102	3295	6749
- Av.	19544	13964	8633	7724	26611	3265	6665
Strontium, Sr ²⁺							
- St. 1	683	328	265	255	605	83	252
- St. 2	696	339	258	261	616	87	262
- Av.	690	334	262	258	611	85	257
Barium, Ba ²⁺							
- St. 1	8.51	5.85	1.86	1.41	6.00	1.24	2.27
- St. 2	8.91	6.03	1.99	1.47	5.42	1.28	2.20
- Av.	8.71	5.94	1.93	1.44	5.71	1.26	2.24
Total cations (Av.)	109287	120469	103341	96822	68271	39846	60972

St. 1, St. 2 and Av.: Standard addition 1, Standard addition 2 and average, respectively.

Table 5. Boron, Iron and Manganese in the Oil-Field Waters Using Different Determination Techniques.

Concentration, mg/L	Water Sample No.						
	1	2	3	4	5	6	7
Boron							
- Carminic method							
- Total	339.2	31.1	42.2	44.6	66.2	18.5	14.9
- Mannitol method							
- Inorganic	325.4	32.5	41.0	41.4	59.9	19.7	17.5
- Organic	0.0	3.1	0.0	1.7	3.9	0.3	0.1
- Total	325.4	35.6	41.0	43.1	63.8	20.0	17.6
- Total (Av.)	332.3	33.4	41.6	43.8	65.0	19.2	16.2
Iron							
- ICP-AES	6.55	63.4	0.088	0.243	528.6	0.068	0.067
- <i>o</i> -Phenanthroline	6.73	64.4	0.107	0.283	574.8	0.146	0.098
- Av.	6.64	63.9	0.098	0.263	551.7	0.107	0.082
Manganese							
- ICP-AES	51.9	65.0	17.0	10.0	181.0	2.49	1.45

Av.: Average.

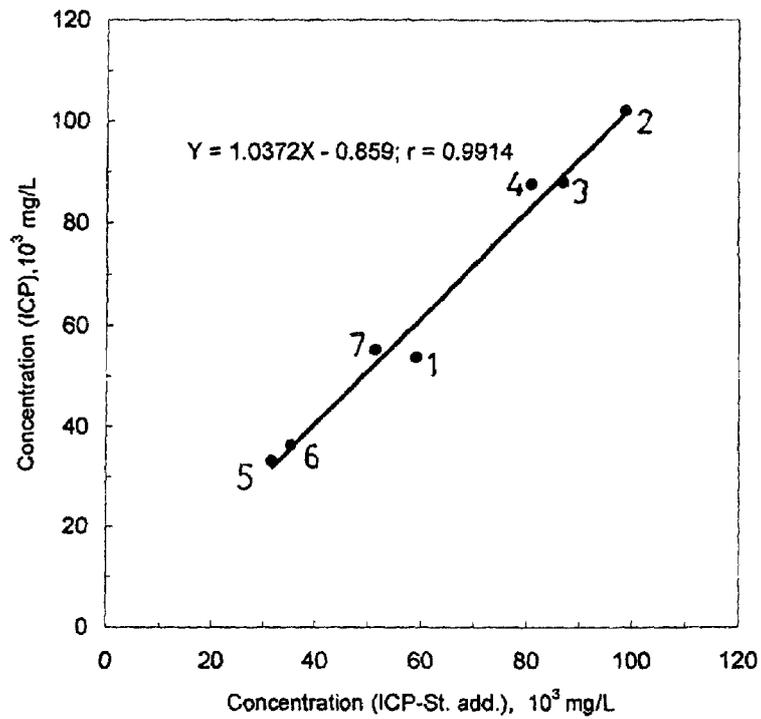


Fig. 14 . Correlation between the ICP-standard additions and ICP methods for determination of sodium in the oil-field waters.

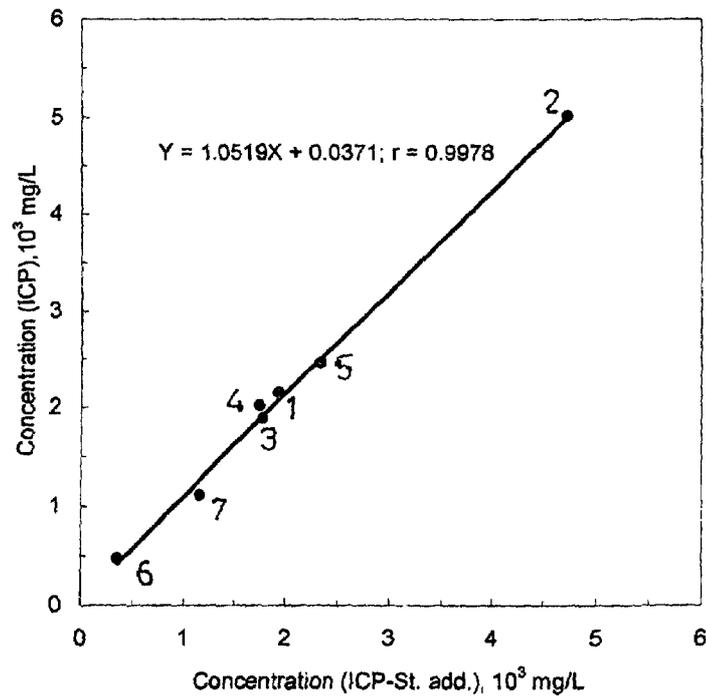


Fig. 15. Correlation between the ICP-standard additions and ICP methods for determination of potassium in the oil-field waters.

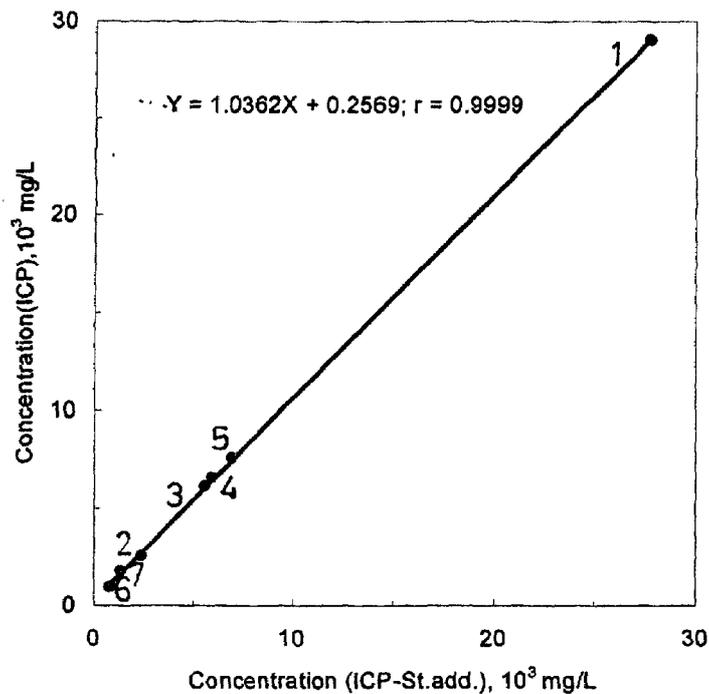


Fig. 16. Correlation between the ICP-standard additions and ICP methods for determination of magnesium in the oil-field waters.

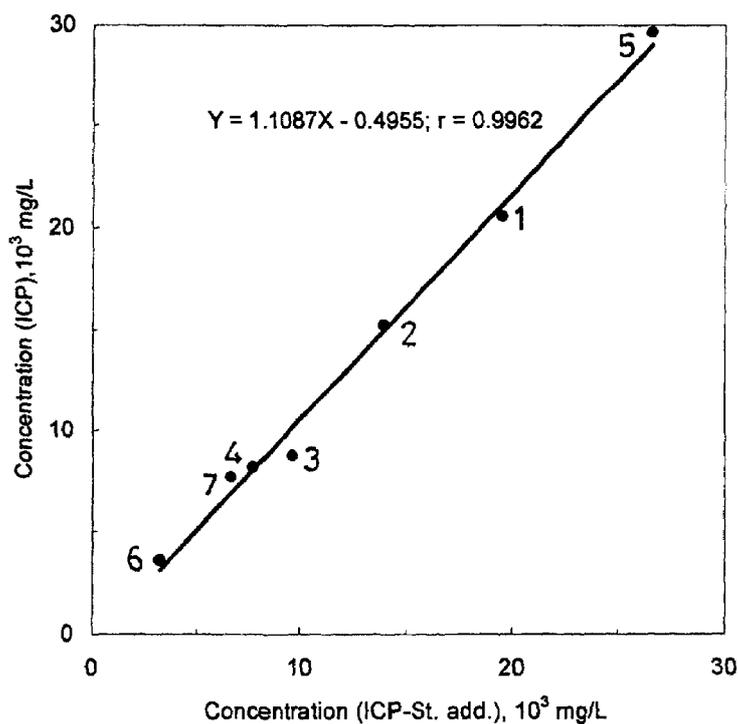


Fig. 17. Correlation between the ICP-standard additions and ICP methods for determination of calcium in the oil-field waters.

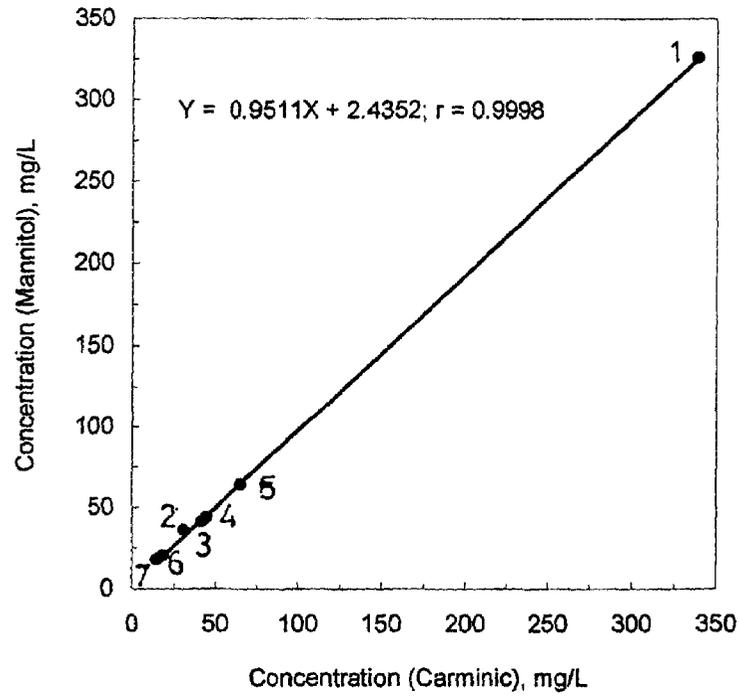


Fig. 18. Correlation between the carminic and mannitol methods for determination of boron in the oil-field waters.

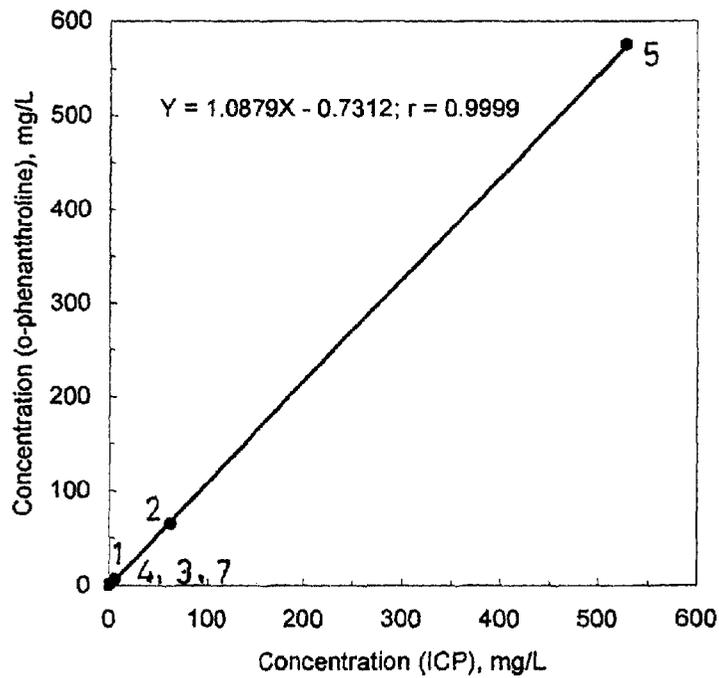


Fig. 19. Correlation between the ICP and *o*-phenanthroline methods for determination of iron in the oil-field waters.

3.6. Determination of Anions in the Oil-Field Waters

Anions, including the halides (F^- , Cl^- , Br^- , I^-), sulphate (SO_4^{2-}), nitrate (NO_3^-), bicarbonate (HCO_3^-) and borate (BO_3^{3-}) have been determined by various procedures. Ion chromatography [1, 2, 292] is applied to give individual halides (F^- , Cl^- , Br^-), while argentometric titration [1-5] yields total halides ($Cl^- + Br^- + I^-$), and colourimetric method [1] determines both the bromide and iodide. The sulphate is carried out by gravimetry [1-5], whereas the nitrate by ultraviolet spectrometry [2]. The bicarbonate is estimated by potentiometric titration [1-3], and the borate is calculated from the boron determined [1-3]. The obtained results of these analyses for anions in the studied oil-field water samples are given in Table 6, and their ion chromatograms are shown in Fig. 20.

It may be noted that the chloride has been determined by two techniques, i.e. ion chromatography and argentometric titration (after subtraction of both bromide and iodide). Both gave results that are very strongly associated, with a correlation coefficient of one ($r = 1.000$) as shown in Fig. 21.

On the other hand, the bromide has been also analyzed by two procedures, i.e. ion chromatography and colourimetry. Both gave results that are also in good agreement, as they are very strongly correlated with a correlation coefficient of about one ($r = 0.999$) as shown in Fig. 22.

The fluoride is present in minor concentrations, being in the range of about 20 to 100 mg/L, while the chloride is found in very high ones ranging from nearly 63000 to 206000 mg/L. The bromide has high values of about 280 to 2520 mg/L. On the other hand the iodide is found in very minor contents, being in the range of approximately 1 to 3 mg/L in five water samples, and 11 and 17 mg/L in two samples (Nos. 1 and 5 respectively).

The predominance occurrence of the halides in the examined water samples indicates that the chloride has the highest figures, followed by the bromide, then the fluoride, and finally the iodide.

The sulphate is present in the range of about 740 to 1580 mg/L in the seven studied water samples. However, the nitrate is present in very minor concentrations, varying from nearly 2 to 6 mg/L in five samples, and about 20 mg/L in two samples (Nos. 1 and 5).

The bicarbonate is only found in four samples, varying from 30 to 300 mg/L. On the other hand, the borate occurs in all the seven samples, being about 90 to 350 mg/L in six samples and 1810 mg/L in the sample No. 1.

Concerning the total anions in the water samples examined, they are in the range of approximately 65000 to 211000 mg/L. The sample No.1 has the highest concentrations, and the sample No. 6 the lowest one. The chloride has the highest values followed by those of the bromide or sulphate, borate, bicarbonate, fluoride, nitrate and iodide.

Table 6. Anions in the Oil-Field Waters Using Different Determination Techniques.

Concentration, mg/L	Water Sample No.						
	1	2	3	4	5	6	7
Fluoride, F ⁻							
- Ion chromatography	101	33.0	33.6	21.6	28.0	46.0	22.0
Chloride, Cl ⁻							
- Ion chromatography	205427	189085	166134	158618	121048	63087	95110
- Titration (Cl ⁻ + Br ⁻ + I ⁻)	208662	190979	167401	159149	122603	63188	95882
- Titration (Cl ⁻)	206136	190058	166439	158335	120385	62905	95491
- Av.	205782	189572	166286	158476	120716	62996	95300
Bromide, Br ⁻							
- Ion chromatography	2575	907	971	818	2279	283	395
- Colourimetric	2454	928	946	806	2122	281	382
- Av.	2515	918	959	812	2201	282	389
Iodide, I ⁻							
- Colourimetric	10.9	2.68	2.53	1.79	16.6	1.19	1.64
Sulphate, SO ₄ ²⁻							
- Gravimetric	736	1577	1054	1072	818	1245	807
Nitrate, NO ₃ ⁻							
- UV spectrometry	19.6	2.34	5.73	5.23	21.5	4.63	5.04
Bicarbonate, HCO ₃ ⁻							
- Titration	0	0	78.5	32.9	0.0	302	172
Borate, BO ₃ ³⁻							
- Calculated from B	1808	182	226	238	354	104	88
Total anions (Av.)	210972	192287	168645	160660	124155	64981	96785

Titration (Cl⁻) = Titration (Cl⁻ + Br⁻ + I⁻) - Av. (Br⁻ + I⁻).

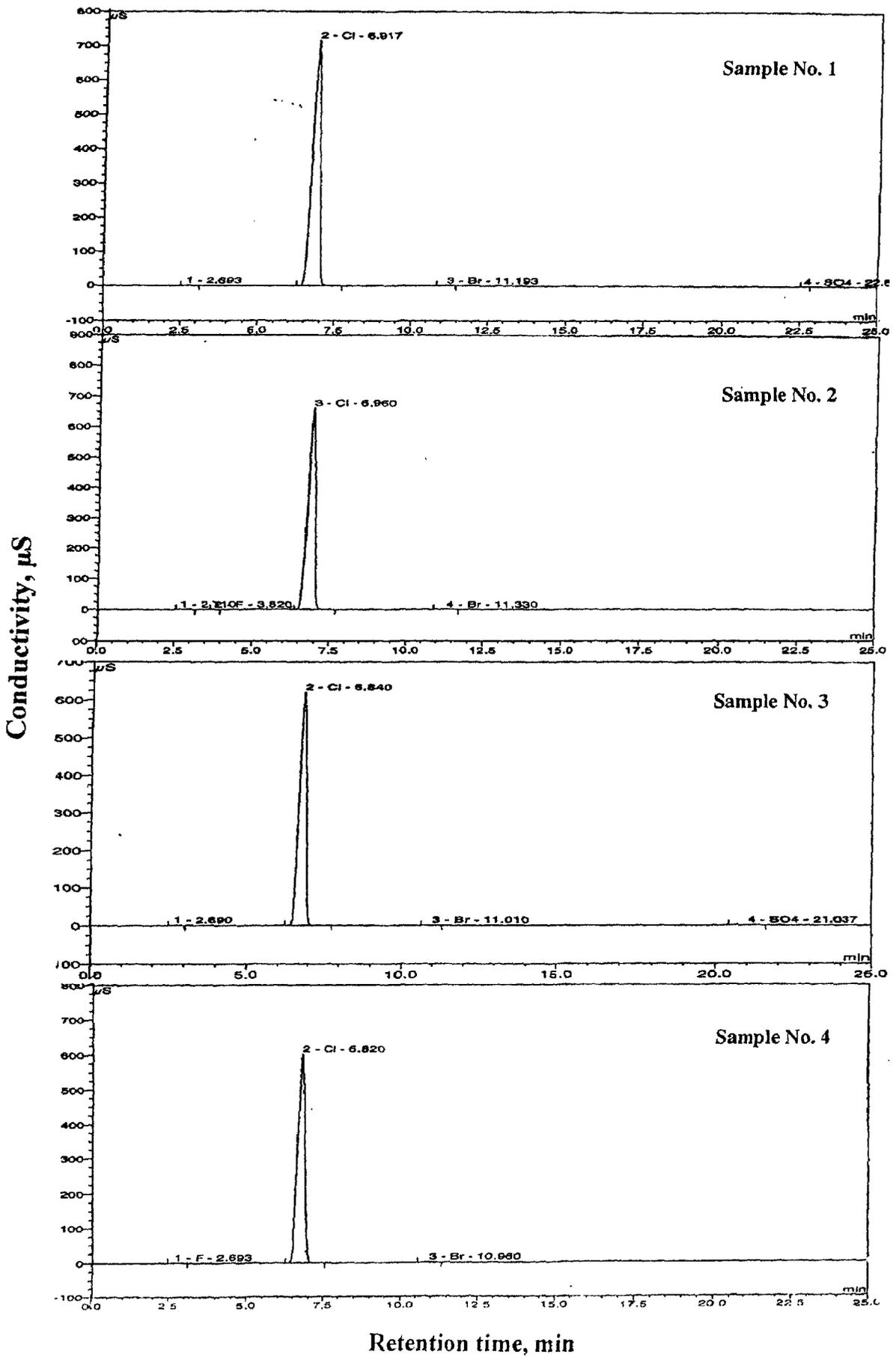


Fig. 20. Ion chromatograms of the anions in the oil-field waters.

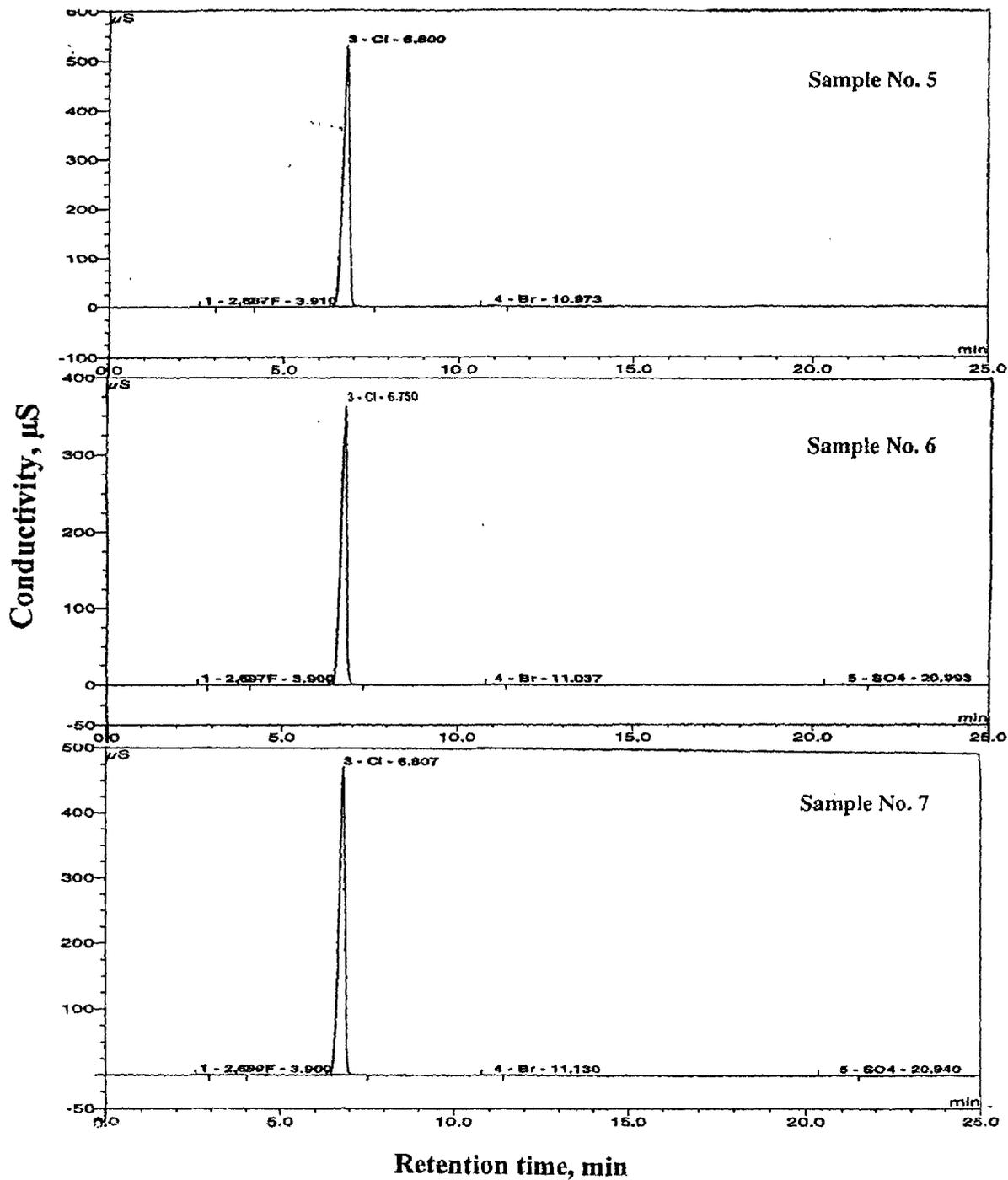


Fig. 20. Continued.

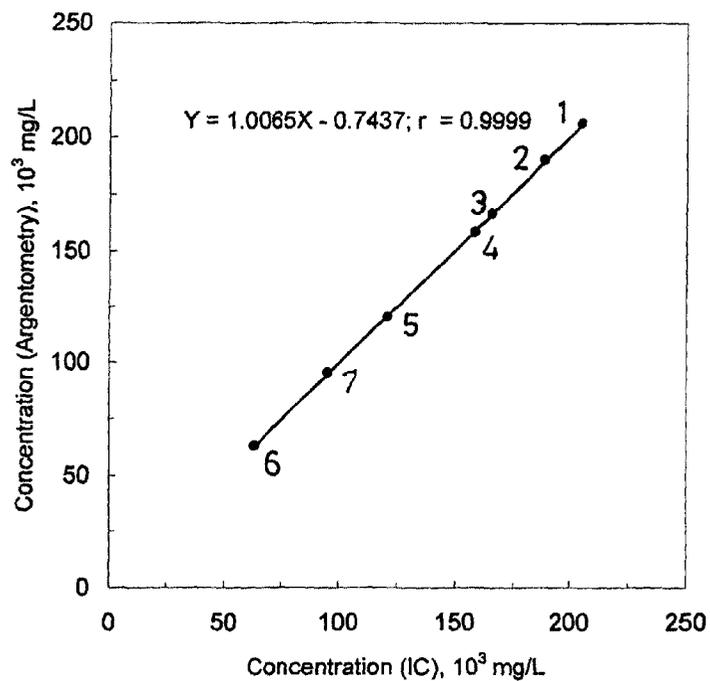


Fig. 21. Correlation between the IC and argentometric methods for determination of chloride in the oil-field waters.

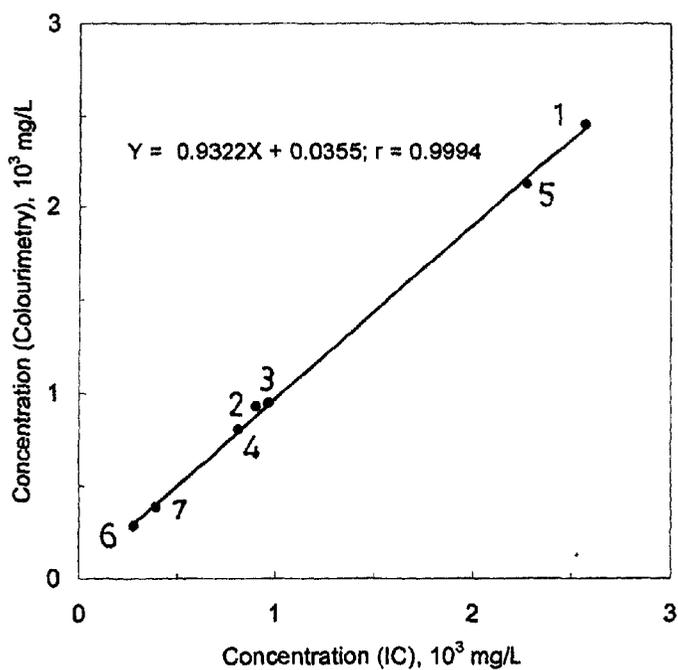


Fig. 22. Correlation between the IC and colourimetric methods for determination of bromide in the oil-field waters.

3.7. Reaction Values of the Cations and Anions in the Oil-Field Waters

Reaction values of the cations and anions in waters are estimated from their determined concentrations by multiplying them with their reaction coefficients (valences per relative atomic or molecular masses).

Average concentrations, in milligrams per litre (mg/L), of the determined cations and anions in the studied water samples as given in Tables 4 to 6, are summarized in Table 7 and represented graphically by Schoeller diagram in Fig. 23.

3.7.1. Reaction values (me/L)

The reaction values, in milliequivalents per litre (me/L), of the cations and anions in the studied water samples are calculated from their determined concentrations, in milligrams per litre (mg/L), by multiplying with their reaction coefficients. The results obtained, are given in Table 8 and represented graphically by the Schoeller [410] diagram in Fig. 24, as well as by the Tickell [430], modified Tickell [431] and Stiff [432] diagrams in Figs. 25.

Reaction values of the alkalis, i.e. sodium, potassium and lithium cations, in the water samples under study are in the order of about 1370 to 4300, 10 to 120, and 4 to 22 me/L, respectively. The highest values of the three alkali cations are present in the sample No. 2, and the lowest ones in the sample No. 6.

The alkaline earths, i.e. Mg, Ca, Sr and Ba cations, are in the range of nearly 70 to 2290, 160 to 1330, 2 to 16, and 0.02 to 0.1 me/L, respectively. The water sample No. 1 has the highest values of Mg, Sr and Ba cations, while the sample No. 6 the lowest values of Ca, Mg, Sr and Ba cations.

Concerning the occurrence of both Mg and Ca cations in the water samples, the former has higher reaction values in the three sample Nos. 1, 3 and 4, while the latter the higher ones in the other four samples, i.e. Nos. 2 and 5 to 7.

Both the iron and manganese cations are generally present in minor values in the examined water samples. The iron is less than 0.01 me/L in four samples and about 0.1, 2 and 20 me/L in the sample Nos. 1, 2 and 5 which may indicate corrosion in their productive wells. On the other hand, manganese is less than 0.1 me/L in two samples, about 0.4 and 0.6 me/L in two samples and 2 to 7 me/L in the other three samples (Nos. 1, 2 and 5).

The reaction values of the total cations in the examined water samples are in the order of 1750 to 5920 me/L. The sample No.1 has the highest values, while No.6 the lowest ones, and Nos. 2 to 5 and 7 the medium values.

Concerning the reactions values of anions in the studied water samples, the halides having the range of : 1780 to 5800, 3.5 to 32, 1.1 to 5.3 and 0.01 to 0.1 me/L for the chloride, bromide, fluoride and iodide anions, respectively.

Table 7. Determined Cations and Anions (mg/L) in the Oil-Field Waters

Concentration, mg/L	Water Sample No.						
	1	2	3	4	5	6	7
Cations:							
- Li ⁺	59.0	156	56.7	57.3	151	29.8	32.1
- Na ⁺	59236	98880	87001	81067	31608	35278	51490
- K ⁺	1942	4727	1791	1754	2342	361	1167
- Mg ²⁺	27807	2402	5595	5960	6942	826	1359
- Ca ²⁺	19544	13964	8633	7724	26611	3265	6665
- Sr ²⁺	690	334	262	258	611	85	257
- Ba ²⁺	8.71	5.94	1.93	1.44	5.71	1.26	2.24
- Fe ²⁺	6.64	63.9	0.098	0.263	551.7	0.107	0.082
- Mn ²⁺	51.9	65.0	17.0	10.0	181.0	2.49	1.45
- Total	109346	120598	103358	96832	69004	39849	60973
Anions:							
- F ⁻	101	33.0	33.6	21.6	28	46	22.0
- Cl ⁻	205782	189572	166286	158476	120716	62996	95300
- Br ⁻	2515	918	959	812	2201	282	389
- I ⁻	10.9	2.68	2.53	1.79	16.6	1.19	1.64
- SO ₄ ²⁻	736	1577	1054	1 072	818	1245	807
- NO ₃ ⁻	19.6	2.34	5.73	5.23	21.5	4.63	5.04
- HCO ₃ ⁻	0	0	78.5	32.9	0	302	172
- BO ₃ ³⁻	1808	182	226	238	354	104	88
- Total	210972	192287	168645	160660	124155	64981	96785

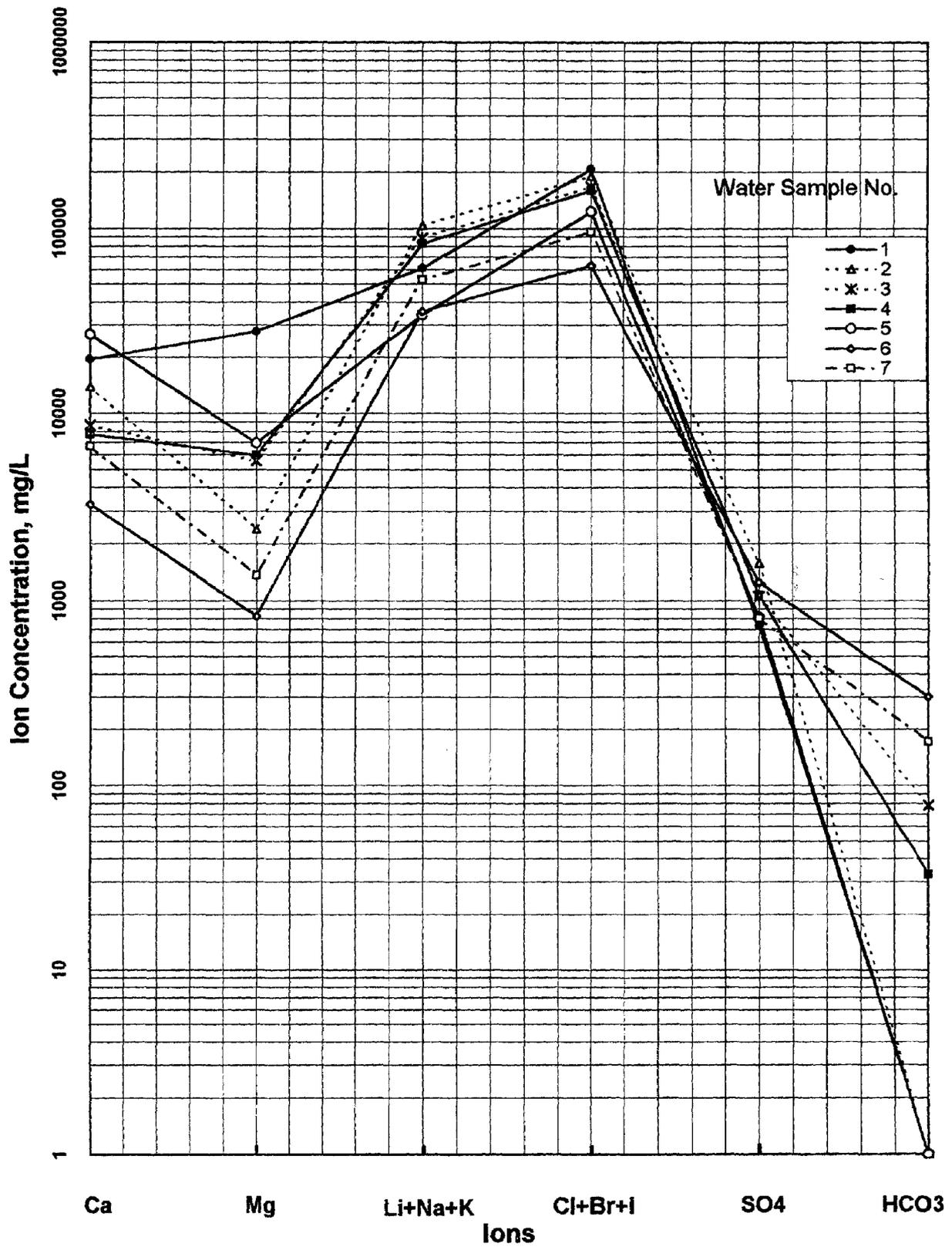


Fig. 23 . Graphical representation of the ion concentrations (mg/L) in the oil-field waters by Schoeller diagram.

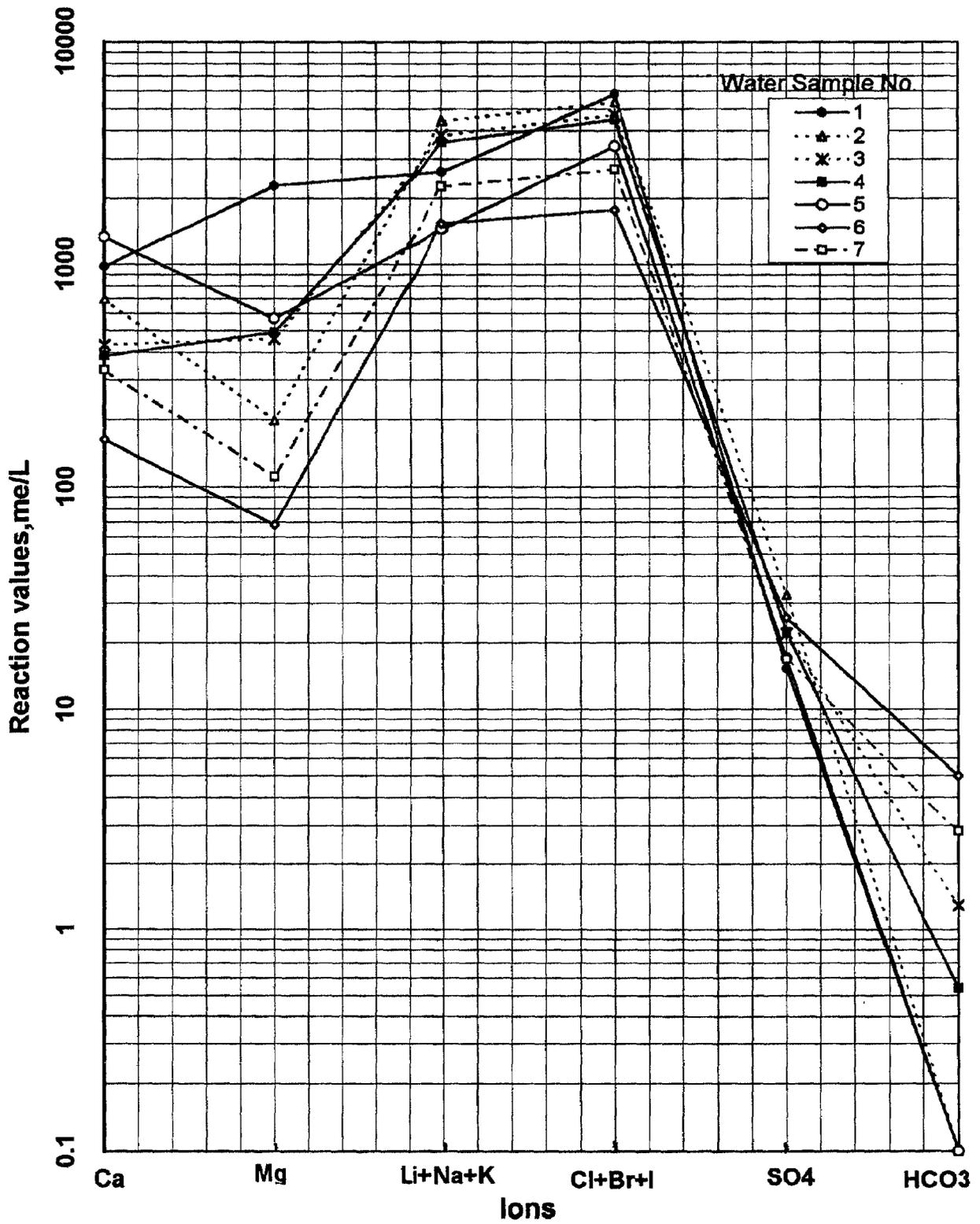


Fig. 24 . Graphical representation of the Ion reaction values (me/L) in the oil-field waters by Schoeller diagram.

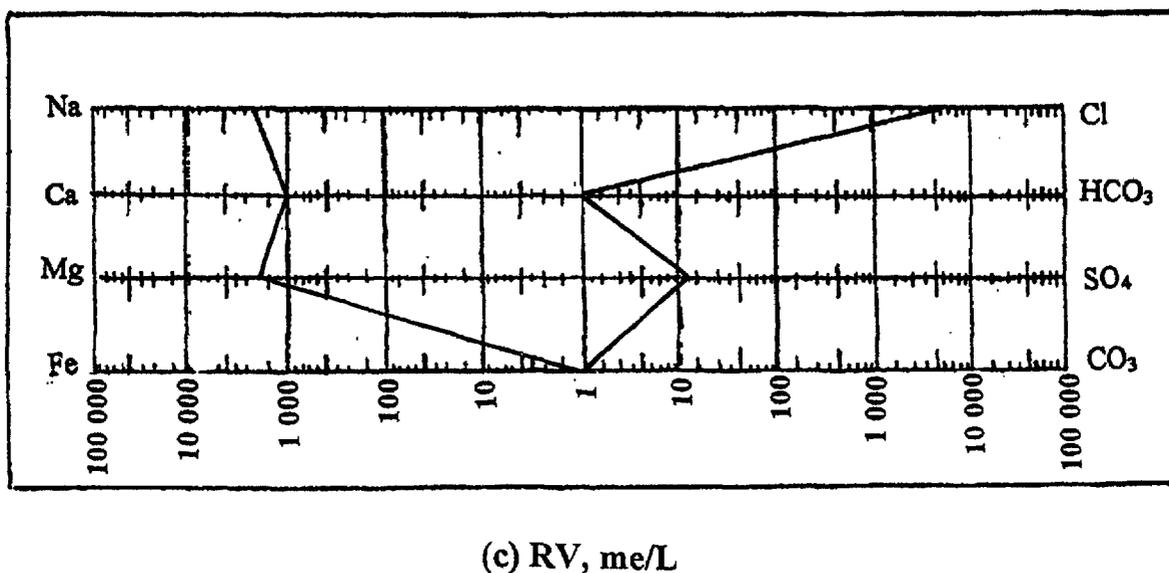
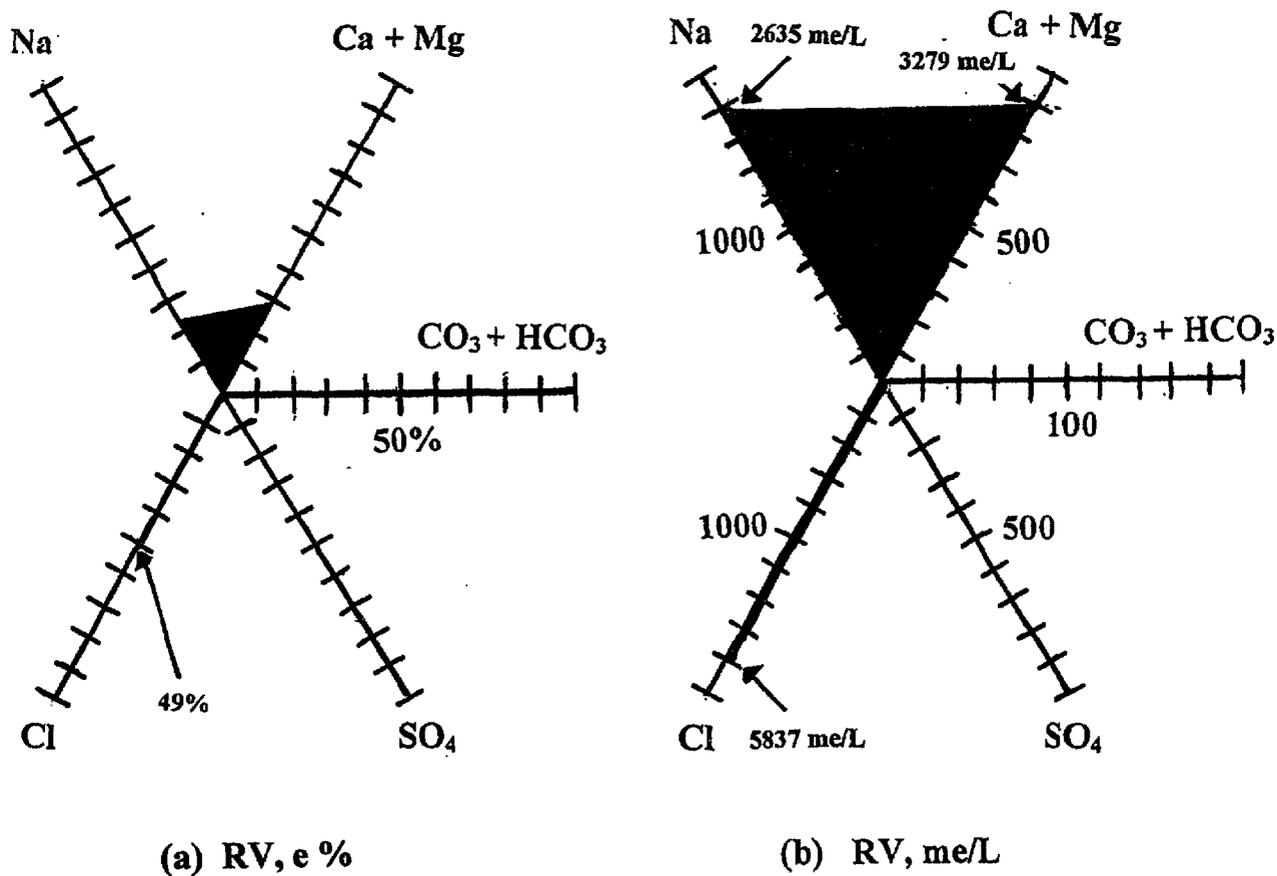


Fig. 25. Graphical representation of the ion reaction values (RV) in sample No. 1 by Tickell (a), modified Tickell (b), and Stiff (c) diagrams.

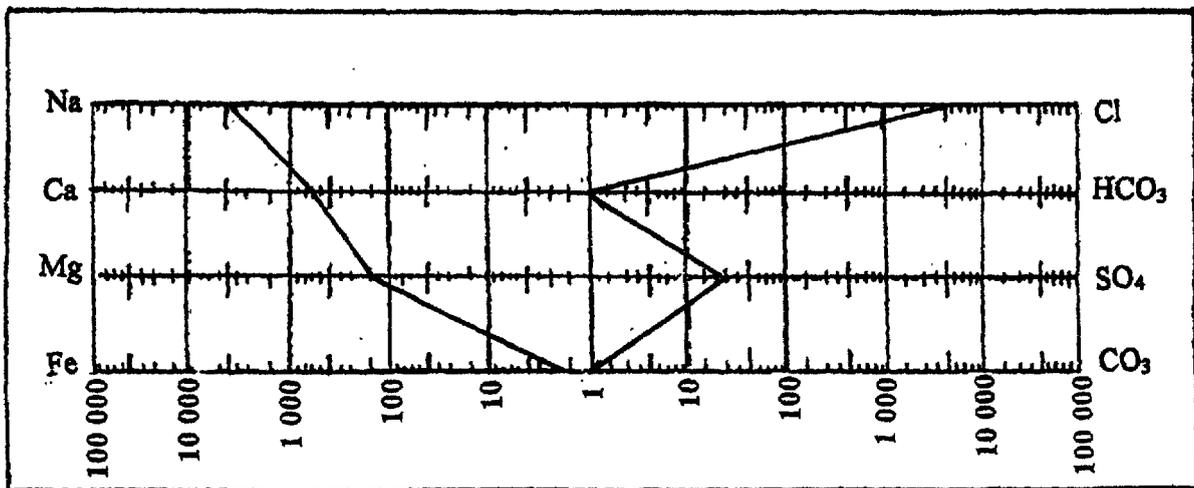
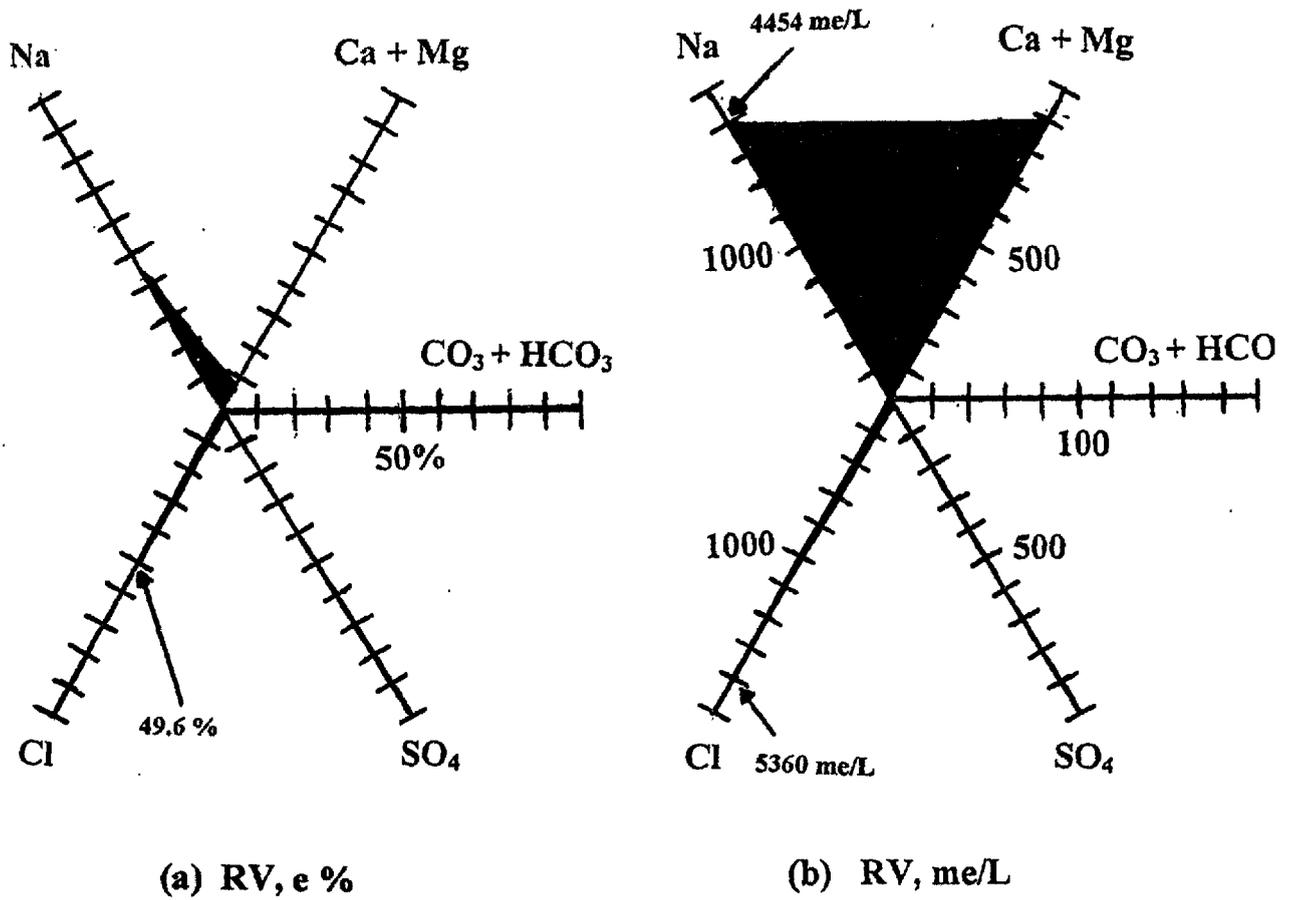
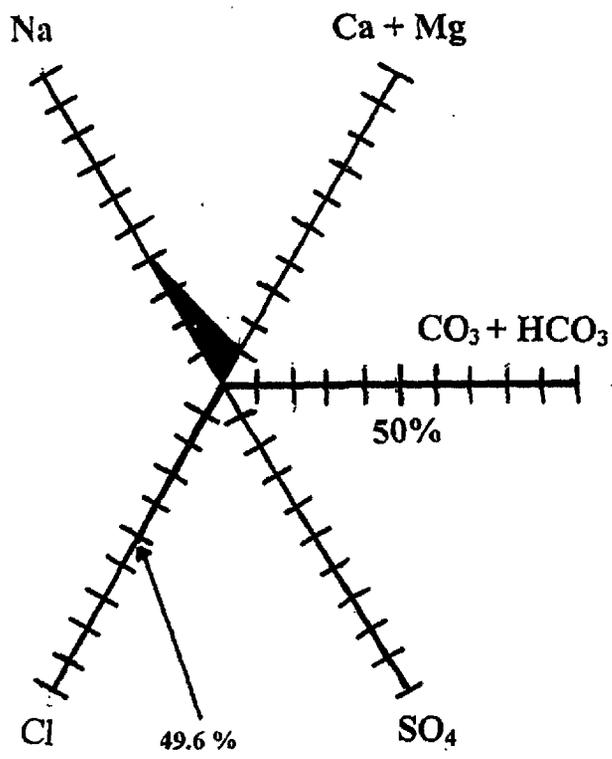
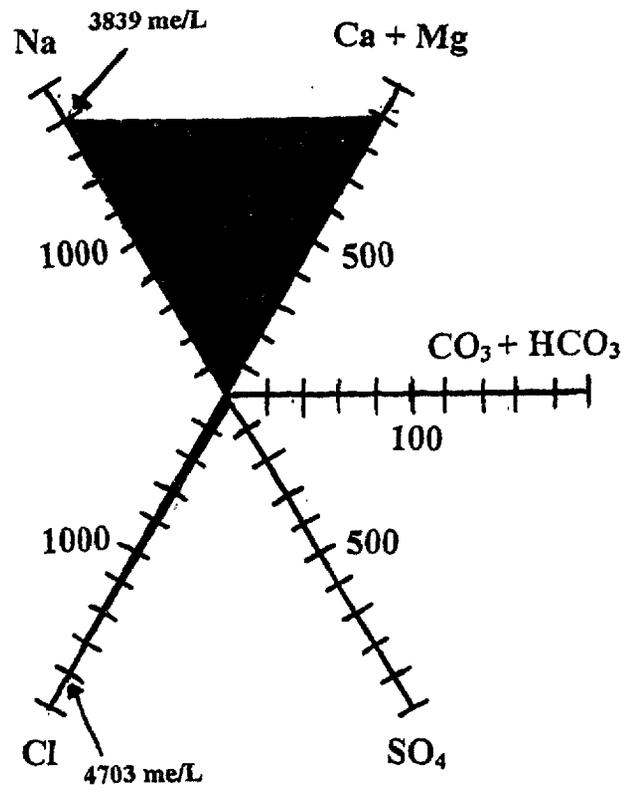


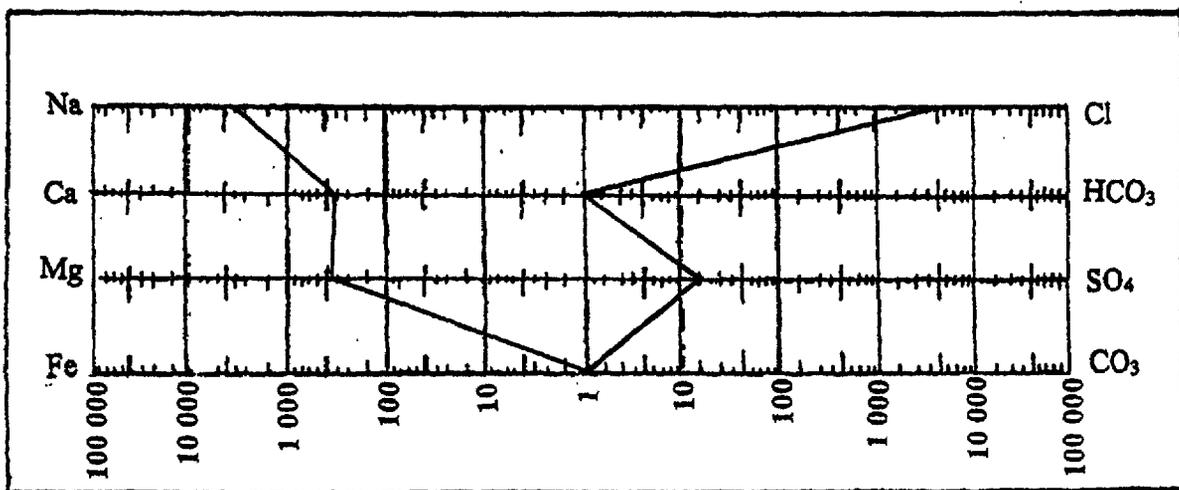
Fig. 25. Graphical representation of the ion reaction values (RV) in sample No. 2 by Tickell (a), modified Tickell (b), and Stiff (c) diagrams.



(a) RV, e %

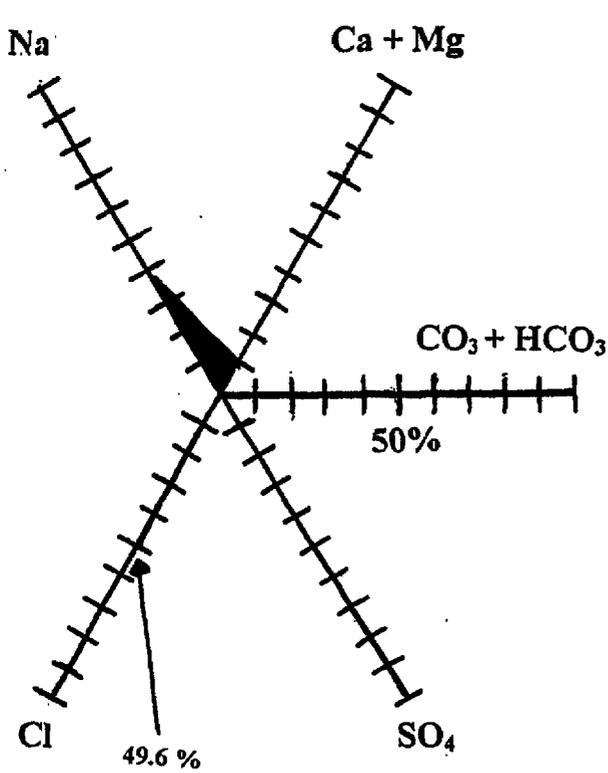


(b) RV, me/L

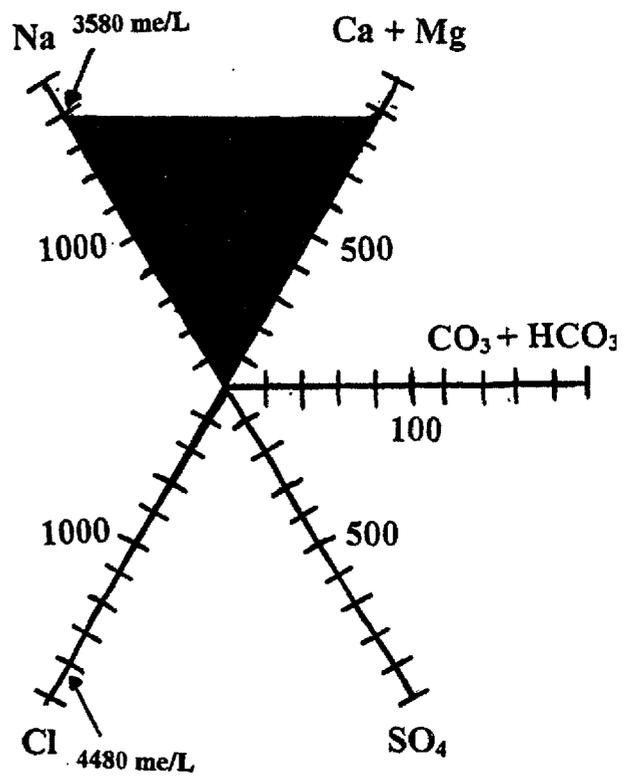


(c) RV, me/L

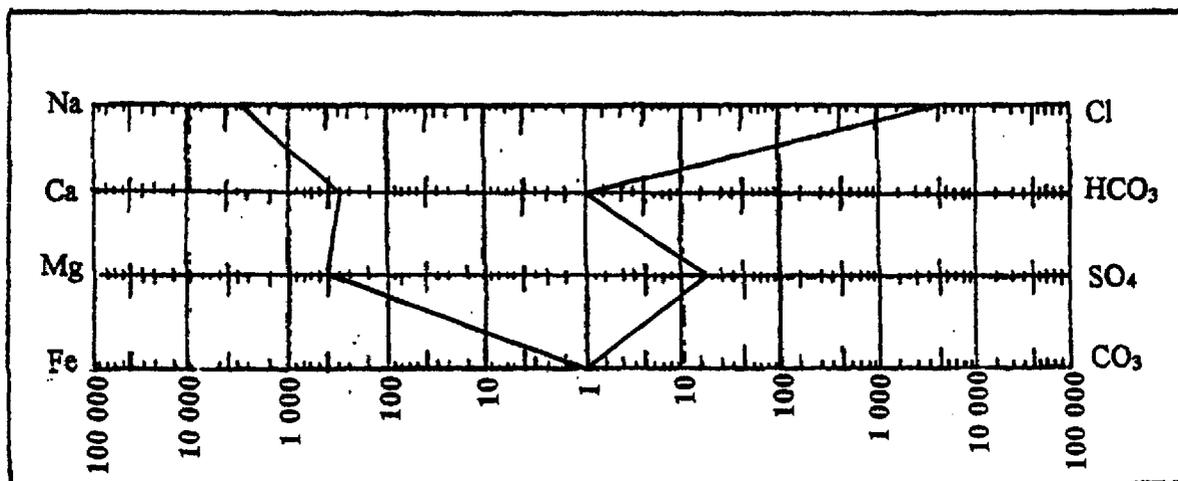
Fig. 25. Graphical representation of the ion reaction values (RV) in sample No. 3 by Tickell (a), modified Tickell (b), and Stiff (c) diagrams.



(a) RV, e %



(b) RV, me/L



(c) RV, me/L

Fig. 25. Graphical representation of the ion reaction values (RV) in sample No. 4 by Tickell (a), modified Tickell (b), and Stiff (c) diagrams.

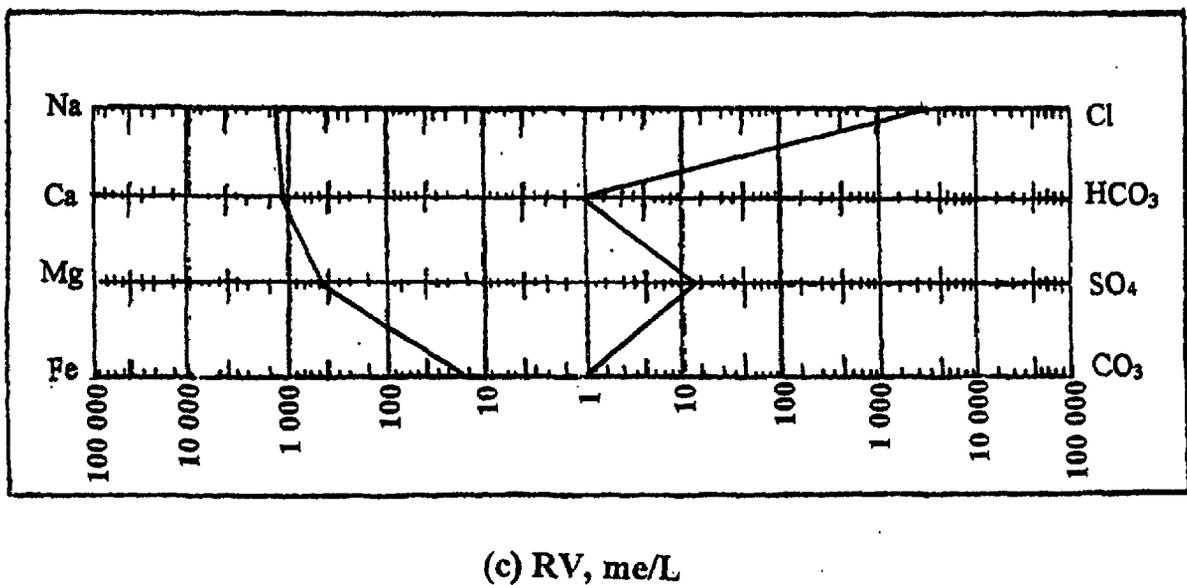
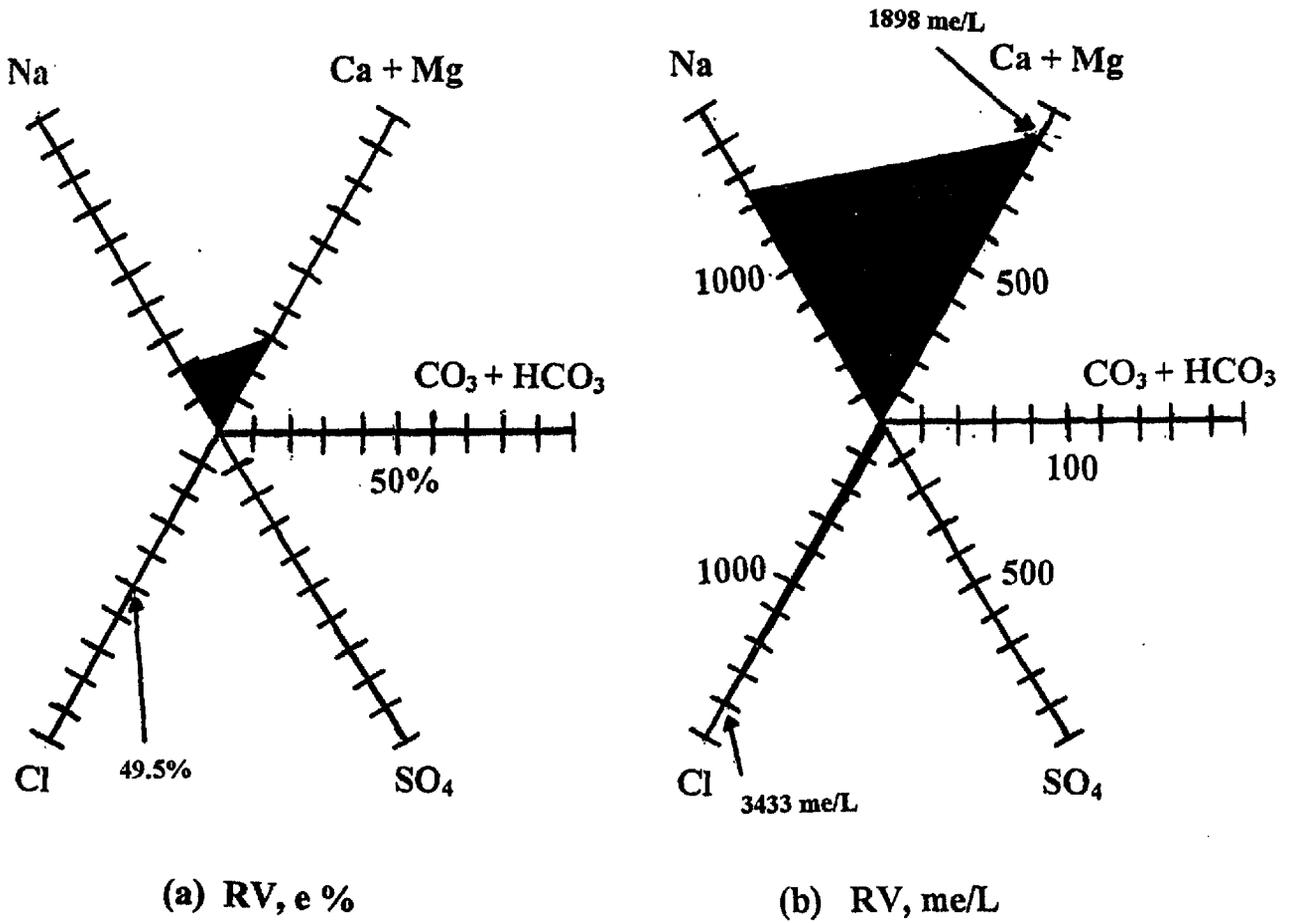


Fig. 25. Graphical representation of the ion reaction values (RV) in sample No. 5 by Tickell (a), modified Tickell (b), and Stiff (c) diagrams.

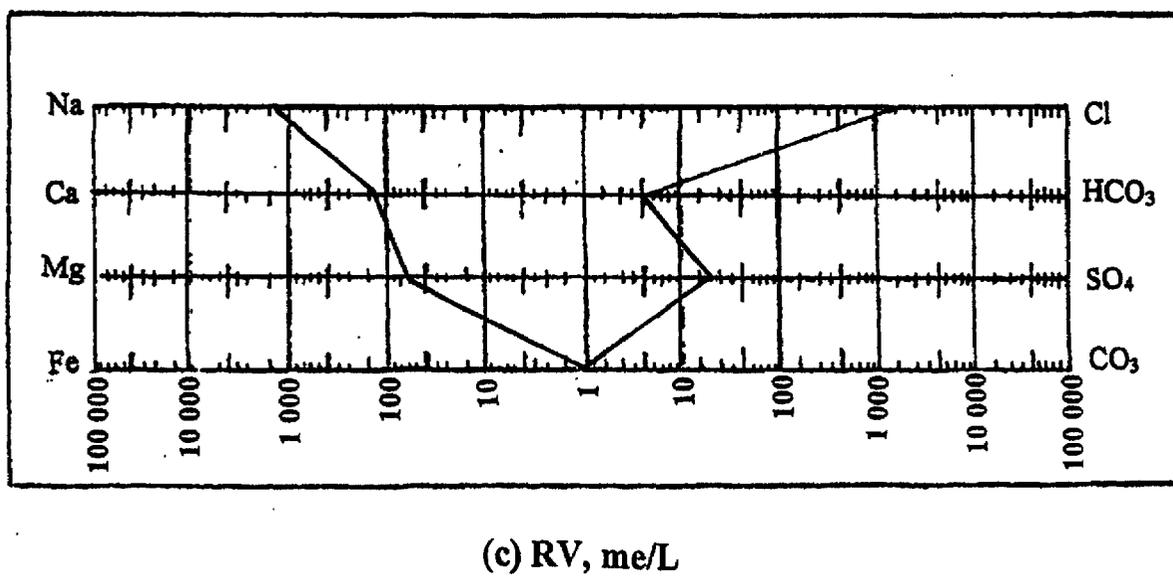
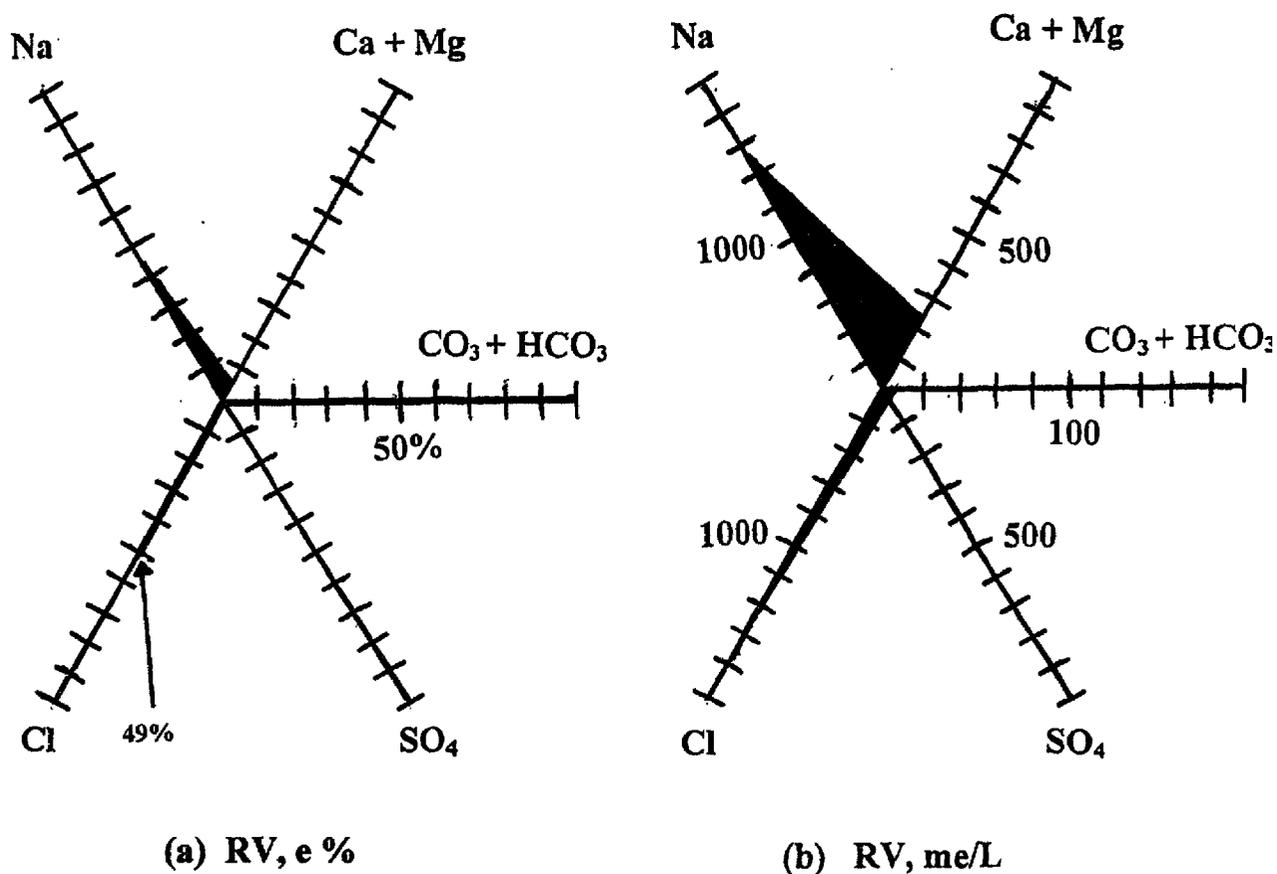


Fig. 25. Graphical representation of the ion reaction values (RV) in sample No. 6 by Tickell (a), modified Tickell (b), and Stiff (c) diagrams.

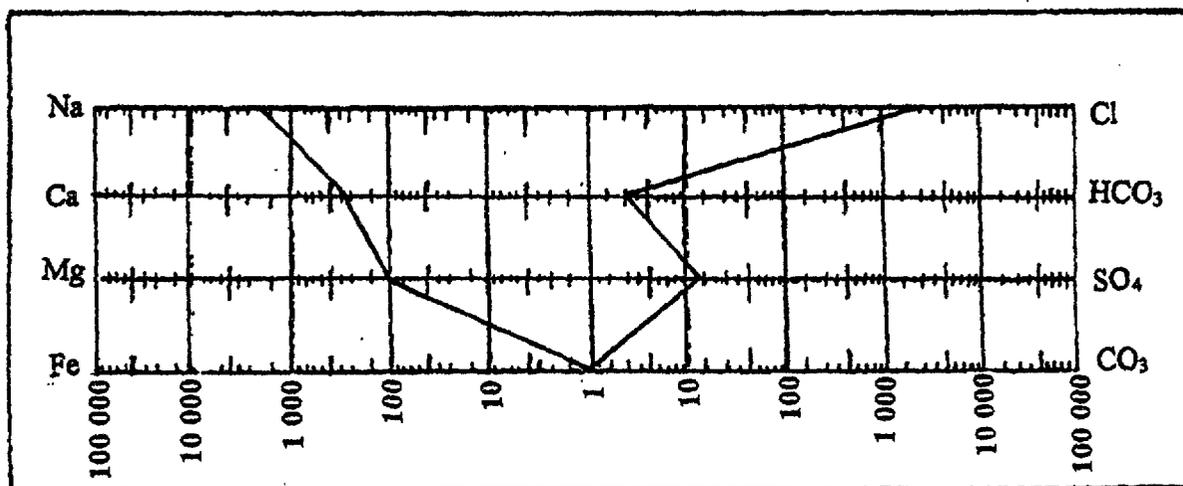
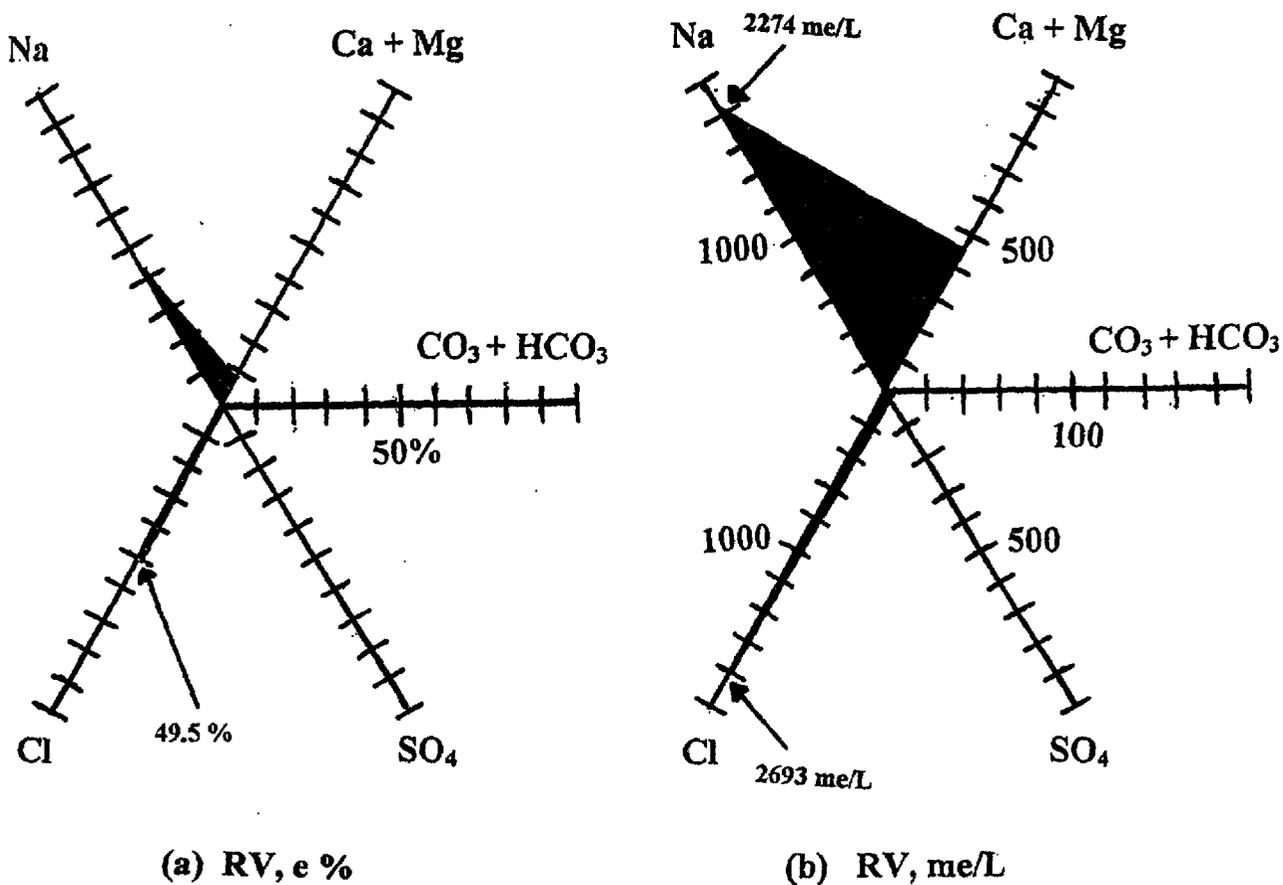


Fig. 25. Graphical representation of the ion reaction values (RV) in sample No. 7 by Tickell (a), modified Tickell (b), and Stiff (c) diagrams.

The sulphate and nitrate anions have the values 15 to 33 and 0.04 to 0.3 me/L respectively, while the bicarbonate and borate are in the order of 0.5 to 5 and 5 to 90 me/L respectively.

The reactions values of total anions in the water samples vary from 1820 to 5950 me/L. They have the same pattern of occurrence of the total cations in the samples, i. e. sample No. 1 has highest value, followed by Nos. 2 to 5 and 7, then No.6.

The deviation from a perfect balance between cations and anions in water samples may be appraised by totaling separately the determined concentrations me/L of cations and anions, and calculating the cations – anions difference.

In the studied oil-field water samples, the percent cations–anions difference has a range of 0.04 to 0.09 in two samples, 0.3 to 0.6 in three samples and 1.1 in two samples, with a mean of 0.52. This indicates that the results reported for the analyses of cations and anions are in good agreements.

3.7. 2. Reaction values (epm)

The reaction values of the determined ions in the oil-field waters under investigation have also been calculated in milliequivalents per kilogram or 1000 g (me/kg or me/1000 g), commonly referred to equivalent per million (epm). This has been calculated from the reaction values in me/L of the ions in the water samples (Table 8) by dividing with the density of the samples (Table 2). The results are presented in Table 9 and represented graphically by Schoeller diagram in Fig. 26.

The distribution of the reaction values (epm) of both cations and anions in the studied water samples will have more or less the same pattern of their reaction values (me/L), but their figures will be reduced by a factor depending on the density of the samples. Thus, the reaction values (epm) of lithium, sodium and potassium vary in the range of about 4 to 19, 1200 to 3550 and 9 to 100 respectively. Those of the magnesium, calcium, strontium and barium are nearly 63 to 1870, 150 to 1160, 2 to 13 and 0.02 to 0.1 epm, respectively.

The sample No. 5 has the highest values of both iron and manganese, followed by those of the Nos. 2 and 1, being about 17 and 6, 2 and 2 and 0.2 and 1.6 epm respectively.

Concerning the total cations, they vary from nearly 1660 to 4840 epm instead of 1780 to 5920 me/L (Table 8), due to reduction caused by dividing with the density of the water samples.

The reaction values of chloride, bromide, fluoride and iodide anions are in the order of approximately 1650 to 4750, 3 to 26, 1 to 4 and 0.01 to 0.1 epm, respectively. Other anions including the sulphate, borate, carbonate and nitrate are in the range of 12 to 27, 4 to 16 (except No. 1, being 75), 0.5 to 5 (except Nos. 1, 2 and 5, being 0) and 0.03 to 0.3 epm, respectively. The total anions vary from about 1690 to 4870 epm.

Table 8. Reaction Values (me/L) of Cations and Anions in the Oil-Field Waters.

Reaction Values, me/L	Water Sample No.						
	1	2	3	4	5	6	7
Cations:							
- Li ⁺	8.50	22.5	8.17	8.26	21.7	4.29	4.62
- Na ⁺	2576.8	4301.3	3784.6	3526.4	1374.9	1534.6	2239.8
- K ⁺	49.7	120.9	45.8	44.9	59.9	9.23	29.8
- Mg ²⁺	2288.2	197.7	460.4	490.4	571.2	68.0	111.8
- Ca ²⁺	975.2	696.8	430.8	385.4	1327.9	162.9	332.6
- Sr ²⁺	15.8	7.62	5.98	5.89	13.9	1.94	5.87
- Ba ²⁺	0.127	0.086	0.028	0.021	0.083	0.018	0.033
- Fe ²⁺	0.238	2.29	0.004	0.009	19.76	0.004	0.003
- Mn ²⁺	1.89	2.37	0.619	0.364	6.59	0.091	0.053
- Total	5916	5352	4736	4462	3396	1781	2724
Anions:							
- F ⁻	5.32	1.74	1.77	1.14	1.47	2.42	1.16
- Cl ⁻	5805.1	5348.0	4690.9	4470.6	3405.4	1777.1	2688.4
- Br ⁻	31.5	11.5	12.0	10.2	27.6	3.53	4.87
- I ⁻	0.086	0.021	0.020	0.014	0.131	0.009	0.013
- SO ₄ ²⁻	15.3	32.8	21.9	22.3	17.0	25.9	16.8
- NO ₃ ⁻	0.316	0.038	0.092	0.084	0.347	0.075	0.081
- HCO ₃ ⁻	0	0	1.29	0.539	0	4.95	2.82
- BO ₃ ³⁻	92.2	9.28	11.5	12.2	18.0	5.32	4.49
- Total	5950	5403	4740	4517	3470	1819	2719
Σ (cations-anions)	-34	-51	-4	-55	-74	-38	5
Difference, %	0.29	0.47	0.04	0.61	1.08	1.06	0.09

Difference, % = 100 x Σ (cations - anion) / Σ (cations + anion).

Table 9. Reaction Values (epm) of Cations and Anions in the Oil-Field Waters.

Reaction Values, epm	Water Sample No.						
	1	2	3	4	5	6	7
Cations:							
- Li ⁺	6.95	18.6	6.91	6.99	19.0	3.99	4.16
- Na ⁺	2108.0	3548.9	3202.4	2985.4	1202.5	1425.9	2014.9
- K ⁺	40.6	99.8	38.8	38.0	52.4	8.58	26.8
- Mg ²⁺	1871.9	163.1	389.6	415.2	499.6	63.2	100.6
- Ca ²⁺	797.8	574.9	364.5	326.3	1161.4	151.4	299.2
- Sr ²⁺	12.9	6.29	5.06	4.99	12.2	1.80	5.28
- Ba ²⁺	0.11	0.07	0.02	0.02	0.07	0.02	0.03
- Fe ²⁺	0.20	1.89	0.0034	0.0076	17.28	0.0037	0.0027
- Mn ²⁺	1.55	1.96	0.52	0.30	5.76	0.084	0.048
- Total	4840	4416	4008	3777	2970	1655	2451
Anions:							
- F ⁻	4.35	1.44	1.50	0.96	1.28	2.25	1.04
- Cl ⁻	4748.9	4412.5	3969.3	3784.8	2978.3	1651.30	2418.5
- Br ⁻	25.8	9.49	10.2	8.64	24.1	3.28	4.38
- I ⁻	0.06	0.02	0.02	0.01	0.11	0.01	0.01
- SO ₄ ²⁻	12.5	27.06	18.5	18.9	14.9	24.1	15.1
- NO ₃ ⁻	0.26	0.03	0.08	0.07	0.31	0.06	0.07
- HCO ₃ ⁻	0.0	0.0	1.09	0.46	0.0	4.60	2.54
- BO ₃ ³⁻	75.4	7.65	9.76	10.3	15.8	4.94	4.04
- Total	4867	4458	4010	3824	3035	1690	2446

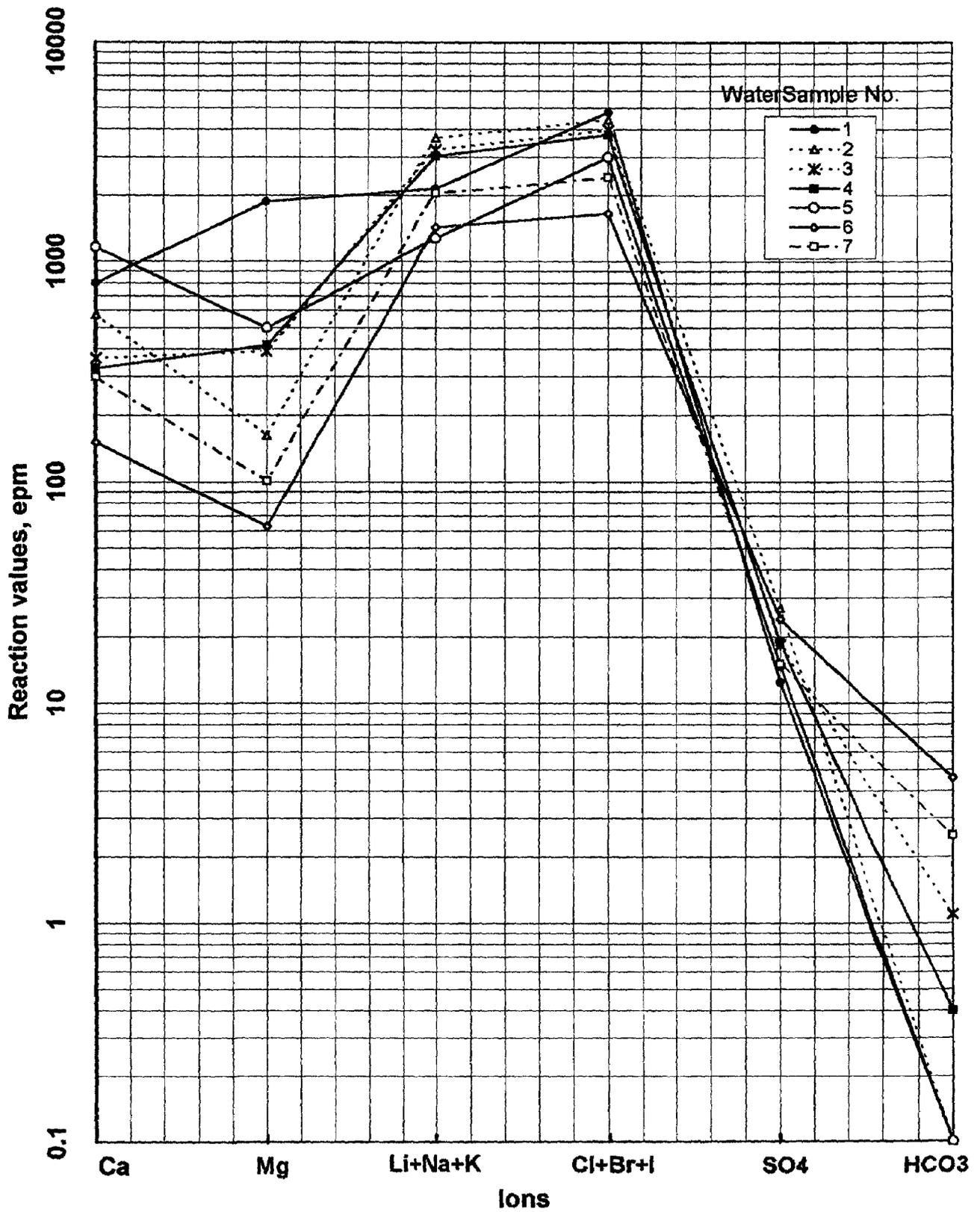


Fig. 26 . Graphical representation of the ion reaction values (epm) in the oil-field waters by Schoeller diagram.

3.7.3. Probable compounds of the ions

Probable compounds dissolved in waters can be calculated from the hypothetical combinations of positive and negative ions according to Collins [5]. This has been carried out for the ions in the examined oil-field water samples, and the results are given in Table 10.

It is indicated that strontium bicarbonate is present in four samples (Nos. 3, 4, 6, and 7) in the range of about 60 to 300 mg/L, and absent in the other three samples (Nos. 1, 2 and 5) having originally no bicarbonate anion.

Strontium sulphate is found in six water samples varying from 280 to 1450 mg/L, and the sample No. 6 is free of it as there is no excess of strontium to combine with the excess sulphate.

Calcium bicarbonate is present only in the sample No. 6, being 150 mg/L. This indicates that there is no excess of strontium cation in this sample to combine with the bicarbonate anion left, so it is combined with calcium cation, and the other samples have no excess of bicarbonate after combination with strontium or originally free of bicarbonate.

Calcium sulphate is found in six water samples (Nos. 2 to 7), ranging from about 210 to 1720 mg/L. The sample No. 1 is free of calcium sulphate as there is no excess sulphate anion to combine with calcium cation after combination first with strontium as sulphate.

Calcium borate is found in all the water samples, varying from nearly 210 to 3650 mg/L, indicating that all borate anions are combined only with calcium cations as there is an excess of the latter.

Calcium chloride and magnesium chloride, both are found in all the samples and vary from about 7140 to 49000 and 3240 to 109000 mg/L, respectively.

Iron chloride is present only in three samples (Nos. 1, 2 and 5), being 15, 145 and 1250 mg/L respectively, mainly depending on the presence of the iron cation as there is an excess of the chloride anion.

Manganese chloride occurs in all the samples, with higher figures (120 to 420 mg/L) in sample Nos. 1, 2 and 5 and lower ones (3 to 40 mg/L) in the other four samples.

Potassium, sodium and lithium chlorides are found in all the samples, having the range of about 690 to 9000, 80000 to 251000 and 180 to 950 mg/L respectively, indicating the presence of excess chloride anions to combine with these alkali cations.

Concerning the distribution of chloride anions among the cations, it is clear that their order of abundance is as follows: $\text{Na}^+ > \text{Mg}^{2+}$ or $\text{Ca}^{2+} > \text{K}^+ > \text{Li}^+ > \text{Fe}^{2+} \simeq \text{Mn}^{2+}$.

The total probable compounds vary from nearly 103000 to 318000 mg/L in the seven water samples, with their order of predominance in them as follows: $1 > 2 > 3 > 4 > 5 > 7 > 6$.

Table 10. Probable Compounds of the Ions in the Oil-Field Waters

Concentration, mg/L	Water Sample No.						
	1	2	3	4	5	6	7
Strontium bicarbonate	0	0	136	57	0	203	295
Strontium Sulphate	1450	698	431	492	1276	0	280
Calcium bicarbonate	0	0	0	0	0	151	0
Calcium Sulphate	0	1716	1172	1154	211	1764	936
Calcium borate	3651	368	455	483	713	211	178
Calcium chloride	49006	36758	22317	19772	72527	7142	17447
Magnesium chloride	108918	9410	21915	23343	27189	3237	5322
Iron chloride	15	145	0	0	1253	0	0
Manganese chloride	119	149	39	23	415	6	3
Potassium chloride	3708	9019	3417	3350	4468	689	2223
Sodium chloride	150485	251196	221021	205942	80294	89621	130658
Lithium chloride	360	954	348	350	920	182	0
Total compounds	317712	310413	271251	254966	189266	103206	157339

3.7. 4. Reaction values (e %)

Reaction values, in equivalent percentage (e %), of the determined ions in the waters can be calculated from their reaction values in me/L, and their reaction groups and properties are determined [407].

3.7.4.1. Reaction groups

The ions may be arranged into three groups: alkali and alkaline earth cations and hydrogen or strong acid anions. These groups have been calculated for the ions in the oil-field water samples under study and are given in Table 11.

It may be noted that the water sample Nos. 1 and 5 have more or less the same percentages of both alkali and alkaline earth cations, being about 22 and 28 e %, respectively. On the other hand, the other five samples have nearly 40 to 43 and 7 to 10 e % of alkalis and alkaline earths, respectively. However, all these seven water samples contain about 49 to 50 e % of the strong acid anions.

3.7.4.2. Reaction properties

The reaction properties or characteristics (e %) of the ions include primary (alkali), secondary (alkaline earth or permanent hardness) and tertiary (acidity) salinity, as well as primary (alkali or permanent) and secondary (alkaline earth or temporary) alkalinity. These properties of the determined ions in the studied oil-field waters have been calculated. The results are given in Table 11.

In the water sample Nos. 1 and 5, the primary and secondary salinity vary from about 43 to 45 and 55 to 57 e %, respectively. However, in the other five water samples, the reaction properties are mainly represented by the primary salinity which varies from nearly 80 to 87 e %, and followed by the secondary salinity which is in the order of about 13 to 19 e %.

Both the tertiary salinity and primary alkalinity are not found in all the studied samples. The secondary alkalinity is only present in four samples, but in minor percentages (0.01 to 0.28 e %).

3.8. Genetic Coefficients of the Ions in the Oil-Field Waters

Genetic coefficients of the major ions in the examined oil-field waters have been calculated from their equivalents. They include fifteen coefficients, formed from relations of the major anions (chloride and sulphate) and cations (sodium, magnesium and calcium) together. The Cl/Br coefficient is also included, although the bromide anion is considered minor. The results are given in Table 12, which indicate the following:

- The genetic coefficients of Cl/Na, Cl/Mg, Cl/Ca, Cl/(Ca + Mg) in the waters under study are in the range of about 1.2 to 2.5, 2.5 to 27, 2.6 to 12 and 1.8 to 7.7 respectively. The Cl/Na is about 1.2 in five samples and 2.2 and 2.5 in the two sample Nos. 1 and 5. The Cl/Mg is nearly 2.5, 6.0, 9.1, 10, 24, 26 and 27 in the sample Nos. 1, 5, 4, 3, 7, 6 and 2

Table 11. Reaction Groups and Properties (e %) of the Ions in the Oil-Field Waters

Reaction values, e %	Water Sample No.						
	1	2	3	4	5	6	7
Reaction groups:							
- Alkali (a)	22.28	41.56	40.53	40.12	21.61	43.46	41.74
- Alkaline earths (b)	27.72	8.44	9.47	9.88	28.39	6.54	8.26
- Strong acid anions (d)	50.00	50.00	49.99	49.99	50.00	49.86	49.95
Reaction properties:							
- Primary (alkali) salinity	44.56	83.12	81.06	80.24	43.22	86.92	83.48
- Secondary (earth) salinity	55.44	16.88	18.91	19.75	56.78	12.80	16.42
- Tertiary salinity (acidity)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- Primary (alkali) alkalinity	0.00	0.00	0.00	0.00	0.00	0.00	0.00
- Secondary (earth) alkalinity	0.00	0.00	0.03	0.01	0.00	0.28	0.10

a : (Li⁺ + Na⁺ + K⁺); b : (Mg²⁺ + Ca²⁺ + Sr²⁺ + Ba²⁺); d: (F⁻ + Cl⁻ + Br⁻ + I⁻ + SO₄²⁻ + NO₃⁻).

Table 12. Genetic Coefficients of the Major Ions in the Oil-Field Waters

Genetic coefficients, (e/e)	Water Sample No.						
	1	2	3	4	5	6	7
Cl/Na	2.25	1.24	1.24	1.27	2.48	1.16	1.20
Cl/Mg	2.54	27.0	10.2	9.12	5.96	26.1	24.0
Cl/Ca	5.95	7.68	10.9	11.6	2.56	10.9	8.08
Cl/(Ca+Mg)	1.78	5.98	5.26	5.10	1.79	7.69	6.05
(Cl-Na)/Mg	1.41	5.29	1.97	1.92	3.55	3.57	4.01
(Na-Cl)/SO ₄	-211	-31.9	-41.4	-42.3	-119	-9.36	-26.7
Na/Cl	0.444	0.806	0.806	0.787	0.403	0.862	0.833
Na/Mg	1.13	21.8	8.22	7.19	2.41	22.6	20.0
Na/Ca	2.64	6.17	8.78	9.15	1.04	9.42	6.73
Na/(Ca+Mg)	0.790	4.81	4.25	4.03	0.724	6.64	5.04
$Na/\sqrt{(Ca + Mg)/2}$	57.7	185	165	155	41.7	138	142
Ca/Mg	0.426	3.52	0.936	0.786	2.32	2.40	2.97
(Ca+Mg)/Mg	1.43	4.52	1.94	1.78	3.32	3.40	3.97
Cl/SO ₄	380	163	215	200	200	68.5	160
(SO ₄ x100)/Cl	0.264	0.613	0.467	0.499	0.499	1.457	0.625
Cl/Br	184	464	389	440	124	516	550

respectively. The Cl/Ca is about 2.6 and 6.0, 7.7 and 8.1 in the water Nos. 5, 1, 2, 7 respectively, and 11 in the other three samples. The Cl/(Ca + Mg) is nearly 1.8 in both the samples Nos. 1 and 5 and 5.1 to 7.7 in the other five samples.

- The (Cl – Na)/Mg and (Na – Cl)/SO₄ coefficients vary from nearly 1.4 to 5.3 and – 9.4 to – 210 respectively. The (Cl – Na)/Mg is about 1.4 in the sample No. 1, 2 in the samples Nos. 3 and 4, and 4 in the samples Nos. 5 to 7, then 5 in the sample No. 2. The (Na – Cl)/SO₄ is nearly – 9 in the sample No. 6, – 30 to – 40 in the other samples except the two sample Nos. 1 and 5 (being – 210 and – 120 respectively).

- The coefficients of Na/Cl, Na/Mg, Na/Ca, Na/(Ca + Mg), Na/ $\sqrt{(Ca + Mg)/2}$ range from approximately 0.44 to 0.86, 1.1 to 23, 1.0 to 9.4, 0.72 to 6.6 and 42 to 185 respectively. The Na/Cl is about 0.4 in the samples 1 and 5, but 0.8 in the four samples 2 to 4 and 7 and 0.86 in the sample 6. The Na/Mg is nearly 1.1, 2.4, 7.2, 8.2, 20, 22 and 23 in the sample Nos. 1, 5, 4, 3, 7, 2 and 6 respectively. The Na/Ca is about 1.0, 2.6 and 6.2 to 9.4 in the sample Nos. 5, 1 and others respectively. The Na/(Ca + Mg) is nearly 0.72, 0.79, 4.0, 4.2, 4.8, 5.0 and 6.6 in the samples 5, 1, 4, 3, 2, 7 and 6 respectively. The Na/ $\sqrt{(Ca + Mg)/2}$ is about 42, 58 and 140 to 185 in the sample Nos. 5, 1 and the others respectively.

- The coefficients of Ca/Mg and (Ca + Mg)/Mg have the values of about 0.43 to 3.5 and 1.4 to 4.5 respectively. The Ca/Mg is about 0.43, 0.79, 0.94 and 2.3 to 3.5 in the samples 1, 4, 3 and others respectively. The (Ca + Mg)/Mg is about 1.4, 1.8, 1.9 and 3.3 to 4.5 in the sample Nos. 1, 4, 3 and rest, respectively.

- The Cl/SO₄ and (SO₄ x 100)/Cl coefficients are in the range of nearly 70 to 380 and 0.26 to 1.5 respectively. For the former coefficient, the sample No.1 has the higher ratio and the sample 6 the lowest one and intermediate ratios are in the other samples. For the latter coefficient, the reverse is true.

- The coefficient of Cl/Br has values of approximately 124 to 550, where the sample No. 5 has the lowest figure, followed in order of increase by the sample Nos.1, 3, 4, 2, 6 and 7.

3.9. Application of the Water Classification Systems to the Oil-Field Waters

Different water classification systems have been applied to the investigated oil-field waters. These systems include those of Palmer [407], Sulin [408], Bojarski modification [411], Chebotarev [409], and Schoeller [410]. Their results are given in Table 13.

3.9.1. Palmer system

Application of the Palmer classification system [407] to the studied water samples is given in Table 13. It is noticed that four water samples (Nos. 3, 4, 6 and 7) belong to the class 3 and three samples (Nos. 1, 2 and 5) to the class 4. This is based on the fact that the samples of the former class have strong acid anions greater than alkali cations, while the samples of the latter class have strong acid anions equal both alkali and alkaline earth cations (Table 11).

Table 13. Application of the Palmer, Sulin, Bojarski, Chebotarev and Schoeller Water Classification Systems to the Oil-Field Waters

Classification system	Water Sample No.						
	1	2	3	4	5	6	7
Palmer System:							
- Class	4	4	3	3	4	3	3
Sulin System:							
- Type	Cl-Ca	Cl-Ca	Cl-Ca	Cl-Ca	Cl-Ca	Cl-Ca	Cl-Ca
- Group	Cl	Cl	Cl	Cl	Cl	Cl	Cl
- Subgroup	Mg	Na	Na	Na	Ca	Na	Na
- Class	S ₂ S ₁	S ₁ S ₂	S ₁ S ₂ A ₂	S ₁ S ₂ A ₂	S ₂ S ₁	S ₁ S ₂ A ₂	S ₁ S ₂ A ₂
Bojarski Modification:							
- Class	V	II	II	II	V	I	II
Chebotarev System:							
- Major group	Cl	Cl	Cl	Cl	Cl	Cl	Cl
- Class	V	V	V	V	V	V	V
- Genetic type	Cl	Cl	Cl	Cl	Cl	Cl	Cl
- Coefficient of exchange:							
- Absolute	0	0	0.0005	0.0002	0	0.0034	0.0019
- Relative	0	0	0.031	0.012	0	0.212	0.119

Table 13. Continued

Classification system	Water Sample No.						
	1	2	3	4	5	6	7
Schoeller System:							
- Chlorinated type	Hyper-						
- Sulphated group	Oligo-	Sulphated	Oligo-	Oligo-	Oligo-	Sulphated	Oligo-
- Bicarbonated group	Hypo-	Hypo-	Hypo-	Hypo-	Hypo-	Normal-	Normal-
- $\sqrt{(SO_4)(Ca)}$ ^A	99.9	124.7	82.1	78.5	131.5	60.4	67.2
- Saturation with CaSO ₄	N. Sat.	U. Sat.	U. Sat.				
- $^3\sqrt{(HCO_3 + CO_3)^2(Ca)}$ ^B	0.00	0.00	7.61	3.74	0.00	14.74	12.32
- Saturation with CaCO ₃	-	-	N. Sat.	U. Sat.	-	N. Sat.	N. Sat.
- Index of Base Exchange	0.556	0.196	0.193	0.211	0.596	0.136	0.167
- Predominance Sequence:							
- Anions	Cl > SO ₄ > CO ₃						
- Cations	Na > Mg > Ca	Na > Ca > Mg	Na > Mg > Ca	Na > Mg > Ca	Na > Ca > Mg	Na > Ca > Mg	Na > Ca > Mg
- HCO ₃ and Ca	HCO ₃ < Ca	HCO ₃ < Ca	HCO ₃ < Ca	HCO ₃ < Ca	HCO ₃ < Ca	HCO ₃ < Ca	HCO ₃ < Ca

A and B: Water saturation with CaSO₄ and with CaCO₃, respectively; N. and U. Sat.: Near and under saturation.

3.9.2. Sulin system

Application of the Sulin system [408] to the studied oil-field waters is given in Table 13. The genetic types of water samples are determined from the genetic coefficients of Na/Cl , $(\text{Na} - \text{Cl})/\text{SO}_4$ and $(\text{Cl} - \text{Na})/\text{Mg}$ (Table 12), the groups and subgroups from the predominance of anions and cations respectively (Table 9), and the classes from the reaction properties (Table 11).

It is clear that all the examined water samples are of the chloride-calcium type, as they have $\text{Na}/\text{Cl} < 1$ and $(\text{Cl} - \text{Na})/\text{Mg} > 1$. They are also of the chloride group due to the predominance of chloride. Five of the water samples (Nos. 2, 3, 4, 6 and 7) belong to the sodium subgroup due to the predominance of primary (alkali) salinity over the secondary (alkaline earth) one, as well as the genetic coefficient $\text{Na}/(\text{Ca} + \text{Mg})$ is > 1 . On the other hand, the sample Nos. 1 and 5 belong to the magnesium and calcium subgroups, respectively. This is due to the predominance of the secondary salinity over the primary one, and the sample Nos. 1 and 5 have the predominance of magnesium and calcium cations, respectively.

Thus, four of the samples (Nos. 3, 4, 6 and 7) belong to the $\text{S}_1\text{S}_2\text{A}_2$ class, one sample (No. 2) to the S_1S_2 class, and two samples (No. 1 and 5) to the S_2S_1 class, where S_1 , S_2 and A_2 represent primary salinity, secondary salinity and secondary alkalinity, arranged in the order of their predominance.

3.9.3. Bojarsky modification

Application of the Bojarsky modification [411] of the chloride-calcium type water in the Sulin system, using the genetic coefficient Na/Cl , to the studied oil-field waters is given in Table 13.

It is clear that one water sample (No. 6) belongs to the class I, four samples (Nos. 2 to 4 and 7) to the class II, and two samples (Nos. 1 and 5) to the class V. This is because the genetic coefficient Na/Cl is: > 0.85 , $0.85-0.75$ and < 0.50 in the classes I, II and V, respectively.

3.9.4. Chebotarev system

Application of the Chebotarev system [409] to the studied oil-field waters is presented in Table 13. The major groups, classes and genetic types of waters are determined from the reaction values in equivalent percentages of anions (Table 8).

It is found that all the water samples under study belong to the chloride major group, class V, and chloride genetic type water. This indicates that all these waters are related to the marine deposits plus weathering of the products, found in zones of accumulation at stagnant conditions of water-exchange.

The absolute and relative coefficients of water-exchange of these water samples have been calculated from their hypothetical combinations, depending mainly on the alkali and

alkaline earth bicarbonate (Table 10), and their results are given in Table 13. However, their values are very low, referred to typical waters of their chloride major group. They are absent in three samples (Nos. 1, 2 and 5) and present in four samples (Nos. 3, 4, 6 and 7), varying from about 0.0002 to 0.0034 and 0.014 to 0.216 for the absolute and relative coefficients, respectively. This may be explained by the presence of acidity in the former three water samples and low values of alkalinity in the latter four samples (Table 2), as well as the decomposition of the bicarbonate and loss of carbon dioxide before their determination.

3.9.5. Schoeller system

Application of the Schoeller system [410] to the oil-field waters under study is presented in Table 13. The concentration or reaction values, in epm, of anions and cations used for their classification are given in Table 9.

The chloride concentrations of these water samples indicate that they are grouped as hyperchlorinated, as they have values greater than 700 epm.

On the other hand, two water samples (Nos. 2 and 6) are sulphated and five ones (Nos. 1, 3 – 5 and 7) are oligosulphated, because the sulphate concentrations are from 58 to 24 epm in the former ones and from 24 to 6 epm in the latter ones. The saturation with calcium sulphate, $\sqrt{(SO_4)(Ca)}$, indicates that five water samples (Nos. 1 to 5) are near saturation, and the other two samples (Nos. 6 and 7) are under saturation, as they have values of > 70 and < 70 epm, respectively.

The bicarbonate plus carbonate concentrations (in epm) show that two water samples (Nos. 6 and 7) are normal carbonated as having values of 7 to 2 epm, while the rest samples (Nos. 1 – 5) are hypocarbonated because they have values less than 2 epm. However, using the water saturation with calcium carbonate, $\sqrt[3]{(HCO_3 + CO_3)^2(Ca)}$, is preferred, instead of the bicarbonate plus carbonate concentration as the latter is proportional to the pressure of gaseous carbon dioxide in equilibrium with calcium carbonate in water. This indicates that three water samples (Nos. 3, 6 and 7) are near saturation and one sample (No. 4) is under saturation as the former samples have values greater than 7 epm, while the latter one less than 7 epm.

The index of base exchange (IBE) calculated for these waters vary from about 0.14 to 0.60 which indicate that they had dissolved alkali cations for alkaline earth ones on the clays. All these water samples have higher values of both IBE and Cl/Na than those of the present sea water (0.129 and 1.17 respectively), thus they probably were not subjected to infiltrating meteoric waters.

In these water samples, the predominant sequences are as follows:

- for anions: $Cl > SO_4 > CO_3$ in all samples,
- for cations: $Na > Mg > Ca$ in three samples (Nos. 1, 3, and 4),
 $Na > Ca > Mg$ in four water samples (Nos. 2 and 5 to 7), and

- for HCO_3 and Ca: $\text{HCO}_3 < \text{Ca}$ in all samples.

3.10. Composition Change of Ions in the Oil-Field Waters during Geologic Ages

The composition change of ions in the studied oil-field waters during their geologic ages has been carried out by determining their concentration ratios referred to those of the present sea water [5]. Results are given in Table 14.

Mechanisms that cause the oil-field waters to differ in composition from waters originally deposited with sediments include ion exchange, infiltrating waters, sediment leaching, mineral formation, sulphate reduction, and ultrafiltration through clay-shale membranes [5].

In the studied water samples, the total ions are found to be enriched by ratios of about 3.0 to 9.3. Both sodium and chloride, the most predominant ions, are similarly concentrated by factors of nearly 3.0 to 9.3 and 3.3 to 11 respectively. Potassium has the same trend (3.1 to 12) in six samples, however it is slightly depleted in the sample No. 6 (0.95). Lithium is highly enriched by a factor of 150 to 780 in all the samples.

Magnesium is enriched, with ratios from 1.8 to 21 in five samples, but without change (1.0) in the sample No.7 and depletion (0.64) in the sample No. 6. However, calcium is enriched with higher ratios (8.2 to 49) in all the samples. Thus, the result of total equivalent magnesium of calcium plus magnesium (Mg') is an enrichment by ratios of about 1.8 to 26.

The Mg'/Mg coefficient varies from nearly 1.2 to 3.3 which is higher than that of the sea water (being 1.19). This coefficient is indicative of the degree of dolomitization, where dolomite is formed. Thus, the concentration of calcium is increased in the water while magnesium is decreased.

Strontium is concentrated from about 1.8 to 86 and barium has also the same trend, but with higher ratios (42 to 290). Iron and manganese are enriched by very high ratios, perhaps due to their low concentration in the present sea water.

Bromide is concentrated by ratios of about 4.3 to 39, while iodide is greatly enriched by factors of about 24 to 332. The source of the high concentration of iodide in these waters is probably from localized sediments enriched in organic iodide [5].

Both Ca/Br and Mg/Br ratios range nearly from 1.3 to 2.8 and 0.13 to 0.55, respectively. These ratios are very lower than those of the present sea water (being 6.2 and 20 respectively). This indicates that the enrichment of calcium is higher than that of bromide, while that of magnesium is lower than of bromide.

Boron is concentrated nearly 69 times in the water sample No. 1 and from 3.4 to 14 times in the other water samples.

The sulphate concentration is greatly depleted by factors of nearly 0.27 to 0.59. This depletion may be due to the anaerobic bacterial reduction of sulphate to hydrogen sulphide and /or dolomitization with the formation of anhydride [5]

Table 14. Composition Changes of Ions during their Geologic Ages Referred to the Present Sea Water

Ion	Water Sample No.							Sea Water, mg/L[5]
	1	2	3	4	5	6	7	
Total ions	9.28	9.06	7.88	7.46	5.58	3.04	4.57	34500
Lithium	295	780	284	286	755	149	160	0.2
Sodium	5.59	9.33	8.21	7.65	2.98	3.33	4.86	10600
Potassium	5.11	12.4	4.71	4.62	6.16	0.950	3.07	380
Magnesium	21.39	1.85	4.30	4.58	5.34	0.635	1.04	1300
Calcium	48.9	34.9	21.6	19.3	66.5	8.16	16.7	400
Strontium	86.2	1.85	32.7	32.2	76.4	10.6	32.1	8
Barium	290	198	64.3	48.0	190	42.0	74.7	0.03
Boron	69.2	6.96	8.67	9.12	13.5	4.00	3.38	4.8
Iron	664	6390	9.80	26.3	55170	10.7	8.20	0.01
Manganese	25950	32500	8500	5000	90500	1245	725	0.002
Chloride	10.8	9.98	8.75	8.34	6.35	3.32	5.02	19000
Bromide	38.7	14.1	14.7	12.5	33.9	4.34	5.98	65
Iodide	217	53.6	50.6	35.8	332	23.8	32.8	0.05
Sulphate	0.273	0.586	0.392	0.398	0.304	0.463	0.300	2690
Mg ¹	25.7	7.05	7.02	6.90	15.0	1.82	3.50	1543
Mg ¹ /Mg	1.20	3.80	1.63	1.50	2.79	2.86	3.34	1.19
Ca / Br	1.26	2.47	1.46	1.55	1.97	1.88	2.79	6.15
Mg / Br	0.553	0.131	0.292	0.367	0.158	0.146	0.175	20.0

Mg¹ = Total equivalent Mg of Ca + Mg (mg/L).

3.11. Statistical Correlations of Data of the Oil-Field Waters

Correlations of data of the studied oil-field waters have been statistically carried out using the linear regression analysis [423, 424].

In this analysis, correlation between any two variables, e.g. independent X and dependent Y, their correlation equation ($Y = m X \pm c$) and coefficient (r) are calculated. The equation gives the slope (m) and intercept (c) of the best-fit straight line, while the coefficient indicates the strength of association or correlation. The slope of the line may be positive or negative, and so the correlation will have the same sign.

3.11.1. Correlations among the density and properties

Correlations among the density and properties of the studied water samples have been carried out using the linear regression analysis. Properties include general physico-chemical properties, concentration of cations and anions, genetic coefficients, probable compounds and depth of productive zones. Correlation results are given in Table 15.

These results indicate that the density is correlated with the physico-chemical properties. These correlations are very strong for the specific gravity, TDS at 180°C, salinity and TDS at 550°C as their correlation coefficients (r) are 1.00, 0.997, 0.998 and 0.963 respectively. They are strong for both the resistivity and conductivity, having ($r = -0.845$ and 0.839 respectively), moderate for both total and Mg hardness ($r = 0.615$ and 0.601 respectively) and minor for Ca hardness ($r = 0.436$).

The density is very strongly correlated with the concentration of total cations ($r = 0.976$), moderately correlated with those of sodium, potassium, magnesium, strontium and barium ($r = 0.709$ to 0.562), and of minor correlation with those of both lithium and calcium ($r = 0.410$ and 0.436 respectively).

The density and concentrations of anions are very strongly associated for those of the chloride and total anions ($r = 0.997$), moderately associated for those of both the bromide and borate ($r = 0.554$ and 0.556 respectively), of minor association for that of the fluoride ($r = 0.389$), and of little or no association for those of the iodide, sulphate and nitrate ($r = 0.213$ to 0.081).

The correlation of the density and genetic coefficients is of little or no correlation for both the Cl/Na and Cl/Ca ($r = 0.272$ and -0.157 respectively), and of minor correlation for other genetic coefficients ($r = -0.52$ to -0.30), except for both the Cl/SO₄ and SO₄ x 100/Cl where it is moderate ($r = 0.751$ and -0.790 respectively).

Association of the density and probable compounds is moderate for the NaCl, KCl and MgCl₂ ($r = 0.709$ to 0.600), and minor for the LiCl and CaCl₂ ($r = 0.457$ and 0.410 respectively).

The density and depth of the productive zone are very strongly correlated for the sample Nos. 1 to 3 ($r = 0.988$) and strongly correlated for the sample Nos. 1 to 4 ($r = 0.800$), while

Table15. Linear Regression Parameters of Correlations among Density (X) and Properties (Y) of the Oil-Field Waters

Properties	$Y = m X \pm c$	r	Properties	$Y = m X \pm c$	r
Specific gravity	$1.0009 X - 0.0002$	1.0000	Cl /Na	$2.8604 X - 1.773$	0.2718
Conductivity	$552.39 X - 436.03$	0.8392	Cl/Mg	$- 93.189 X + 123.2$	- 0.4814
Resistivity	$- 0.1605 X - 0.2365$	- 0.8452	Cl/Ca	$- 9.5415 X + 19.318$	- 0.1572
TDS at 180°C	$149395 X - 1501294$	0.9972	Cl/ (Ca+Mg)	$- 21.191 X + 29.415$	- 0.5085
TDS at 550°C	$1295272 X - 1285098$	0.9632	(Cl-Na)/Mg	$- 7.7045 X + 12.05$	- 0.2966
Salinity	$1591590 X - 1612905$	0.9976	(Na-Cl)/SO ₄	$- 698.48 X + 742.29$	- 0.5208
Ca hardness	$167926 X - 164178$	0.4361	Na/Cl	$- 1.25 X + 2.1574$	- 0.3432
Mg hardness	$432898 X - 472541$	0.6006	Na/Mg	$- 85.618 X + 111.33$	- 0.4917
Total hardness	$600824 X - 636719$	0.6153	Na/Ca	$- 18.388 X + 27.629$	- 0.2982
Lithium	$409.34 X - 397.92$	0.4101	Na/(Ca+Mg)	$- 21.407 X + 28.613$	- 0.5172
Sodium	$345960 X - 338230$	0.7086	Ca/Mg	$- 8.9259 X + 12.273$	- 0.4001
Potassium	$17508 X - 18318$	0.6901	(Ca+Mg)/Mg	$- 8.9138 X + 13.26$	- 0.3996
Magnesium	$104687 X - 114295$	0.5975	Cl/SO ₄	$1318 X - 1332.5$	0.7508
Calcium	$67252 X - 65751$	0.4361	(SO ₄ x100)/Cl	$- 5.6526 X + 7.196$	- 0.7896
Strontium	$2264 X - 2272.3$	0.5616	Cl/Br	$- 1269.7 X + 1855.4$	- 0.4130
Barium	$33.974 X - 35.562$	0.6278	Ca Cl ₂	$172092 X - 167700$	0.4096
Total cations	$538116 X - 539303$	0.9757	MgCl ₂	$410049 X - 447685$	0.5975
Fluoride	$202.54 X - 194.45$	0.3890	KCl	$33427 X - 34978$	0.6905
Chloride	$965478 X - 978408$	0.9976	NaCl	$879315 X - 859769$	0.7088
Bromide	$8971 X - 9263.7$	0.5535	LiCl	$3074.1 X - 3124.9$	0.4566
Iodide	$23.862 X - 22.38$	0.2126	Depth (S 1- 3)	$34428 X - 35951$	0.9881
Sulphate	$449.25 X + 522.6$	0.0812	Depth (S 1- 4)	$22806 X - 21800$	0.7999
Nitrate	$30.034 X - 25.722$	0.2037	Depth (S 1- 4, 7)	$- 14207 X + 22732$	- 0.6062
Borate	$6396.7 X - 6999.5$	0.5563	Depth (S 1-4, 6, 7)	$- 6433.2 X + 13435$	- 0.4108
Total anions	$979684 X - 992140$	0.9972	Depth (S1- 7)	$- 11964 X + 20617$	- 0.2879

the correlation is moderate ($r = -0.606$), minor ($r = -0.411$), and little ($r = -0.288$) for the sample Nos. 1 to 4 and 7, 1 to 4, 6 and 7, and 1 to 7 respectively.

3.11.2. Correlations of the depth and properties

The depth of the productive zone and some physico-chemical properties of the studied water samples have been correlated using the linear regression analysis, and the results are given in Table 16.

For the sample Nos. 1 to 4, it is clear that the depth is strongly correlated with the Ca hardness, calcium and strontium concentrations ($r = 0.800$ for all), moderately correlated with those of the total anions, chloride, iodide, bromide and sodium ($r = 0.745, 0.738, 0.729, 0.714$ and -0.590 respectively), of minor correlation with those of both the nitrate and total cations ($r = 0.468$ and 0.309 respectively), and of little or no correlation with those of both the sulphate and lithium ($r = -0.261$ and 0.127 respectively).

For the sample Nos. 1 to 7, correlation of the depth is moderate with concentrations of the iodide, Ca hardness, calcium, sodium and nitrate ($r = 0.784, 0.696, 0.696, -0.687$ and 0.678 respectively), and minor with those of the strontium, sulphate, lithium, bromide, total cations, chloride and total anions ($r = 0.514, -0.472, 0.469, 0.461, -0.412, -0.326$ and -0.317 respectively).

3.11.3. Intercorrelations of physico-chemical properties

Intercorrelations among selected physico-chemical properties of the studied water samples have been performed using the linear regression analysis. Results of the correlation, equations and coefficients, are given in Tables 17 and 18, respectively.

These intercorrelations indicate the followings:

- Correlations of the density are: very strong ($r = 0.998$ to 0.963) with both the TDS at 180°C and 550°C , salinity, chloride, total cations and total anions, strong ($r = 0.839$) with conductivity, moderate ($r = 0.709$ to 0.601) with the sodium, total and Mg hardness, and minor ($r = 0.436$) with the Ca hardness.
- Correlations of the conductivity are: very strong ($r = 0.935$ and 0.905) with the TDS at 550°C and total cations, strong ($r = 0.873$ to 0.810) with the TDS at 180°C , salinity, sodium, chloride and total anions, and little ($r = 0.218$ to 0.116) with the Ca, Mg and total hardness.
- Correlations of the TDS at 180°C are: very strong ($r = 0.996$ to 0.906) with the TDS at 550°C , salinity, total cations, chloride and total anions, moderate ($r = 0.756$ to 0.559) with the Mg and total hardness, as well as sodium, and minor ($r = 0.382$) with the Ca hardness.
- Correlations of the TDS at 550°C are: very strong ($r = 0.994$ to 0.950) with the salinity, total cations, chloride and total anions, strong ($r = 0.856$) with the sodium, minor ($r = 0.387$ and 0.368) with the Mg and total hardness respectively, and little ($r = 0.292$) with the Ca hardness.

Table 16. Linear Regression Parameters of Correlations among Depth (X) and Properties (Y) of the Oil-Field Waters

Properties	Sample Nos. 1 to 4		Sample Nos. 1 to 7	
	$Y = m X \pm c$	r	$Y = m X \pm c$	r
Ca hardness	$18.178 X - 69810$	0.7997	$6.4522 X - 12565$	0.6963
Lithium	$0.0104 X + 24.59$	0.1269	$0.0113 X + 1.6157$	0.4694
Sodium	$-16.336 X + 172255$	-0.5899	$-8.0719 X + 117787$	-0.6870
Calcium	$7.2802 X - 27959$	0.7997	$2.584 X - 5031.9$	0.6963
Strontium	$0.2736 X - 1133.3$	0.7983	$0.0499 X + 21.25$	0.5142
Total cations	$5.1741 X + 78749$	0.3090	$-5.4731 X + 122376$	-0.4123
Chloride	$26.657 X + 32011$	0.7384	$-7.5893 X + 193766$	-0.3259
Bromide	$0.9659 X - 4062.1$	0.7140	$0.1797 X - 54.767$	0.4608
Iodide	$0.0052 X - 24.434$	0.7294	$0.0021 X - 8.92$	0.7843
Sulphate	$-0.1512 X + 1949.5$	-0.2610	$-0.063 X + 1468.1$	-0.4722
Nitrate	$0.0084 X - 38.221$	0.4682	$0.0024 X - 7.0228$	0.6782
Total anions	$28.454 X + 25144$	0.7454	$-7.4856 X + 195834$	-0.3167

Table 17. Linear Regression Equations of Intercorrelations of Physico-Chemical Properties of the Oil-Field Waters

X - Y	Y = m X ± c	X - Y	Y = m X ± c
Density-		Salinity-	
Conductivity	552.39X - 436.03	Ca hardness	0.0989 X + 7552
TDS at 180°C	149395X - 1501294	Mg hardness	0.2825 X - 36321
TDS at 550°C	1295272X - 1285098	Total hardness	0.3814 X - 28769
Salinity	1591590X - 1612905	Sodium	0.2168 X + 12503
Ca hardness	167926X - 164178	Total cations	0.3368 X + 6324.8
Mg hardness	432898X - 472541	Chloride	0.6066 X + 0.0371
Total hardness	600824X - 636719	Total anions	0.6157 X + 633.68
Sodium	345960X - 338230	Ca hardness-	
Total cations	538116X - 539303	Mg hardness	0.9636 X + 450.41
Chloride	965478X - 978408	Total hardness	1.9636 X + 450.41
Total anions	979684X - 992140	Sodium	-0.2674 X + 71752
Conductivity-		Total cations	0.4099 X + 72939
TDS at 180°C	1954.2 X - 167943	Chloride	1.03 X + 110985
TDS at 550°C	1909.2 X - 173260	Total anions	1.0747 X + 112372
Salinity	1984.6 X - 172397	Mg hardness-	
Ca hardness	127.16 X + 4700.1	Total hardness	1.275 X + 22531
Mg hardness	126.97 X + 4068.8	Sodium	-0.0233 X + 64210
Total hardness	254.13 X + 8768.9	Total cations	0.335 X + 75472
Sodium	647.15 X - 69435	Chloride	0.8396 X + 117417
Total cations	758.23 X - 70189	Total anions	0.869 X + 119294
Chloride	1203.9 X - 104579	Total hardness-	
Total anions	1208.6 X - 102782	Sodium	-0.0542 X + 66816
TDS at 180°C-		Total cations	0.2463 X + 70557
TDS at 550°C	0.8766 X + 14323	Chloride	0.6176 X + 105074
Salinity	1.0612 X - 12500	Total anions	0.6406 X - 106437
Ca hardness	0.0982 X + 7903.4	Sodium-	
Mg hardness	0.2688 X - 32610	Total cations	0.9505 X + 25205
Total hardness	0.3669 X - 24707	Chloride	1.404 X + 35365
Sodium	0.2463 X + 6004.9	Total anions	1.4001 X + 56578
Total cations	0.364 X + 576.97	Total cations-	
Chloride	0.6437 X - 7582.8	Chloride	1.7094 X - 3541.8
Total anions	0.6525 X - 6860.9	Total anions	1.728 X - 2375.6
TDS at 550°C-		Chloride-	
Salinity	1.133 X - 12850	Total anions	1.0149 X + 633.64
Ca hardness	0.0835 X + 12533		
Mg hardness	0.1973 X - 13065		
Total hardness	0.2808 X - 531.72		
Sodium	0.3108 X - 4565.7		
Total cations	0.4078 X - 3740.4		
Chloride	0.6873 X - 7795.2		
Total anions	0.6941 X - 6521.4		

Table 18. Correlation Coefficients (r) of Intercorrelations of Physico-Chemical Properties of the Oil-Field Waters

Properties X Y	Density	Conduc- tivity	TDS at 180°C	TDS at 550°C	Salinity	Ca hardness	Mg hardness	Total hadness	Sodium	Total cations	Chloride
Conductivity	0.8392										
TDS at 180°C	0.9972	0.8587									
TDS at 550°C	0.9632	0.9347	0.9765								
Salinity	0.9976	0.8188	0.9065	0.9550							
Ca hardness	0.4361	0.2175	0.3818	0.2917	0.4098						
Mg hardnes	0.6006	0.1158	0.5587	0.3681	0.6253	0.5148					
Total hadness	0.6153	0.1712	0.5629	0.3868	0.6231	0.7743	0.9411				
Sodium	0.7086	0.8725	0.7556	0.8561	0.7083	-0.2110	-0.0346	-0.1086			
Total cations	0.9757	0.9049	0.9886	0.9943	0.9742	0.2862	0.4377	0.4360	0.8414		
Chloride	0.9976	0.8188	0.9965	0.9550	1.0000	0.4098	0.6253	0.6231	0.7083	0.9742	
Total anions	0.9972	0.8098	0.9950	0.9502	0.9998	0.4212	0.6376	0.6367	0.6958	0.9413	0.9998

- Correlations of the salinity are: very strong ($r = 1.00$ to 0.974) with the total cations, chloride and total anions, moderate ($r = 0.708$ to 0.623) with the Mg and total hardness and sodium, and minor ($r = 0.410$) with the calcium.
- Correlations of the Ca hardness are: moderate ($r = 0.774$) with the total hardness, minor ($r = 0.515$ to 0.410) with the Mg hardness, chloride and total anions, and little ($r = -0.211$ and 0.286) with the sodium and total cations.
- Correlations of the Mg hardness are: very strong ($r = 0.941$) with the total hardness, moderate ($r = 0.638$ to 0.625) with the chloride and total anions, minor ($r = 0.438$) with the total cations, and none ($r = -0.035$) with the sodium.
- Correlations of total hardness are: moderate ($r = 0.637$ to 0.623) with the chloride and total anions, minor ($r = 0.436$) with the total cations, and little ($r = -0.109$) with the sodium.
- Correlations of the sodium are: strong ($r = 0.841$) with the total cations, and moderate ($r = 0.708$ to 0.696) with the chloride and total anions.
- Correlations of the total cations are: very strong ($r = 0.974$ and 0.941) with the chloride and total anions.
- Correlation of the chloride is: very strong ($r = 1.00$) with the total anions.

3.12. Organic Constituents in the Oil-Field Waters

Organic constituents in the studied water samples have been investigated through extraction of fatty acids by sodium carbonate, extraction of oils by methylene chloride, fractionation of the oils into their components of saturates, aromatics and resins by column chromatography, determination of the extracted fatty acids by gas chromatography, determination of *n*-paraffins in the saturates by gas chromatography, determination of polyaromatics in the aromatics by high performance liquid chromatography, and determination of functional groups of the extracted oils by infrared spectrometry.

3.12.1. Extraction of fatty acids by sodium carbonate

Fatty acids in the five studied water samples have been extracted by sodium carbonate [425]. Results are given in Table 19. The concentration of fatty acids is in the range of 0.9 to 2.0 mg/L in the water samples, where the sample No. 5 has the lowest value, followed by both the sample Nos. 4 and 6, then the sample No. 3, and finally the sample No. 7 has the highest value.

3.12.2. Extraction of oils by methylene chloride

Oils in the studied water samples have been extracted with methylene chloride (instead of conventionally used fluorocarbon) using the gravimetric method [1, 2].

Table 19. Fatty Acids and Oils Extracted from the Oil-Field Waters and Oil Components Fractionated by Column Chromatography

Analysis	Water Sample No.						
	1	2	3	4	5	6	7
Fatty acids, mg/L	n.d.	n.d.	1.6	1.5	0.9	1.5	2.0
Oils, mg/L	8.70	9.00	11.0	8.00	10.8	12.6	8.70
Fatty acids/oils, m/m %	n.d.	n.d.	14.5	18.8	8.33	11.9	23.0
Oil components, m/m %:							
- Saturates	25.3	26.8	24.6	23.7	21.3	22.2	24.7
- Aromatics	39.3	34.7	39.0	38.0	38.0	37.0	38.0
- Resins	32.0	35.0	33.0	35.0	37.0	38.0	35.0
- Loss	3.4	3.5	3.4	3.3	3.7	2.8	2.3

n.d.: not determined.

The obtained results are given in Table 19, which indicate that concentration of the oils varies from 8.00 to 12.6 mg/L. The oil concentration has the following trend in the water samples: $4 < 1 = 7 < 2 < 5 < 3 < 6$.

It is clear that the fatty acids represent about 8.3, 12, 14, 19 and 23 m/m % of the oils in the water sample Nos. 5, 6, 3, 4 and 7, respectively.

3.12.3. Fractionation of the oils into their components by column chromatography

The extracted oils from the studied water samples have been fractionated into their components, i.e. saturates, aromatics and resins, by silica-gel column chromatography [426]. The results are included in Table 19.

It is noted that the three oil components, i.e. the saturates, aromatics and resins, constitute about 21 to 27, 35 to 39 and 32 to 38 m/m % of the oils, respectively. The saturates have the lowest percentages, followed by the resins, while the aromatics are the highest ones. Generally, the saturates consist of *n*-, *iso*- and *cycloparaffins* (alkanes), the aromatics of mono-, di- and polyaromatics, and the resins of non-hydrocarbons including polar N-, O- and S-compounds.

3.12.4. Determination of the fatty acids by gas chromatography

The extracted fatty acids from the studied water samples, after methylation, have been determined by gas chromatography [425]. Results are given in Table 20, and gas chromatograms of the methyl esters of fatty acids in the water samples are shown in Fig. 27, and their concentration-carbon number in Fig. 28.

It is clear from Fig. 28 that the methyl esters of fatty acids identified in the water sample Nos. 3 to 7 are in the range of C₈- to C₂₀-fatty acids. They constitute about 84, 60 and 42 % of those of the sample Nos. 3, 4 and 7, then 5, and 6, respectively. In other words, the unidentified esters are about 16, 40 and 58 %, respectively.

Concerning the predominance of the esters of odd-numbered carbon fatty acids, it follows the sequence in the sample Nos. $5 < 4 < 6 < 7 < 3$, being about 9, 10, 13, 15 and 25 % respectively. On the other hand, the esters of even-numbered carbon fatty acids, the abundance follows the order in the sample Nos. $6 < 5 < 3 < 7 < 4$, being nearly 29, 51, 59, 69 and 74 %, respectively.

Consequently, the ratios of the esters of odd- to even-carbon numbered fatty acids vary from 0.13 to 0.44, with the values of 0.13, 0.18, 0.21, 0.42 and 0.44 in the sample Nos. 4, 5, 7, 3 and 6, respectively.

The identified fatty acid methyl esters vary from those of C₈- to C₂₀-fatty acids in the water sample No. 3, while they are in the range of those of C₁₁- to C₂₀- in the sample Nos. 4 to 6 and C₁₂- to C₂₀-fatty acids in sample No. 7.

It is noticed that the highest concentration in the methyl esters of fatty acids is that of C₁₂-fatty acid in the water sample Nos. 5 and 6 (being about 38 and 15 % respectively).

Table 20. Gas Chromatographic Analysis of the Methyl Esters of the Fatty Acids Extracted from the Oil-Field Waters

Concentration, m/m %	Water Sample No.				
	3	4	5	6	7
<i>n</i> -C ₈	0.492	-	-	-	-
<i>n</i> -C ₉	0.153	-	-	-	-
<i>n</i> -C ₁₀	0.163	-	-	-	-
<i>n</i> -C ₁₁	0.510	2.58	1.22	0.769	-
<i>n</i> -C ₁₂	0.336	7.56	38.02	15.32	16.08
<i>n</i> -C ₁₃	20.03	4.20	3.96	6.13	11.92
<i>n</i> -C ₁₄	17.06	3.56	3.35	2.51	17.85
<i>n</i> -C ₁₅	1.56	0.844	3.14	4.61	-
<i>n</i> -C ₁₆	3.91	1.47	2.74	3.80	4.62
<i>n</i> -C ₁₇	2.35	0.64	0.696	1.52	2.55
<i>n</i> -C ₁₈	2.26	2.43	0.570	0.767	0.74
<i>n</i> -C ₁₉	0.308	1.76	-	-	0.271
<i>n</i> -C ₂₀	34.94	59.31	6.30	6.97	30.08
Total <i>n</i> -A:	84.07	84.35	60.00	42.40	84.11
- Odd	24.91	10.02	9.02	13.03	14.74
- Even	59.16	74.33	50.98	29.37	69.37
- Odd/Even	0.42	0.13	0.18	0.44	0.21
Unidentified	15.93	15.65	40.00	57.60	15.89

n-A: *n*-alkanoic or fatty acids; - : not present at detectable concentration.

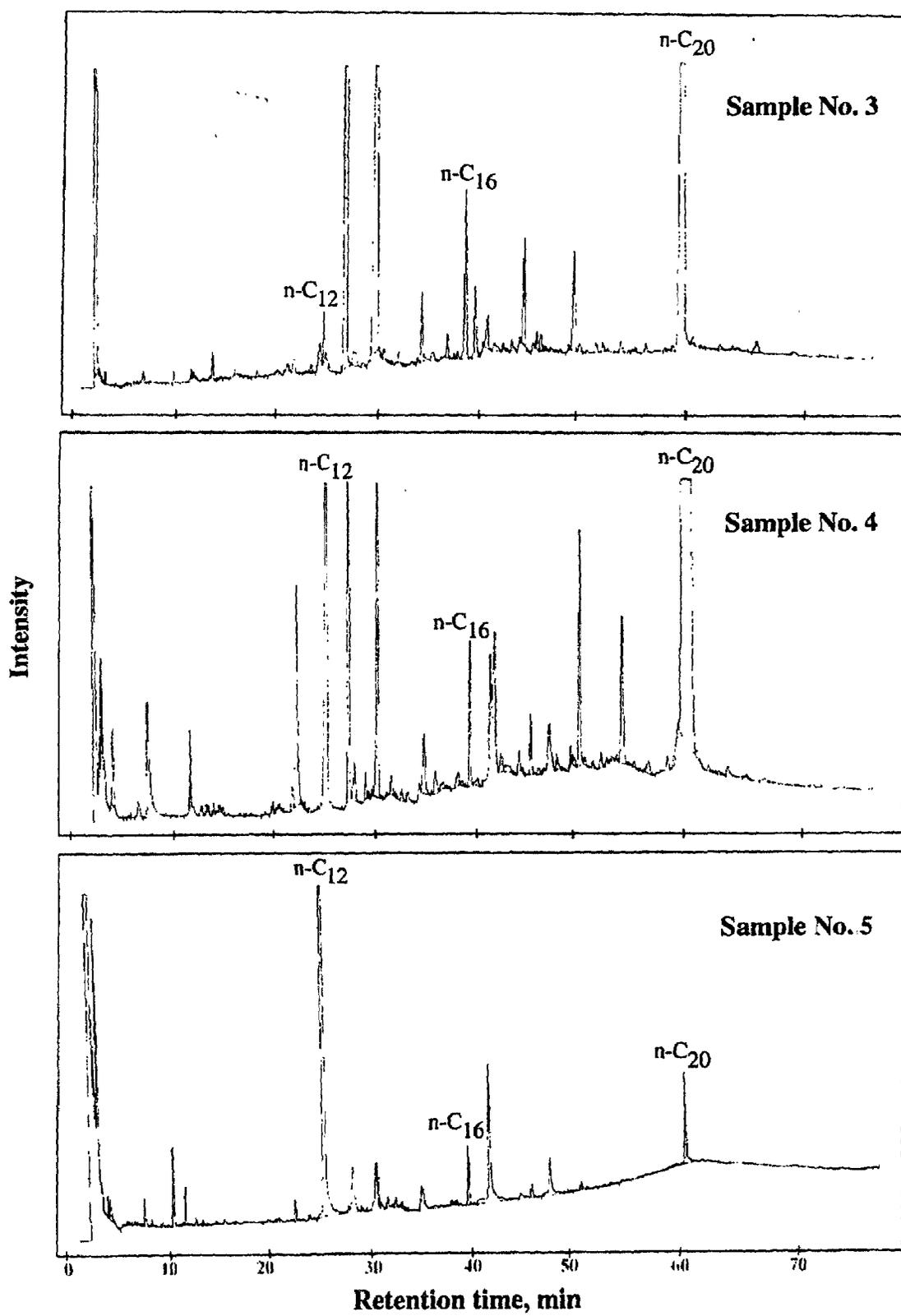


Fig. 27. Gas chromatograms of methyl esters of fatty acids in the oil-field waters.

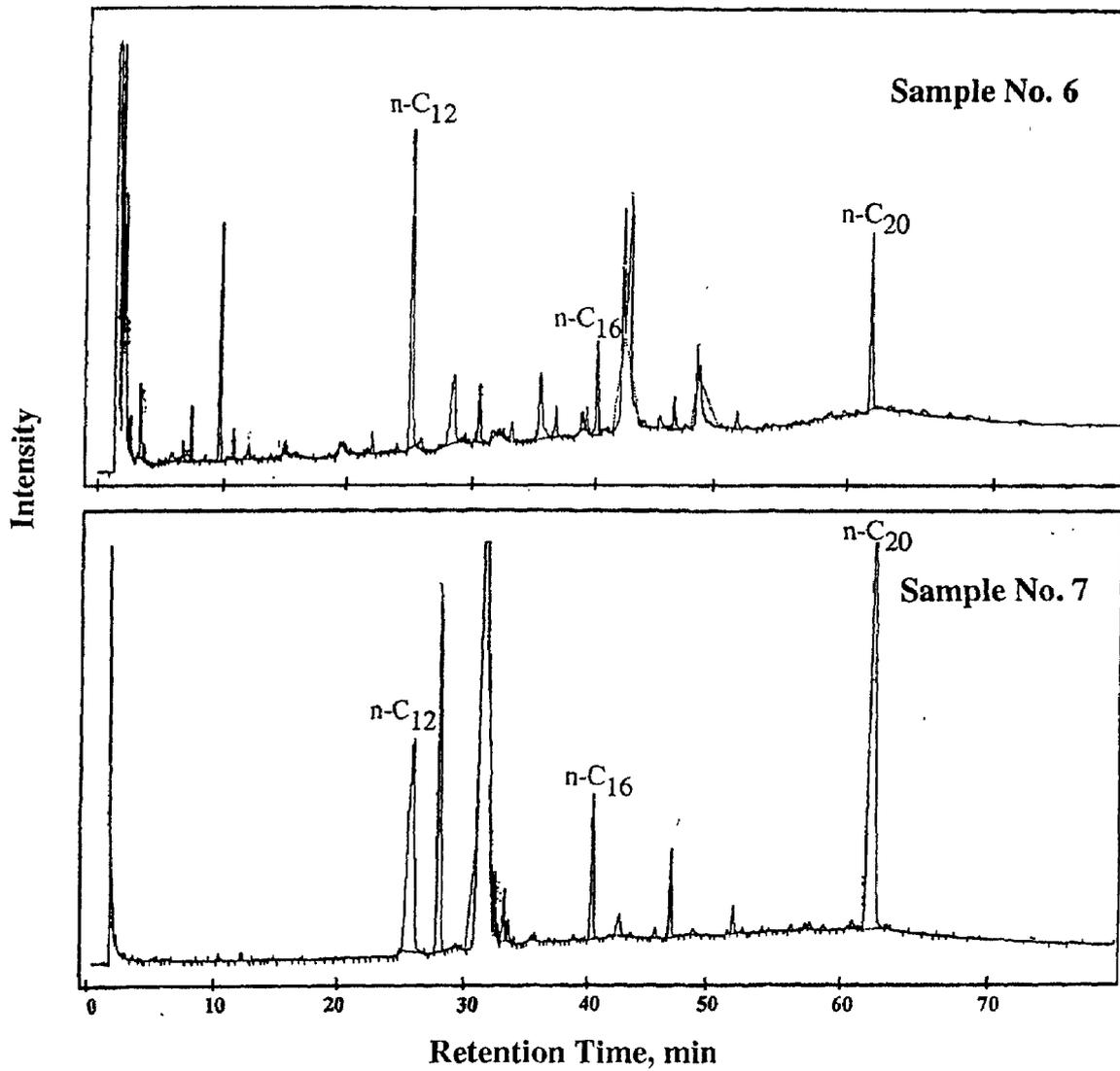


Fig. 27. Continued.

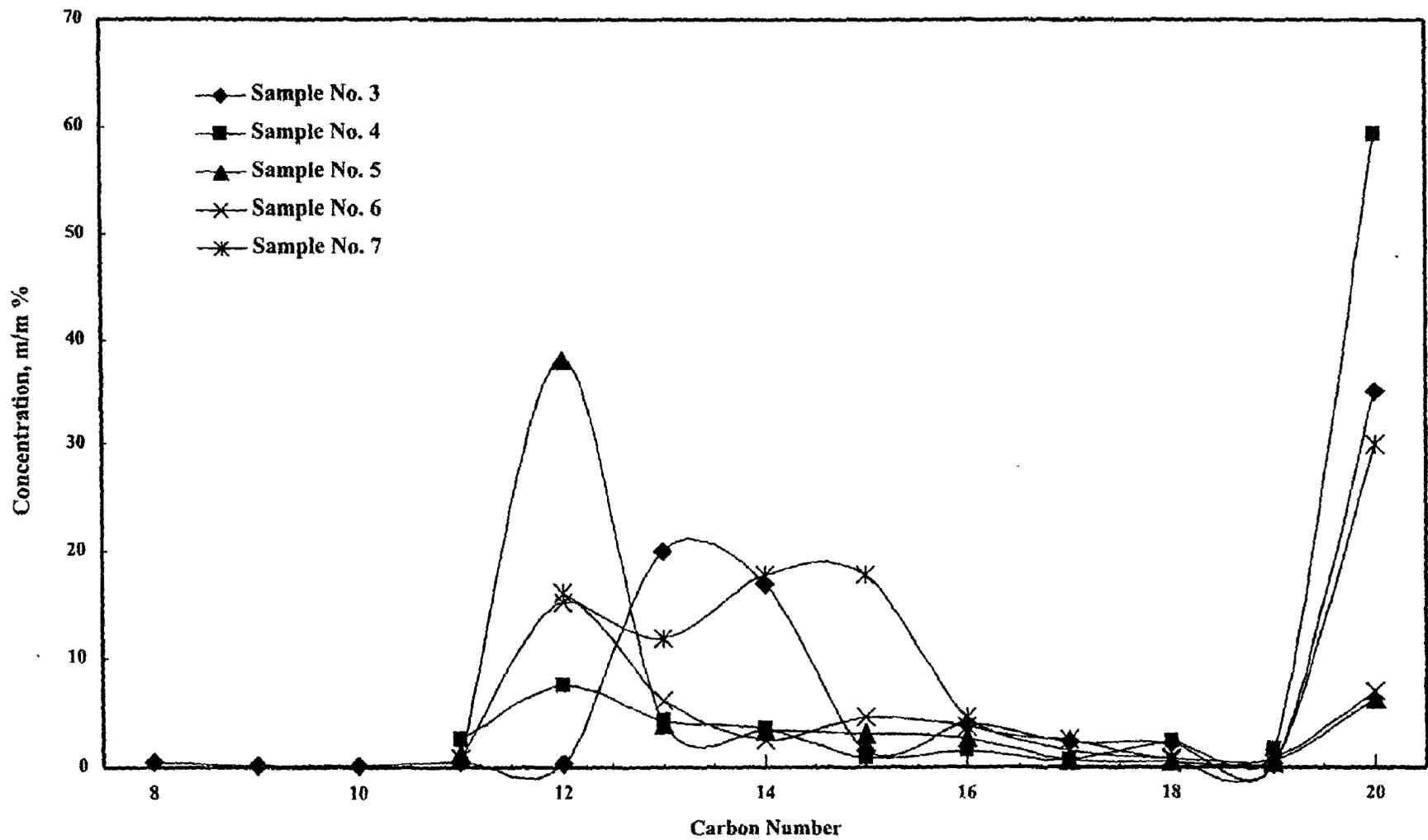


Fig. 28. Concentration-carbon number of methyl esters of fatty acids in the oil-field waters.

However, it is that of C₂₀-fatty acid in the other sample Nos. 3, 4 and 7 (being about 35, 59 and 30 % respectively).

3.12.5. Determination of *n*-paraffins in the saturates by gas chromatography

The *n*-paraffins in the saturates separated by silica gel column chromatography from the extracted oils of the studied water samples have been determined by gas chromatography. Results obtained are given in Table 21, and gas chromatograms of the saturates, as well as the concentration-carbon number of their *n*-paraffins identified are depicted in Figs. 29 and 30 respectively.

Each chromatogram is composed of resolved components of *n*- and non-*n*- paraffins superimposed on unresolved complex of hydrocarbons.

It is clear that the *n*-paraffins appear at *n*-C₁₁ in the sample Nos. 2 and 7, at *n*-C₁₇ in the sample Nos. 1, 4 and 6, and at *n*-C₁₈ in the sample Nos. 3 and 5. However, they disappear at *n*-C₄₀, *n*-C₄₁ and *n*-C₄₂ in the sample Nos. 2, 4, 5 and 6, 3 and 7, and 1, respectively.

Total *n*-paraffins represent about 7.3 to 8.2, 14 to 15 and 19 to 20 % of the saturates in the sample Nos. 2 to 4, 1 plus 5, then 6 and 7 respectively. Non-*n*-paraffins are in the range of about 3.8, 5.9 to 6.3 and 7.5 to 8.2 % of the saturates in the sample Nos. 1 and 4, 2, 3 and 7, then 5 and 6, respectively. Consequently, the unresolved complex form about 81 to 89 and 73 to 77 % of the saturates in the sample Nos. 1 to 4 and 5 to 7, respectively.

The odd-numbered carbon *n*-paraffins are in the range of 3.3 to 4.0, 6.8 to 7.3 and 10 % in the sample Nos. 2 to 4, 1 and 5, then 6 and 7, respectively. The even-carbon numbered ones have values of 4.1 to 4.4 and 7.2 to 9.9 in the sample Nos. 2 to 4 and others, respectively. Consequently, the ratios of both odd- to even-carbon numbered *n*-paraffins are 0.76 to 0.95 and 1.0 to 1.2 in the saturates of the sample Nos. 1 to 4 and 5 to 7, respectively.

3.12.6. Determination of polyaromatics in the aromatics fraction by high performance liquid chromatography

The polyaromatics in the separated aromatic fractions by silica gel column chromatography from the extracted oils of the studied water samples have been analyzed by the high performance liquid chromatography (HPLC) standard method [1].

Results obtained from this analysis are given in Table 22, and HPLC chromatograms of the aromatics are depicted in Fig. 31.

It is noticed that the total polyaromatics, in the five analyzed aromatics of the water samples Nos. 1, 3 and 5 to 7, are in the range of about 60 to 125 µg/L. The sample No. 6 has the lowest value, followed by the sample Nos. 5, 3, 7 and 1. In the same time, dibenzo(a, h)anthracene has the highest concentration among the polyaromatics identified, being in the range of about 48 to 116 µg/L. Thus, its concentration forms about 79 to 93 %

Table 21. Gas Chromatographic Analysis of the Saturates Separated from the Extracted Oils

Concentration, m/m%	Water Sample No.						
	1	2	3	4	5	6	7
<i>n</i> -C ₁₁	-	0.1026	-	-	-	-	2.9063
<i>n</i> -C ₁₂	-	0.2526	-	-	-	-	1.8445
<i>n</i> -C ₁₃	-	0.2510	-	-	-	-	1.8895
<i>n</i> -C ₁₄	-	0.2818	-	-	-	-	1.2895
<i>n</i> -C ₁₅	-	0.3486	-	-	-	-	1.1392
<i>n</i> -C ₁₆	-	0.4519	-	-	-	-	0.6650
<i>n</i> -C ₁₇	0.0024	0.3744	-	0.0400	-	0.0282	1.1890
<i>n</i> -C ₁₈	0.0180	0.4213	0.2557	0.0230	0.0544	0.0310	1.4008
<i>n</i> -C ₁₉	0.0297	0.3495	0.2026	0.0551	0.0449	0.0875	0.9338
<i>n</i> -C ₂₀	0.0930	0.6001	0.3881	0.1567	0.1416	0.5848	1.1947
<i>n</i> -C ₂₁	0.2135	0.5417	0.2589	0.2970	0.4466	1.1515	0.8854
<i>n</i> -C ₂₂	0.4696	0.3078	0.8446	0.3996	0.7853	1.5766	1.3209
<i>n</i> -C ₂₃	0.5090	0.2753	0.5465	0.4998	0.9727	1.7525	0.5259
<i>n</i> -C ₂₄	0.9062	0.2505	0.7370	0.6370	1.1783	1.9366	0.5160
<i>n</i> -C ₂₅	0.2788	0.2177	0.6635	0.1822	1.0874	1.8862	0.3526
<i>n</i> -C ₂₆	1.0439	0.3854	0.6701	0.8824	1.5122	2.1206	0.2817
<i>n</i> -C ₂₇	1.1256	0.3962	0.5002	0.9706	1.4113	2.0538	0.1645
<i>n</i> -C ₂₈	1.1679	0.4714	0.5918	0.9048	1.2126	1.7410	0.0681
<i>n</i> -C ₂₉	0.9199	0.4286	0.3824	0.6703	1.1623	1.4718	-
<i>n</i> -C ₃₀	0.6204	0.3594	0.3996	0.5084	0.8897	1.0301	-
<i>n</i> -C ₃₁	0.4885	0.2460	0.2623	0.3630	0.9530	0.8801	-
<i>n</i> -C ₃₂	0.4157	0.2145	0.1954	0.2602	0.7291	0.5591	0.0730
<i>n</i> -C ₃₃	0.2513	0.1585	0.1963	0.1680	0.6699	0.4536	0.0400
<i>n</i> -C ₃₄	0.2400	0.0868	0.1595	0.1918	0.4702	0.2156	0.0350
<i>n</i> -C ₃₅	0.2100	0.0639	0.1868	-	0.4192	0.1774	0.0471
<i>n</i> -C ₃₆	0.5574	0.0438	0.1423	0.0261	0.1674	0.0475	0.0276
<i>n</i> -C ₃₇	0.7573	0.0507	0.1186	0.0153	0.0750	0.0457	0.0593
<i>n</i> -C ₃₈	0.8114	0.0058	0.0183	0.0620	0.0081	0.0056	0.0285
<i>n</i> -C ₃₉	0.9328	0.1946	0.0199	0.0218	0.0456	0.0290	0.0065
<i>n</i> -C ₄₀	1.0404	0.0639	0.0151	0.0252	0.0176	0.0335	0.0047
<i>n</i> -C ₄₁	1.0603	-	0.0066	-	-	-	0.0029
<i>n</i> -C ₄₂	1.0403	-	-	-	-	-	-
Total <i>n</i> -P:	15.20	8.20	7.76	7.34	14.45	19.90	18.89
-Odd	6.78	4.00	3.34	3.28	7.29	10.02	10.14
-Even	8.42	4.20	4.42	4.08	7.17	9.88	8.75
-Odd/Even	0.81	0.95	0.76	0.80	1.02	1.01	1.16
Non- <i>n</i> -P	3.79	6.27	5.91	3.75	8.20	7.47	6.10
U.R.C.	81.01	85.53	86.32	88.91	77.34	72.63	75.01

- : Not present at detectable concentration.

n-P : *n*-Paraffins; non-*n*-P : non-*n*-Paraffins ; U.R.C. : Unresolved complex.

Table 22. High Performance Liquid Chromatographic Analysis of the Aromatics Separated from the Extracted Oils

Concentration, µg/L	Water Sample No.				
	1	3	5	6	7
Naphthalene	-	-	-	-	-
Acenaphthylene	-	-	-	2.330	-
Unknown peak	-	-	-	x	-
Acenaphthene	-	-	-	-	-
Fluorene	-	-	-	-	-
Phenanthrene	1.275	0.296	1.104	1.446	1.784
Unknown peak	-	x	-	-	-
Anthracene	-	-	-	-	-
Fluoranthene	1.693	3.770	2.437	2.244	2.677
Pyrene	4.327	4.214	3.778	3.986	6.092
Unknow peak	x	x	x	x	x
Benzo(a)anthracene	-	-	-	0.883	0.394
Chrysene	0.166	0.173	0.126	0.146	0.161
Unknow peak	x	x	x	x	x
Benzo(b)fluoranthene	0.326	0.368	0.353	1.659	-
Benzo(k)fluoranthene	1.413	-	0.704	-	2.629
Benzo(a) pyrene	-	-	-	1.962	-
Dibenzo(a,h)anthracene	115.9	98.21	88.02	47.69	102.5
Benzo(g,h,l)perylene	-	-	-	-	-
Indeno(1,2,3-cd)pyrene	-	-	-	-	-
Total	125.1	107.0	96.5	60.4	116.2
Dibenzo(a,h)anthracene/total	0.92	0.77	0.91	0.79	0.88

x : unknown peak present; - : not present at detectable concentration.

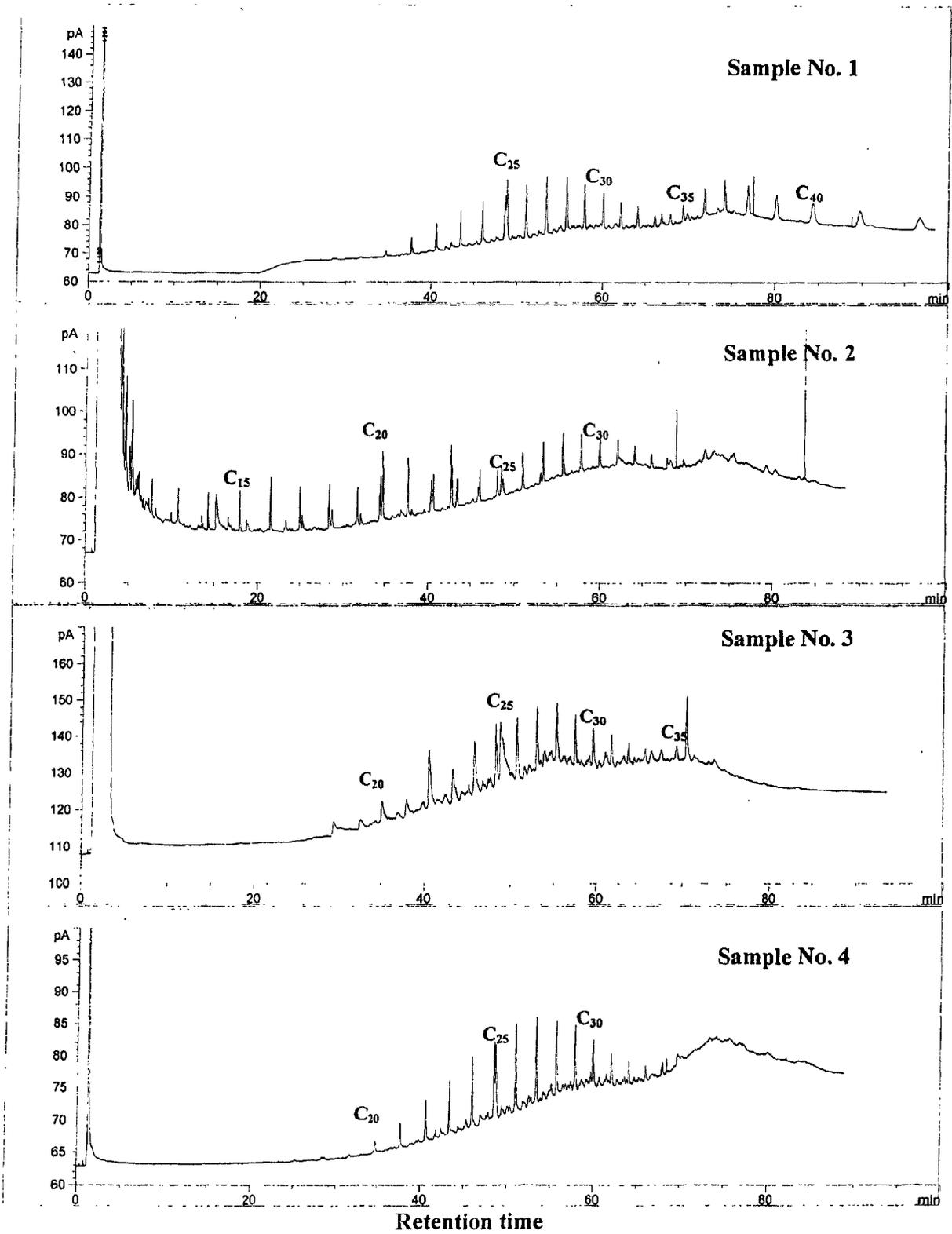


Fig. 29. Gas chromatograms of the saturates separated from the extracted oils of the oil-field waters.

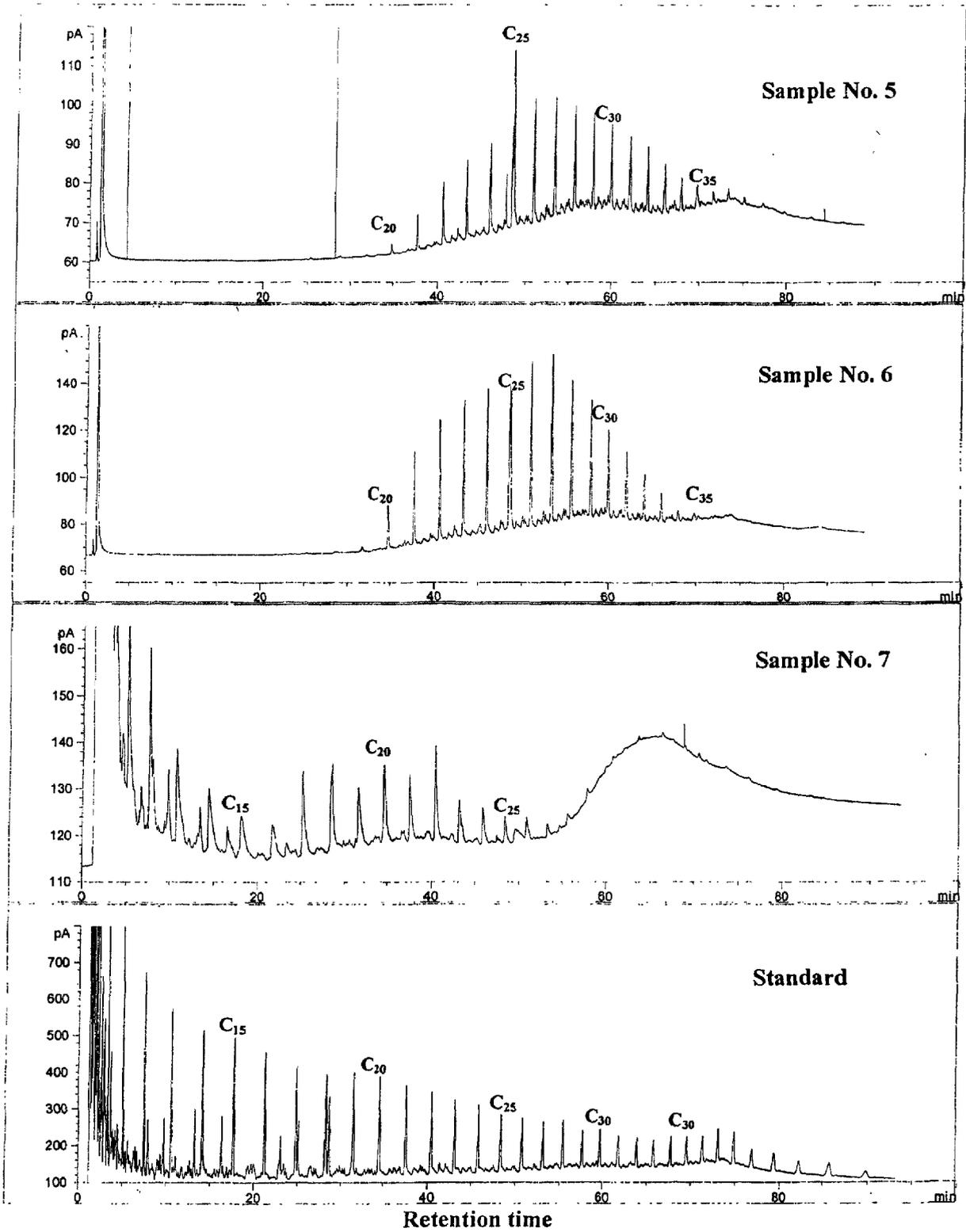


Fig. 29. Continued.

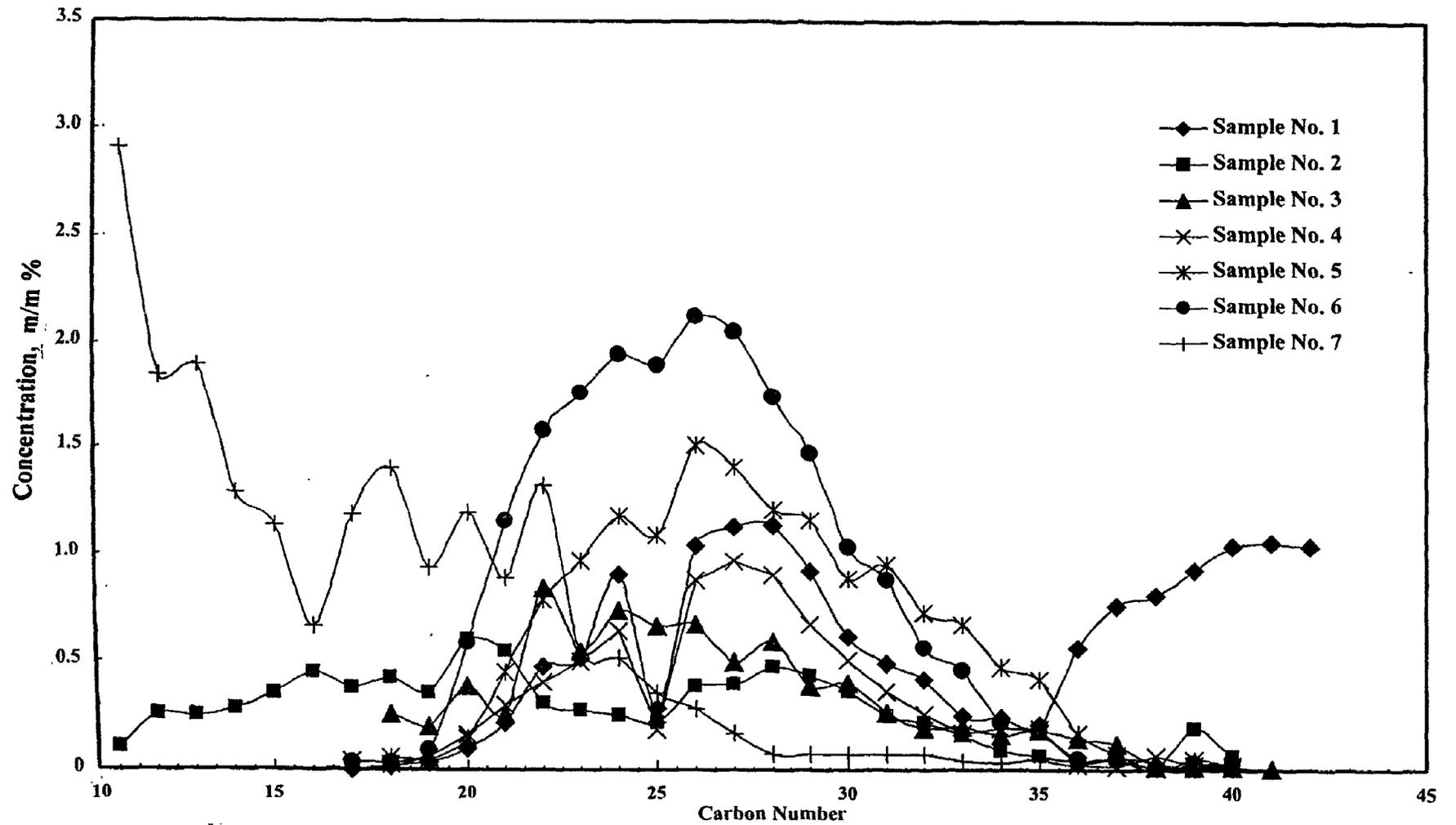


Fig. 30. Concentration-carbon number of *n*-paraffins in the saturates separated from the extracted oils of the oil-field waters.

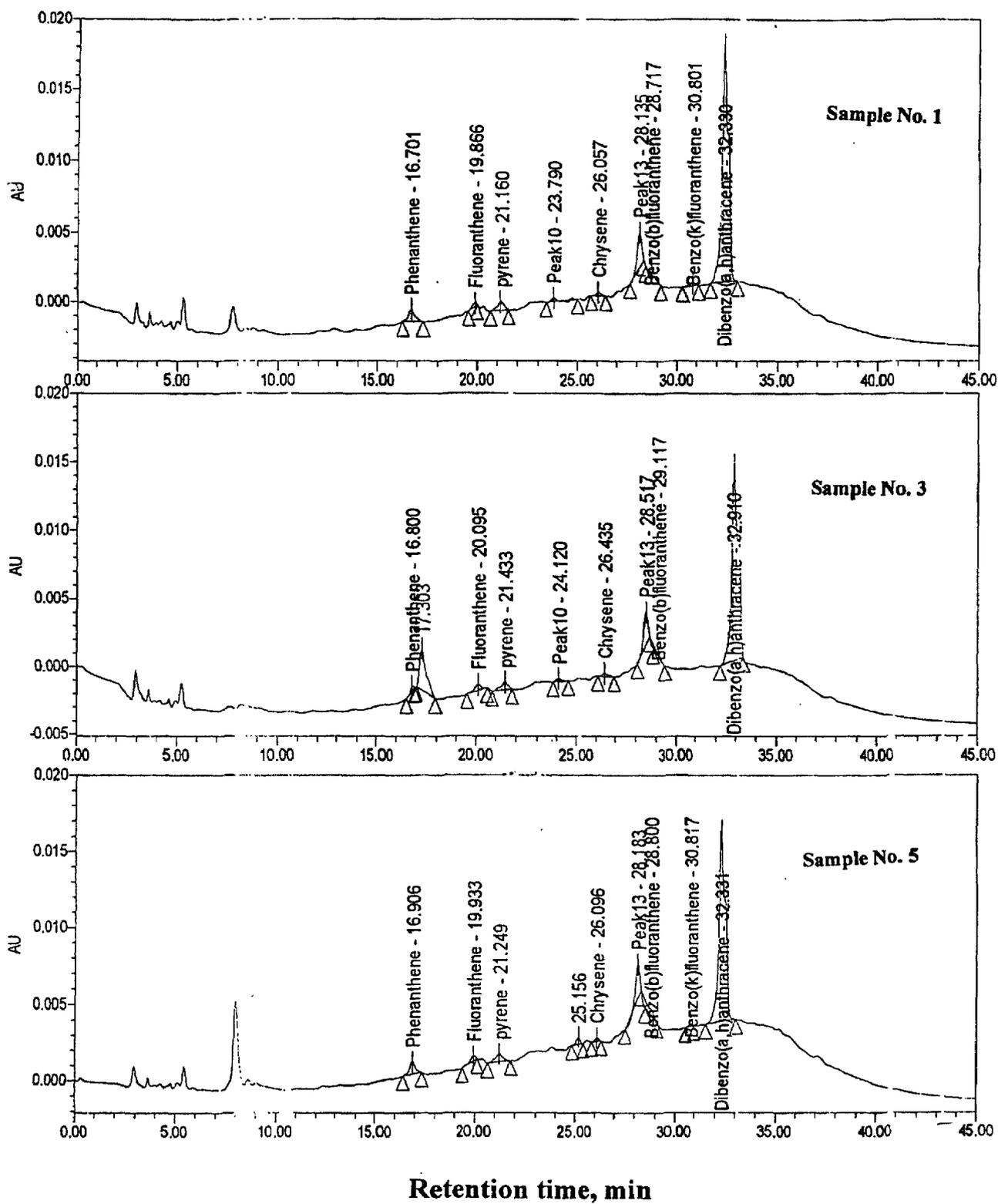


Fig. 31. High performance liquid chromatography of the polyaromatics in the aromatics of the oil-field waters.

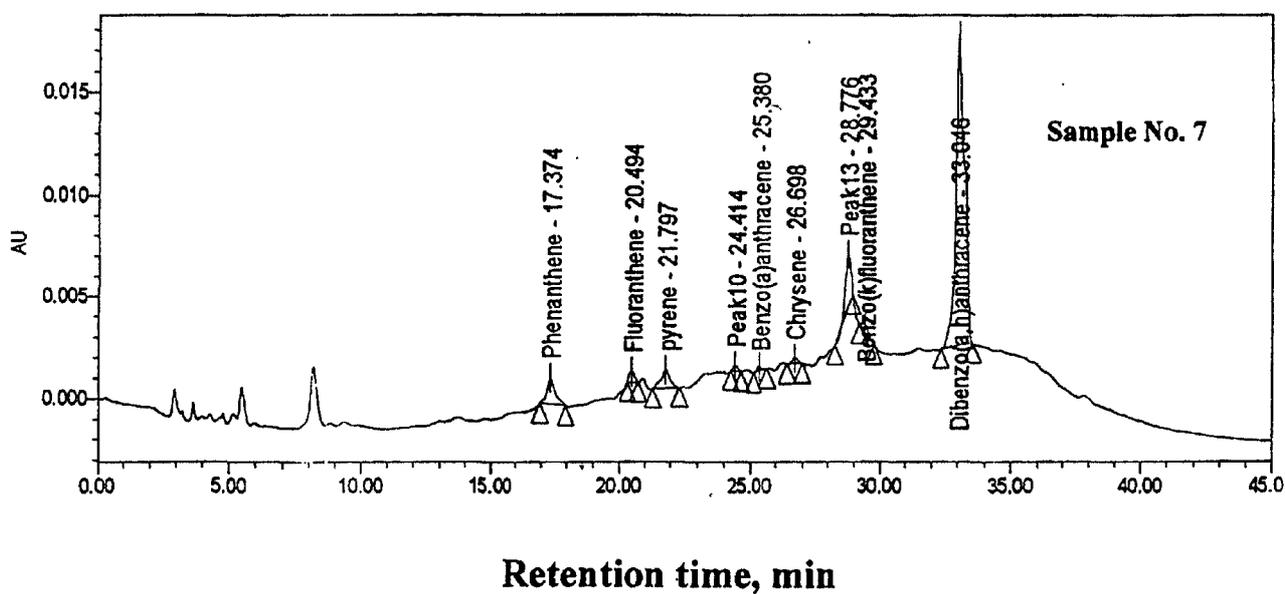
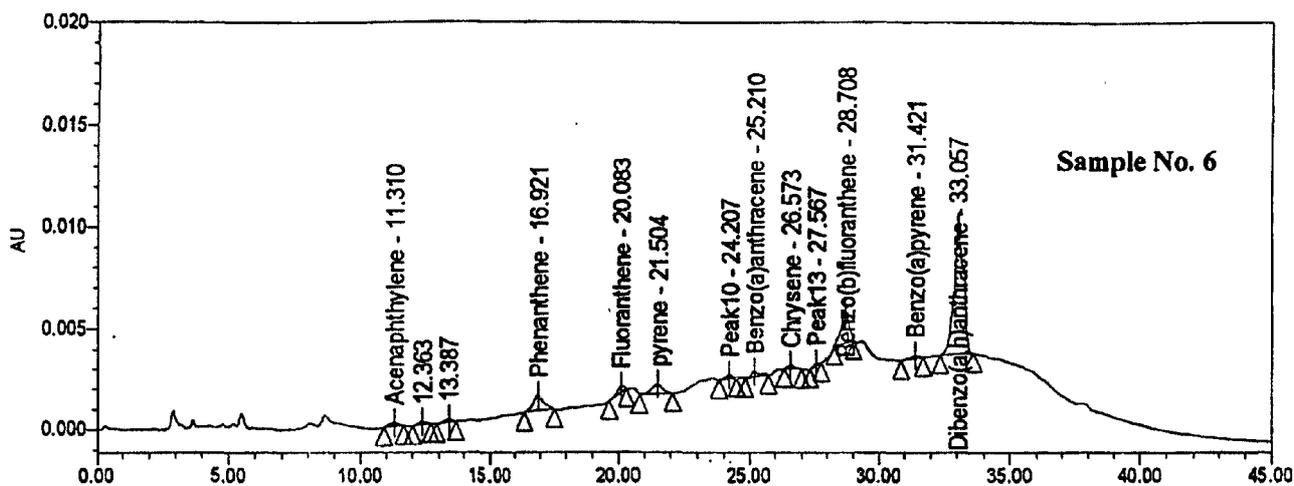


Fig. 31. Continued.

of the total polyaromatics identified in the studied samples. The sample No. 6 has the lowest percentage (as well as the total polyaromatics), followed by those of the sample Nos. 7, 5, 3 and 1.

So, the predominance of polyaromatics identified is as follows:

dibenzo(a, h)anthracene >> pyrene > fluoranthene > phenanthrene >
benzo(b)fluoranthene > chrysene.

It is clear that acenaphthylene is present in the sample No. 6, benzo(a)anthracene in the sample Nos. 6 and 7, benzo(k)fluoranthene in the sample Nos. 1, 5 and 7, and benzo(a)pyrene in the sample No. 6.

It is noted that dibenzo(a, h)anthracene is the major polyaromatic hydrocarbon present in all the studied samples. Its ratio to the total polyaromatics varies from 0.77 to 0.93, being 0.77, 0.79, 0.88, 0.91 and 0.93 in the sample Nos. 3, 6, 7, 5 and 1 respectively.

3.12.7. Determination of functional groups in the extracted oils by infrared spectrometry

Functional groups in the extracted oils from the examined oil-field waters have been determined by measurement of their infrared absorption spectra in the range of wavenumbers 4000 to 400 cm^{-1} using FT-IR spectrometer and applying the KBr disc technique.

The measured infrared spectra, in wavenumber – % transmittance and wavenumber – absorbance, of these oils are shown in Figs. 32 and 33 respectively. The position (in wavenumber, cm^{-1}) and intensity (in absorbance) of the main bands present in these infrared spectra are given in Table 23. The assignments of vibrations of the functional groups, which give rise to their bands in the infrared spectra [433-435], are given in Table 24.

The infrared bands of the functional groups reflect the chemical composition of the studied oils, which are formed of *n*-, *iso*- and *cyclo*paraffins (alkanes) and mono-, di- and polyaromatics, as well as non-hydrocarbons, such as oxygen (e. g. fatty or alkanolic acids), nitrogen and sulphur compounds.

In the measured infrared spectra of the oils, the paraffins are indicated by the presence of vibrations of their functional groups:

- CH_3 asymmetric stretching at 2955 cm^{-1} ,
- CH_2 asymmetric stretching at 2925 cm^{-1} ,
- CH_2 symmetric stretching at 2855 – 2850 cm^{-1} ,
- CH_3 and CH_2 asymmetric deformation at 1460 – 1450 cm^{-1} and 1420 – 1400 cm^{-1} ,
- CH_3 symmetric deformation (scissoring) at 1380 – 1375 cm^{-1} ,
- CH_2 wagging in long paraffinic chains at 1350 cm^{-1} .
- CH in *cyclo*paraffinic (naphthenic) rings at 1000 – 945 cm^{-1} , and
- CH_2 rocking in long paraffinic chains $(\text{CH}_2)_n$, $n \geq 4$ at 725 – 715 cm^{-1} .

Table 23. Wavenumbers and Absorbances of the Main Bands in the Infrared Spectra of the Oil Extracted from the Oil-Field Waters.

Water Sample No.													
1		2		3		4		5		6		7	
ν , cm^{-1}	A												
3430	0.1610	3419	0.0538	3409	0.1262	3431	0.1456	3413	0.1022	3436	0.1363	3443	0.2026
2954	0.2009	2954	0.1679	2954	0.1678	2953	0.1424	2952	0.1863	2952	0.1437	2954	0.1118
2925	0.2743	2923	0.2523	2925	0.2457	2923	0.2345	2923	0.3030	2924	0.2103	2923	0.1797
2854	0.1516	2852	0.1513	2853	0.1445	2853	0.1332	2853	0.1699	2853	0.1136	2853	0.1023
-	-	-	-	-	-	-	-	-	-	-	-	2671	0.0331
2587	0.0300	-	-	-	-	-	-	-	-	2569	0.0113	-	-
2359	0.0312	2362	0.0068	-	-	2360	0.0175	2360	0.0268	2385	0.0057	2360	0.0437
2335	0.0281	2336	0.0066	-	-	2336	0.0144	2335	0.0234	2343	0.0038	2336	0.0411
1838	0.0412	1885	0.0160	1871	0.0225	1874	0.0226	1830	0.0245	1860	0.0305	1818	0.0345
1719	0.2000	1728	0.0906	1719	0.1138	1727	0.1088	1726	0.0969	1706	0.1752	1725	0.0589
1648	0.0864	1649	0.1930	1658	0.1144	1646	0.0721	1659	0.0666	1646	0.0783	1633	0.0801
-	-	-	-	1603	0.0842	-	-	1616	0.0485	-	-	-	-
1526	0.0405	-	-	-	-	1537	0.0232	-	-	1531	0.0303	1542	0.1073
-	-	1511	0.0183	1507	0.0231	1508	0.1727	1517	0.0241	-	-	1520	0.0353
1455	0.1170	1461	0.0736	1452	0.0949	1459	0.0863	1459	0.0909	1459	0.0846	1460	0.0692
1412	0.0673	1413	0.0582	1418	0.0696	1408	0.1928	1408	0.2499	1415	0.0656	1402	0.0812
1378	0.0816	1377	0.0499	1379	0.0741	1379	0.0609	1377	0.0596	1380	0.0693	1377	0.0438
-	-	-	-	-	-	-	-	1352	0.0458	-	-	1352	0.0386
1276	0.1234	1270	0.0593	1283	0.0765	1282	0.0753	1283	0.0820	1280	0.1009	1284	0.0471
1171	0.1024	1165	0.0615	1166	0.0619	1158	0.1855	-	-	1174	0.0825	1180	0.0429
1121	0.1145	1119	0.0587	1122	0.0810	1120	0.0919	1116	0.1451	1121	0.0811	1110	0.0987
1073	0.0782	-	-	1073	0.0546	1074	0.0781	1078	0.1482	1077	0.0695	-	-
-	-	1040	0.0411	1015	0.0624	1038	0.0688	1037	0.0600	1040	0.0565	1035	0.0991
998	0.1325	-	-	-	-	-	-	952	0.0267	-	-	947	0.0390
873	0.0309	879	0.0088	890	0.0188	872	0.0259	-	-	874	0.0165	873	0.1049
811	0.0405	808	0.0306	846	0.0218	-	-	833	0.0084	839	0.0089	828	0.0387
785	0.0408	-	-	-	-	776	0.0290	-	-	-	-	794	0.0383
-	-	764	0.0198	-	-	766	0.0292	-	-	-	-	-	-
748	0.0369	748	0.2128	748	0.0277	745	0.0253	749	0.0247	750	0.0393	758	0.0376
713	0.0432	721	0.0233	721	0.0256	720	0.0282	721	0.0213	717	0.0273	726	0.0339

Table 24. Assignment of Vibrations of the Functional Groups in the Infrared Spectra of the Oils Extracted from the Oil-Field Waters

Wavenumber, cm ⁻¹	Assignment of the Vibrations of the Functional Groups
3445 – 3410	OH stretching; NH stretching
2955	CH ₃ asymmetric stretching
2925	CH ₂ asymmetric stretching
2855 – 2850	CH ₂ symmetric stretching
2670	OH stretching in carboxylic acid bonded
2585 – 2570	C–O stretching overtones in ketones and acids
2385 – 2360	CH deformation overtones in aromatic rings
2345 – 2335	CH deformation overtones in aromatic rings
1885 – 1820	CH deformation overtones in aromatic rings
1730 – 1705	C=O stretching in carbonyl groups
1660 – 1630	C=O stretching in carbonyl groups
1615 – 1605	C=C stretching in aromatic rings
1540 – 1525	C=C stretching in aromatic rings
1520 – 1505	C=C stretching in aromatic rings
1460 – 1450	CH ₃ and CH ₂ asymmetric deformation
1420 – 1400	CH ₃ and CH ₂ asymmetric deformation
1380 – 1375	CH ₃ symmetric deformation (scissoring)
1350	CH ₂ wagging in long paraffinic chains
1285 – 1270	C–O stretching in ketones and acids
1180 – 1160	CH aromatic in-plane deformation
1120 – 1110	C–O asymmetric stretching
1080 – 1075	C–O asymmetric stretching
1040 – 1015	C–O stretching; C–N stretching; S=O stretching
1000 – 945	CH in naphthenic rings
890 – 870	CH aromatic out-of-plane deformation (one free hydrogen)
845 – 810	CH aromatic out-of-plane deformation (two free adjacent hydrogens)
795 – 775	CH aromatic out-of-plane deformation (three free adjacent hydrogens)
765 – 760	CH aromatic out-of-plane deformation (four free adjacent hydrogens)
750 – 745	CH aromatic out-of-plane deformation (five free adjacent hydrogens)
725 – 715	CH ₂ rocking in long paraffinic chains (CH ₂) _n , n ≥ 4

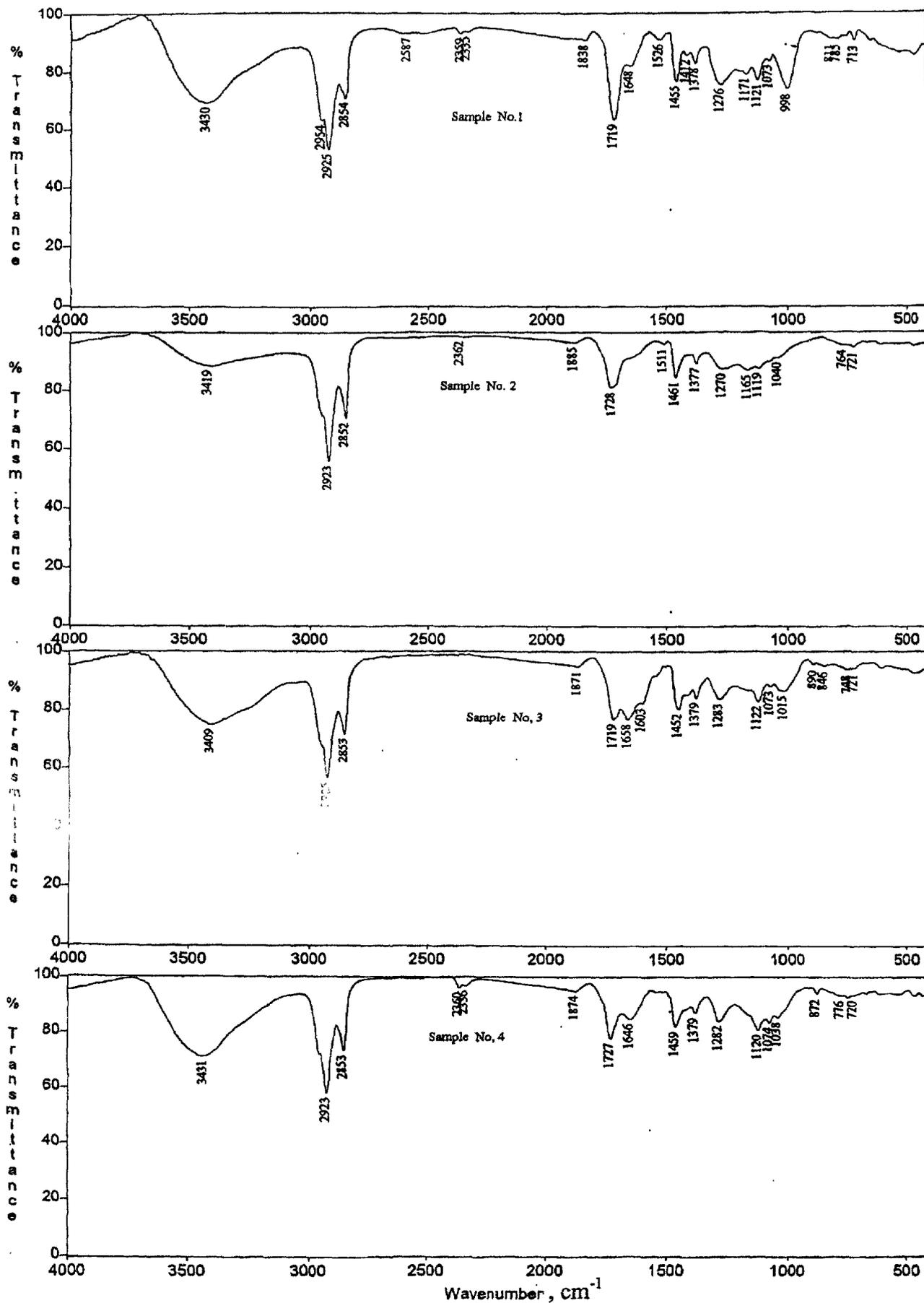


Fig. 32. Infrared spectra (wavenumber-% transmittance) of the oils extracted from oil-field waters.

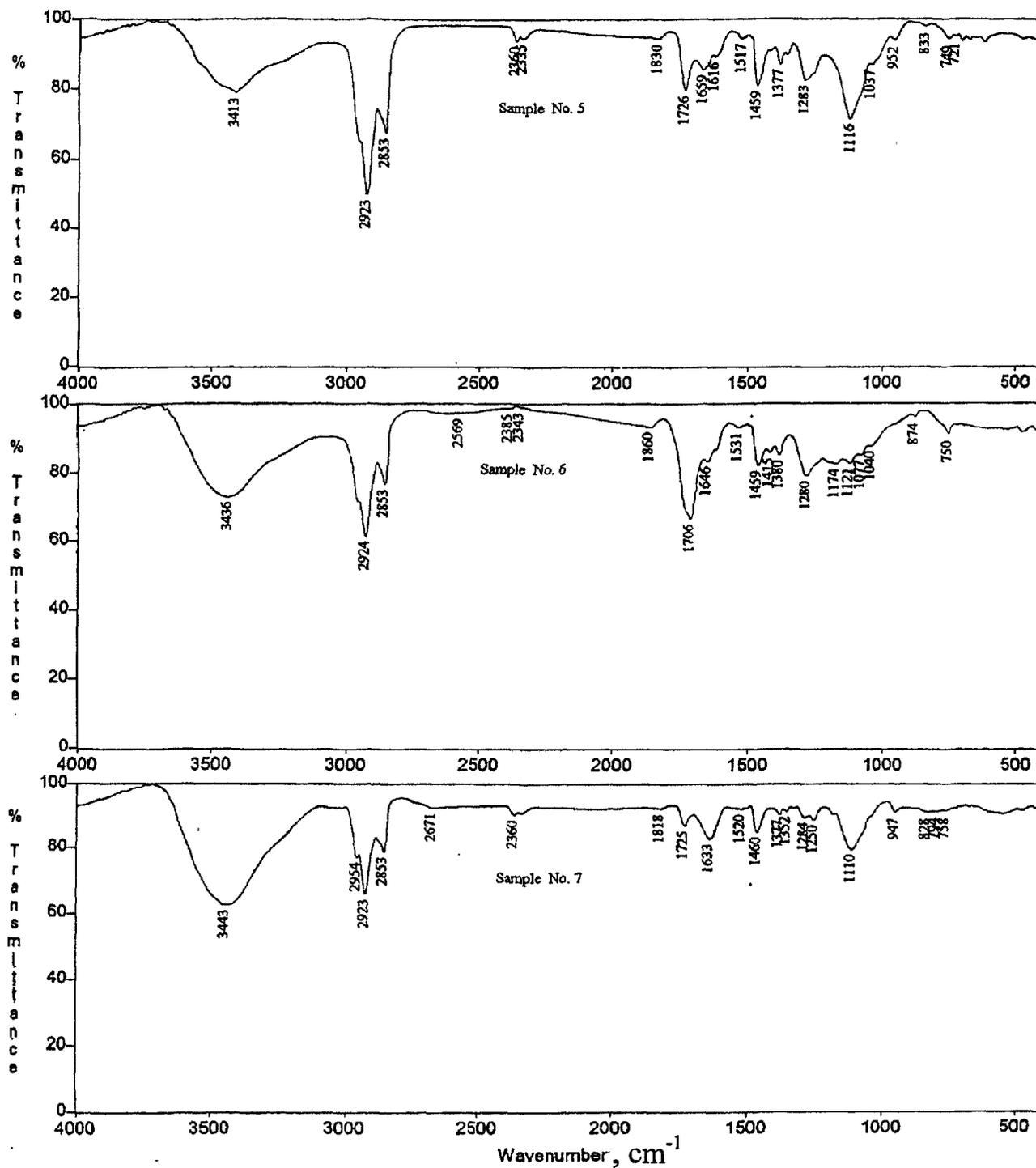


Fig. 32. Continued.

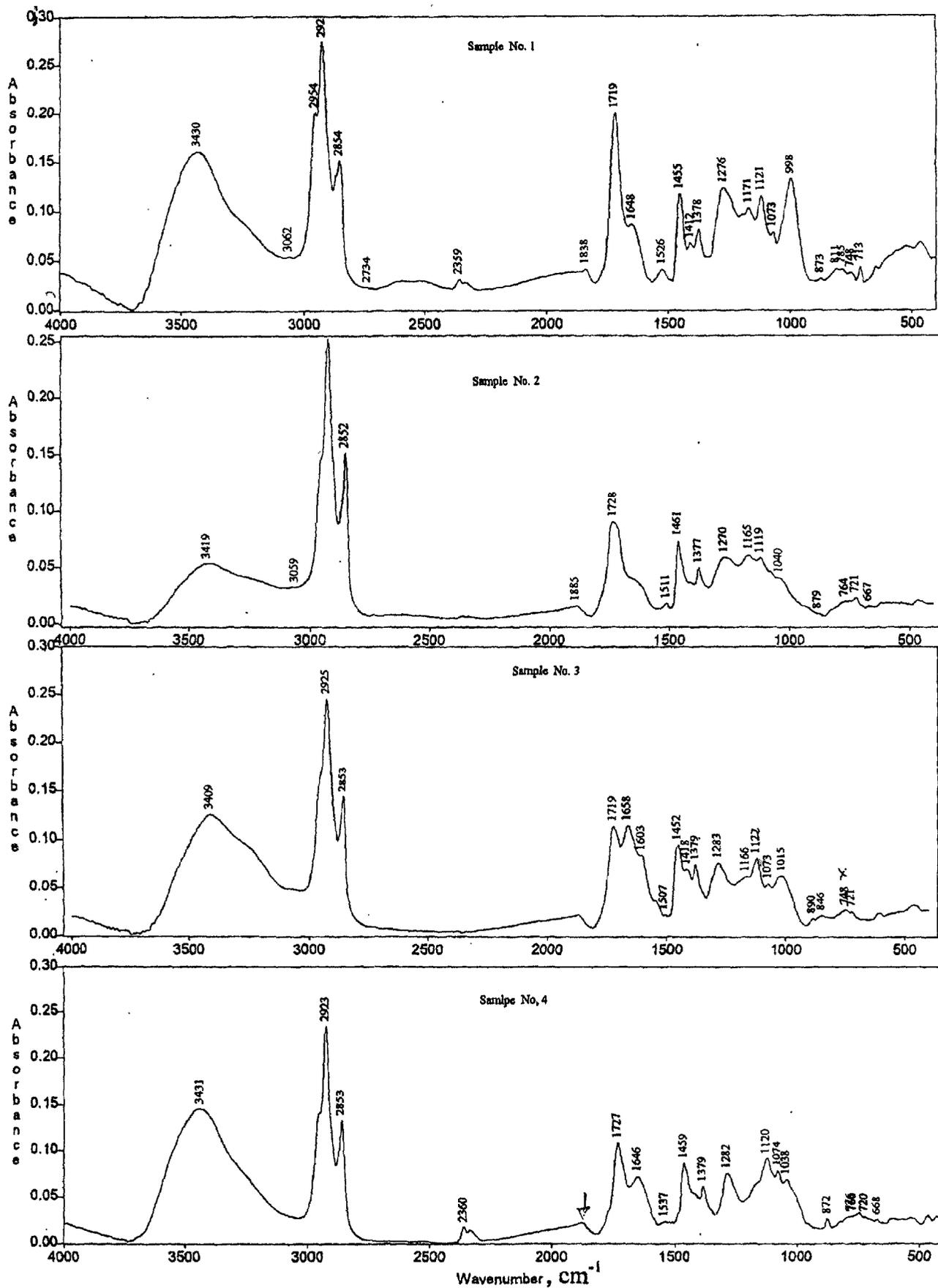


Fig. 33. Infrared spectra (wavenumber-absorbance) of the oils extracted from oil-field waters.

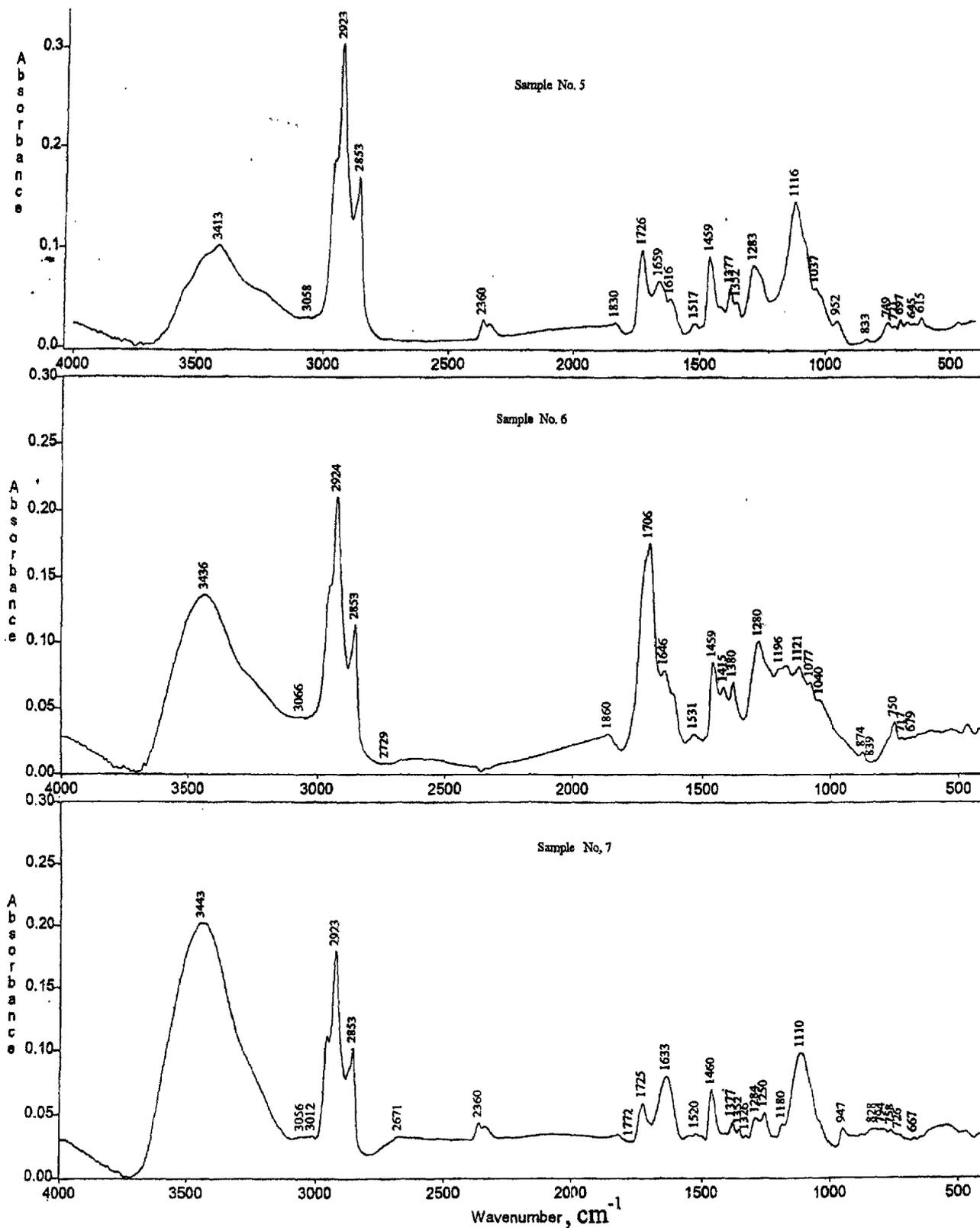


Fig. 33. Continued.

In these spectra, the aromatics are confirmed by the presence of vibrations of their functional groups:

- CH stretching in aromatic rings at $3100 - 3000 \text{ cm}^{-1}$ is not clear, as it is hidden by strong bands on both its sides,
- CH deformation overtones in aromatic rings at $2385 - 2360$ and $2345 - 2335$, and $1885 - 1820 \text{ cm}^{-1}$,
- C=C stretching in aromatic rings at $1615 - 1605$, $1540 - 1525$ and $1520 - 1505 \text{ cm}^{-1}$,
- CH aromatic in-plane deformation at $1180 - 1160 \text{ cm}^{-1}$, and
- CH aromatic out-of-plane deformation for one, two, three, four and five free adjacent hydrogen atoms at $890 - 870$, $845 - 810$, $795 - 775$, $765 - 760$ and $750 - 745 \text{ cm}^{-1}$, respectively.

In these spectra, the fatty or alkanolic acids are indicated by the presence of vibrations of their functional groups:

- CH_3 and CH_2 stretching and deformation as fore-mentioned with the paraffins.
- OH stretching at $3445 - 3410 \text{ cm}^{-1}$,
- C-O stretching overtones in acids and ketones at $2585 - 2570 \text{ cm}^{-1}$,
- OH stretching in carboxylic acids bonded at 2670 cm^{-1} ,
- C=O stretching in carbonyl groups at $1730 - 1705$ and $1660 - 1630 \text{ cm}^{-1}$,
- C-O stretching in acids and ketones at $1285 - 1270 \text{ cm}^{-1}$,
- C-O asymmetric stretching at $1120 - 1110$ and $1080 - 1075 \text{ cm}^{-1}$, and
- C-O stretching at $1040 - 1015 \text{ cm}^{-1}$.

In these spectra, the nitrogen and sulphur compounds may be indicated by the presence of vibrations of their functional groups:

- NH stretching at $3445 - 3410 \text{ cm}^{-1}$, and
- C-N stretching and S=O stretching at $1040 - 1015 \text{ cm}^{-1}$.