

PART TWO
PRESENT WORK

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1. AIM OF THE WORK

Chemical analyses of waters produced with the oil are useful in oil production problems, such as identifying the source of intrusive water, planning water-flood and salt-water disposal projects, and treating to prevent corrosion problems in primary and secondary recovery. Electrical well-log interpretation requires a knowledge of the dissolved solids concentration and composition of interstitial water. Such information also is useful in correlation of stratigraphic units and of the aquifers within these units, and in studies of the movement of subsurface waters. It is impossible to understand the processes that accumulate petroleum or other minerals without insight into the nature of these waters. Oil-field waters generally contains ions in high concentrations, which might be economically recovered as salts, e.g. NaCl, KCl and MgCl₂, or as elements, e.g. Cl, Br, I, Li, Na, K, Mg, Ca and B. These salts or elements might be used as sources for the preparation of other valuable compounds, e.g. HCl, NaOH, NaBr and NaI [1-6].

In Egypt, the main oil-fields have been discovered in the Gulf of Suez region, from which the oils have been produced since more than a century. This region includes the Gulf eastern coast in Sinai, the Gulf itself and its western coast in the Eastern Desert. Recently, some oil-fields have been discovered in the northern part of the Western Desert. Actually, many studies [413 – 421] have been carried out on the oil-field waters in the Gulf of Suez region, and only one study [422] on those in the northern part of the Western Desert has been done.

The present work will be carried on seven waters associated with crude oils produced from seven individual wells of six oil-fields, namely, Belayim (in Sinai), Ashrafi, Ramadan and Zeit Bay (in the Gulf of Suez), Meleiha and Razzak (in Western Desert).

The analysis of these waters includes the determination of their general physico-chemical properties (pH, density/specific gravity, electrical conductivity/ resistivity, total dissolved solids, acidity, alkalinity and hardness), alkali cations (lithium, sodium and potassium), alkaline earth cations (magnesium, calcium, strontium and barium), iron, manganese, halides (fluoride, chloride, bromide and iodide), sulphate, nitrate, borate, carbonate, bicarbonate and hydroxide. The reaction values of the determined cations and anions, probable compounds of their hypothetical combinations and their genetic coefficients will be calculated to apply different systems of water geochemical classification on the studied waters.

Organic constituents, including fatty acids and oils, will be investigated through their extractions by sodium carbonate and methylene chloride, respectively. The extracted oils will be fractionated into their saturates, aromatics and resins. The extracted fatty acids will be analyzed by gas chromatography. The *n*-paraffins in the saturates and polyaromatics in the aromatics will be determined by gas chromatography and high performance liquid

chromatography, respectively. The functional groups in the oils will be identified by infrared spectrometry.

The obtained results will be discussed in relation of the studied oil-field waters to their general physico-chemical properties, ion compositions, geochemical classifications, enrichments, and the geological data of their productive zones in the wells of the oil-fields. Statistical correlation among these data will be calculated using the linear regression analysis.

2. EXPERIMENTAL

2.1. Collection of the Studied Oil-Field Water Samples

Seven samples of formation waters associated with crude oils produced from individual wells of six oil-fields were kindly provided by the Belayim Petroleum, Agiba Petroleum, Gulf of Suez Petroleum and Suez Oil Company.

Water samples were collected from Belayim oil-field located in Sinai, from Ashrafi, Ramadan and Zeit Bay oil-fields located in the Gulf of Suez, and from Meleiha and Razzak oil-fields located in the Western Desert of Egypt. The locations of these oil-fields are shown in Fig.1.

2.2. Methods Used in the Analysis of the Oil-Field Waters

The analysis of the studied oil-field waters was carried out using ASTM [1] and/or APHA [2] standard methods for the water analysis, unless otherwise indicated.

The water samples were filtered using ashless filter papers (Whatman No. 42) before they were subjected to the analysis.

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

General physico-chemical properties, including the pH, density, specific gravity, electrical conductivity, resistivity, total dissolved solids, salinity, acidity, alkalinity and hardness were determined for the oil-field waters under study.

2.3.1. pH

The pH was determined using the electrometric method according to the ASTM D1293 [1], APHA 4500H⁺ [2] and API [3] methods.

The pH of the water samples was measured at 25°C using a digital pH-meter, Hanna model pH 213, equipped with a combination pH electrode, HI 1230 B, consisting of glass electrode and silver-silver chloride reference electrode.

The pH-meter with the combination electrode was standardized under controlled parameters using three buffer solutions of pH 4.01, 6.86 and 9.18 at 25°C before measurements of the pH of the water samples were carried out.

2.3.2. Density and specific gravity

The density and specific gravity were determined using the pycnometer method according to the ASTM D1429 [1], APHA 2710 F and API [3] methods.

The specific gravity of the water samples was measured at 60/60°F using a capillary stoppered pycnometer. The water sample was introduced into the pycnometer, stabilized at the test temperature and weighed. The specific gravity was calculated from this weight and

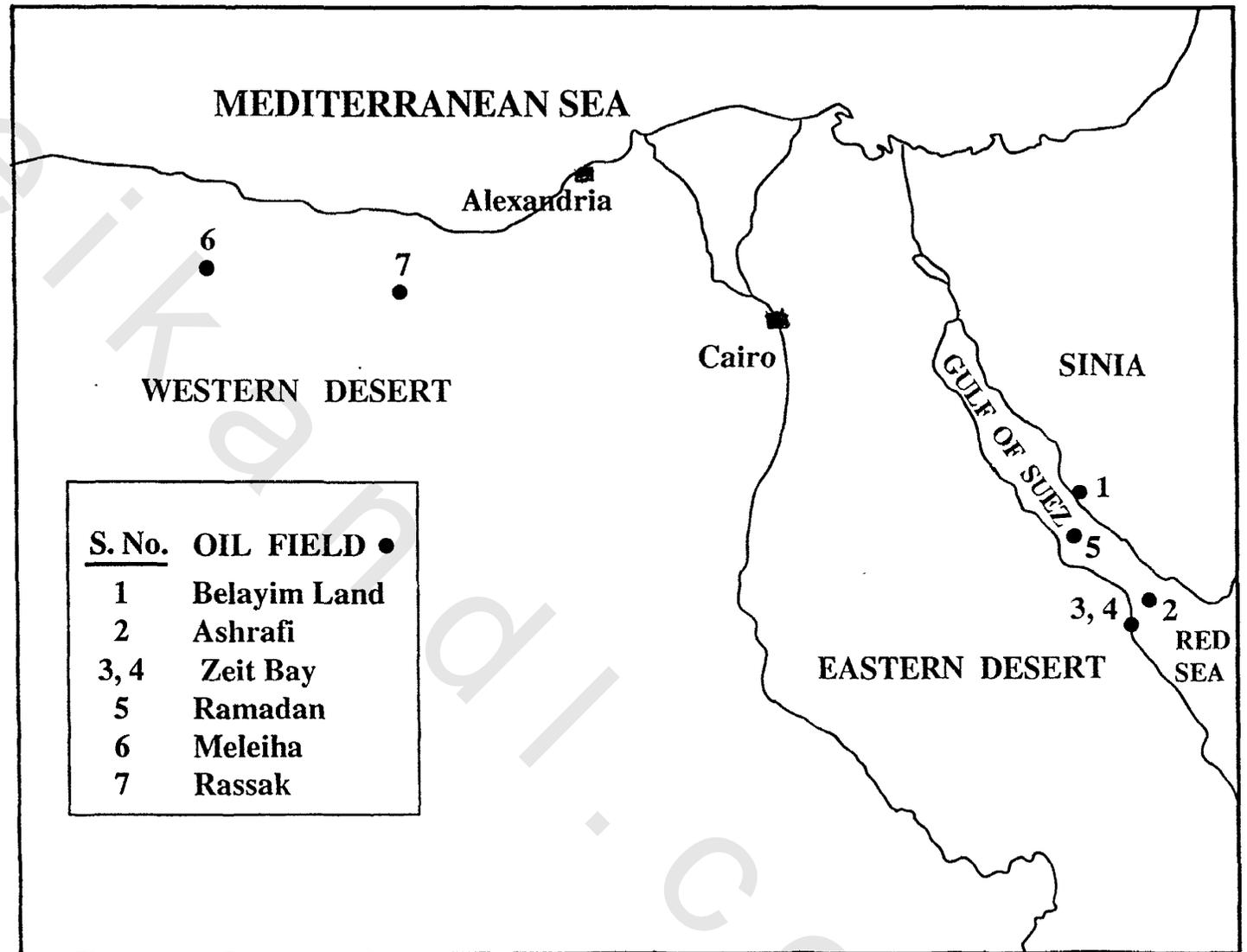


Fig. 1. Location map of the oil-fields producing the studied water samples.

the previously determined weight of distilled water that was required to fill the pycnometer at the same temperature.

The density, at 15°C of the water samples was calculated from their obtained results of specific gravity at 60/60°F.

2.3.3. Electrical conductivity and resistivity

The electrical conductivity was determined using the instrumental method according to the ASTM D1125 [1] APHA 2510 [2] and API [3] methods.

The conductivity of the water samples was determined at 25°C using a digital conductivity meter, WTW, model Cond 330i, equipped with a conductivity cell. The cell was rinsed thoroughly several times with deionized water and then with the sample to be measured. The temperature of the sample was stabilized at 25°C in a thermostat.

The resistivity of the water samples was calculated from their obtained conductivity values.

2.3.4. Dissolved solids

Dissolved solids were determined according to the ASTM D1888 [1], APHA 2540 [2] and API [3] methods.

The dissolved solids in the water samples at 105, 180, 550°C were determined by drying suitable aliquots of the water samples at 105°C and then at 180°C in an oven, and finally ignition at 550°C in a muffle furnace.

2.3.5. Salinity

The salinity of the water samples were estimated from the determined chloride concentration to give the salinity as sodium chloride, as will be described later (2.6.1 and 2.6.2).

2.3.6. Acidity

The acidity was determined for samples Nos. 1, 2 and 5 by the potentiometric titration method according to the ASTM D1067 [1] and APHA 2310 [2] and API [3] methods.

Apparatus used: A potentiometric automatic titrator, model AT-400, Kyoto Electronics, equipped with a glass and calomel reference electrodes.

Procedure: A suitable aliquot of the water sample was titrated potentiometrically to the pH 8.3 with a standard sodium hydroxide solution. The alkali solution was added automatically, while the sample was gently mixed with a magnetic stirrer. The total acidity, as calcium carbonate, was then calculated.

2.3.7. Alkalinity

The bicarbonate alkalinity was determined for samples Nos. 3, 4, 6 and 7 by the potentiometric titration method according to the ASTM D1067 and D3875 [1] and APHA 2320 [2] and API [3] methods.

Apparatus used: Described before in (2.3.6).

Procedure: A suitable aliquot of the water sample was titrated potentiometrically to the pH 4.5 with a standard hydrochloric acid solution. The acid solution was added automatically, while the sample was gently mixed with a magnetic stirrer. The bicarbonate alkalinity, as calcium carbonate, was calculated.

2.3.8. Hardness

The hardness, according to the ASTM D1126 [1] and APHA 2340 B [2] methods, was estimated from the calcium and magnesium concentrations determined by the ASTM D1976 [1] and APHA 3120 B [2] methods.

The calcium, magnesium and total hardness, as calcium carbonate, of the water samples were calculated from the determined calcium, magnesium and their total concentrations, as described later in (2.4.1).

2.4. Determination of Alkali and Alkaline Earth Cations in the Oil-Field Waters

Concentrations of alkali and alkaline earth cations, including lithium, sodium, potassium, magnesium, calcium, strontium and barium, were determined in the water samples using different analytical techniques, such as ICP-AES, IC and EDTA titration.

2.4.1. Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

Lithium, sodium, potassium, magnesium, calcium, strontium and barium were determined by the inductively coupled plasma-atomic emission spectrometry according to the ASTM D1976 [1] and APHA 3120 [2] methods. The standard additions method was also used to overcome the effect of the sample matrix.

Apparatus used: ICP Spectrometer, Flame-ICP Modula, Spectro, GmbH; having: RF generator: 27.12 MHz \pm 10 kHz; Plasma power: 2.5 kW; Nebulizer chamber: Glass Scott; Sample pump: peristaltic; Argon gas flow: Coolant (plasma): 12 to 18, auxiliary (intermediate): 0.8 to 2, and nebulizer (carrier): 0.7 to 1, L/min.

Procedure: Standard solutions of Li, K, Na, Mg, Ca, Sr and Ba in deionized water were prepared using analytical grade reagents. Measurements were determined by:

- Direct method: Each water sample, diluted to a suitable concentration, was measured at the specific wavelength of the analyte. Its concentration was calculated from the calibration curve of its prepared standard solutions measured at the same conditions.

- Standard additions method: For each water sample, after dilution to be suitable for measurements, three identical samples were prepared and different amounts of the analyte standard were added to two of them. The three samples were measured at the specific wavelength of the analyte, where their concentration readings were recorded, then the concentration of the analyte in the original water sample was calculated.

The analysis of Li, Na, K, Mg, Ca, Sr and Ba were measured at wavelengths of 670.784, 589.592, 766.491, 279.806, 315.887, 421.552 and 445.403 nm, respectively.

2.4.2. Ion chromatography (IC) for lithium, sodium, potassium, magnesium and calcium

Lithium, sodium, potassium, magnesium and calcium were determined by ion chromatography according to the Kadnar [202] method.

Apparatus used: Ion chromatograph: Dionex OX 600; column: Ion Pac CS12A (250 x 4 mm); eluent: 20 mmol methanesulfonic acid solution, with flow rate of 1 mL/min; auto suppressed conductivity ASRS-ULTRA (auto suppression recycle mode); the background conductivity : 1 μ S.

Procedure: An aliquot of the water sample was diluted with measured volume of deionized water to a suitable volume to be within the measuring range, and 25 μ L of the solution was injected into the column. The elution was then carried out by the eluent. The separated peaks of cations were identified by their retention times and areas as compared to those of prepared cation standards.

2.4.3. EDTA complexometric titration method for calcium and magnesium

Calcium and magnesium were determined by the EDTA complexometric titration method according to the ASTM D511 [1], APHA 2340 C [2] and API [3] methods.

An aliquot of the water sample was adjusted to pH 10, and Eriochrome Black T indicator was added, then the titration was carried out with ethylene diamine tetraacetic acid disodium salt (EDTA- Na_2) standard solution for the determination of calcium plus magnesium.

Another aliquot of the water sample was adjusted to pH 12-13 and Murexide indicator was added, then titrated with EDTA- Na_2 standard solution for the determination of calcium alone.

Magnesium was estimated as the difference between the two titrations.

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

Boron, iron and manganese in the water samples studied were determined using different techniques.

2.5.1. Boron

Boron in the water samples was determined by two different methods: carminic acid and mannitol.

2.5.1.1. Carminic acid colourimetric method

Carminic acid colourimetric method was carried out according to the ASTM D3082 [1] and APHA 4500-B [2] methods:

In this method, boron in concentrated sulphuric acid forms a coloured complex with carminic acid (carmine). The colour ranges from a bright red to a bluish red or blue depending on the concentration of boron present.

Apparatus used: An UV-VIS spectrometer, ATI Unicam model 8625, equipped with glass cells.

Procedure: Series of standard boron solutions were prepared, and their absorbances were measured at 585 nm.

The boron concentrations in the water samples were calculated from the concentration-absorbance calibration curve of boron standard solutions or from its equation estimated by the linear regression analysis, as shown in Fig. 2.

2.5.1.2. Mannitol titration method

Mannitol titration method was carried out according to the ASTM D3082 [1] and API [3] methods.

In this method, an aliquot of the water is treated with dilute hydrochloric acid to decompose borates and boiled to expel carbon dioxide. Potassium permanganate is added to break the bonds of the organo-boron compounds and oxidize the boron to borates. EDTA is added to chelate interfering metal ions. Mannitol reacts with boron to produce an acid complex that acts like a fairly strong acid, which is titrated with standard sodium hydroxide to an equivalent point of pH 7.6. Boron in inorganic compounds is determined with the same steps without using potassium permanganate.

The concentrations of total, inorganic and organic boron in the water samples were calculated from the alkali titration results.

2.5.2. Iron

Iron was determined by two techniques: visible spectrometry and ICP-AES.

2.5.2.1. Spectrophotometric *o*-phenanthroline method

Spectrophotometric *o*-phenanthroline method was carried out according to the ASTM D1068 [1] and APHA 3500-Fe [2] methods.

Apparatus used: Described in (2.5.1.1).

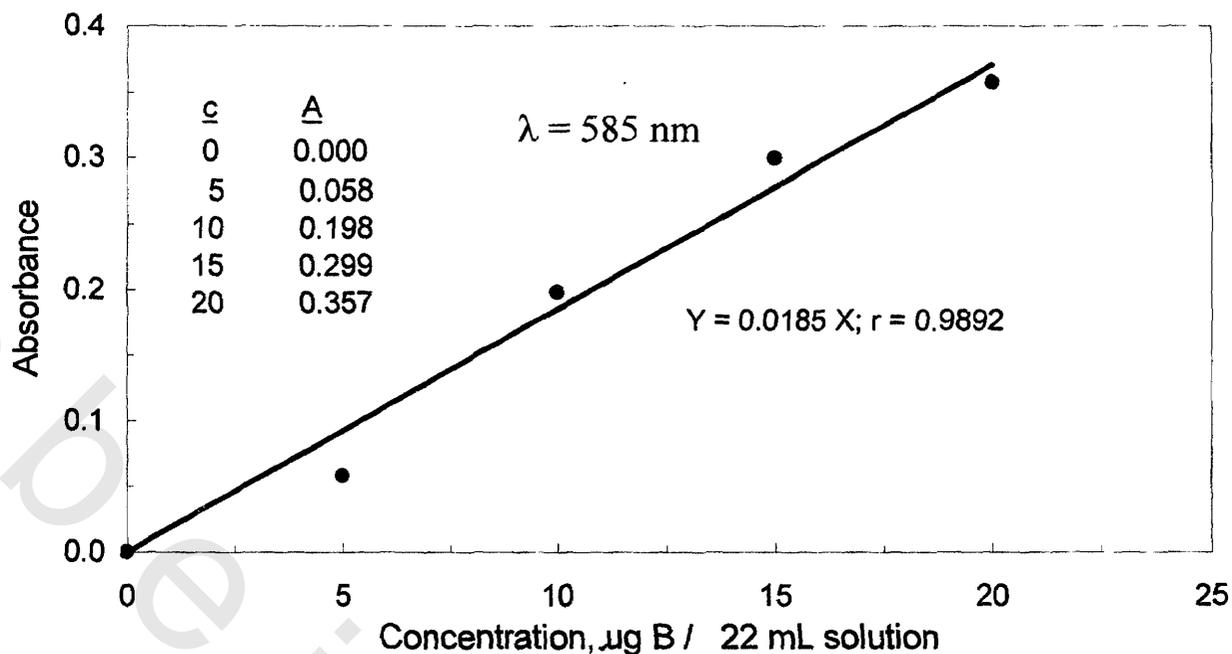


Fig. 2. Calibration curve of the standard boron solutions according to APHA 4500-B, C: Carmine Method.

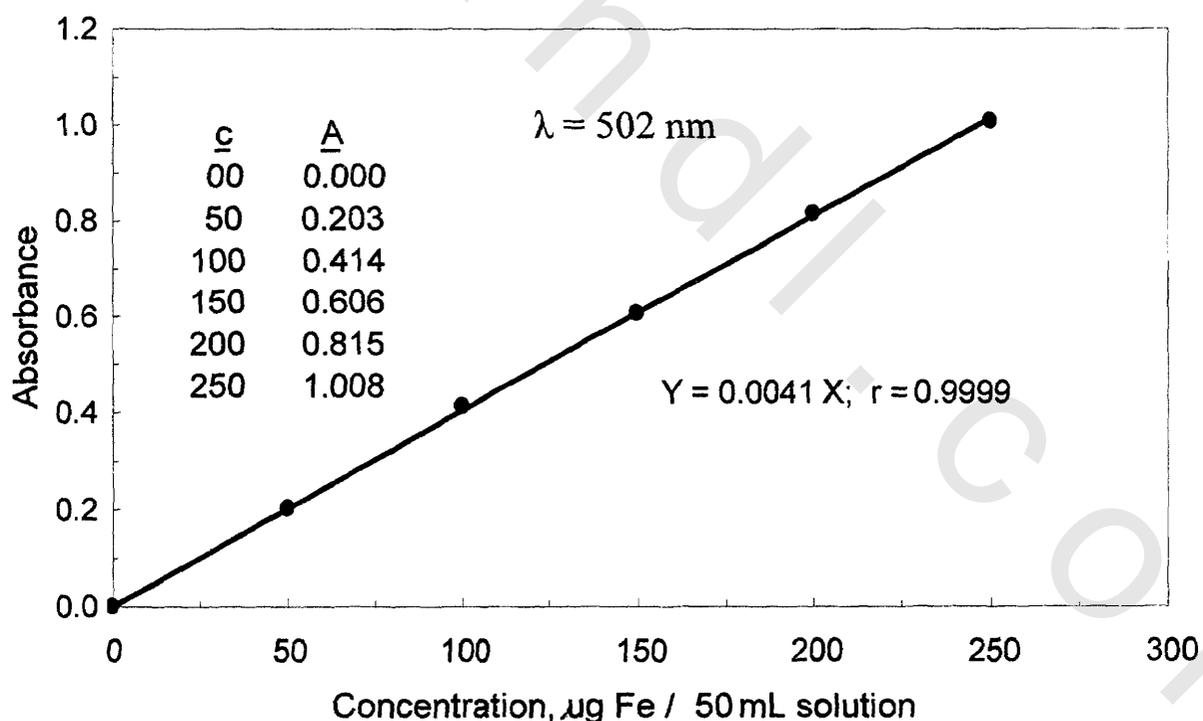


Fig. 3. Calibration curve of the standard iron solutions according to ASTM D 1608 and APHA 3500-Fe: *o*-Phenanthroline Method.

Procedure: An aliquot of sample was treated with *o*-phenanthroline solution at pH 3.2-3.3, and the absorbance of the complex was measured at 502 nm.

The iron concentrations in the water samples were calculated from the concentration-absorbance calibration curve of iron standard solutions, or from its equation estimated by the linear regression analysis, as shown in Fig. 3.

2.5.2.2. ICP-AES

The ICP-AES technique was carried out, as previously described in (2.4.1), according to the ASTM D1976 [1] and APHA 3120 [2] methods.

Each water sample was diluted to a suitable concentration was measured at 238.204 nm. The concentration of the iron was calculated from the calibration curve of the iron standard solutions carried out at the same conditions of measurement.

2.5.3. Manganese

Manganese was determined by the ICP-AES technique, as previously mentioned in (2.5.2.2), according to the ASTM D1976 and APHA 3120 [2] methods. Measurement was carried out at 257.610 nm.

2.6. Determination of Anions in the Oil-Field Waters

Concentrations of anions, including fluoride, chloride, bromide, iodide, sulphate, bicarbonate and nitrate, were determined in the water samples using different analytical techniques as follows. Borate anion was calculated from the boron determined previously in (2.5.1).

2.6.1. Ion chromatography for fluoride, chloride and bromide

Fluoride, chloride and bromide were determined by the ion chromatography according to the ASTM D4327 [1], APHA 4110 [2] and by the method described by Kadnar and Rieder [202] methods.

Apparatus used: Ion chromatograph: Dionex OX 600; column: Ion Pac AS9-HC (250 x 4 mm); eluent: 9.0 mmol Na₂CO₃ solution, with flow rate of 1 mL/min; auto suppressed conductivity ASRS-ULTRA (auto-suppression recycle mode); background conductivity: 1 μS.

Procedure: An aliquot of the water sample was diluted with deionized water to a suitable volume, 25 μL of the solution was injected into the column. The elution was carried out with the eluent. The separated peaks of anions were identified by their peak retention times and areas as compared to those of prepared anion standards.

2.6.2. Titration method for chloride (bromide and iodide)

Chloride was also determined with the argentometric titration method according to the ASTM D512 and D4458 [1], APHA 4500-Cl⁻ [2], API [3] and Collins [4] methods.

This method is based upon the Mohr procedure for determining chloride ion with silver nitrate at pH between 6.0 and 8.5 in presence of potassium chromate indicator. The chloride reacts with the silver ion before silver chromate formation, due to the lower solubility of silver chloride. Potassium chromate indicator reacts with the excess silver ions to form a red silver chromate precipitate. The end point is the appearance of the first permanent orange colour.

In this method, bromide and iodide anions are also determined together with the chloride.

2.6.3. Colourimetric method for bromide and iodide

Bromide and iodide were determined by the colourimetric method according to the ASTM D3869 method [1].

The apparatus used was an UV-VIS spectrometer, ATI Unicam model 8625, equipped with glass cells.

Procedure: bromide is oxidized to bromine in an acid solution by chromium trioxide, then bromine is extracted into carbon tetrachloride and the absorbance is measured at 417 nm against carbon tetrachloride.

The bromide concentrations in the water samples were calculated from the prepared concentration-absorbance calibration curve of bromide standard solutions, or from its equation estimated by the linear regression analysis, as shown in Fig. 4.

In an aliquot of the water sample that is free of hydrocarbons and hydrogen sulfide, iodide is oxidized with nitrous acid and extracted into carbon tetrachloride. A violet colour in the carbon tetrachloride indicates the presence of iodide in the sample. The concentration is proportional to the intensity of the violet colour which is measured at 517 nm against the blank as a reference

The iodide concentrations in the water samples were calculated from the prepared concentration-absorbance calibration curve of iodide standard solutions, or from its equation estimated by the linear regression analysis, as shown in Fig. 5.

2.6.4. Potentiometric titration method for bicarbonate, carbonate and hydroxide

Bicarbonate, carbonate and hydroxide anions were determined by the potentiometric titration method according to the ASTM D1067 [1], APHA 2320 [2] and API [3] methods, as previously mentioned in the alkalinity (2.3.7).

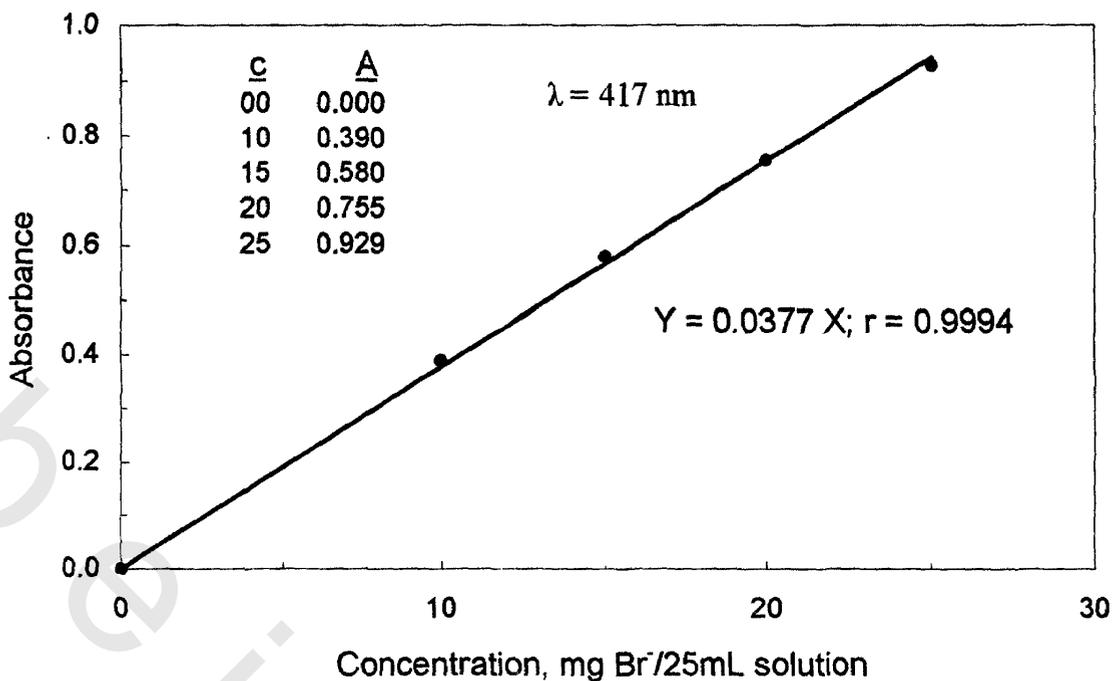


Fig.4. Calibration curve of the standard bromide solutions according to ASTM D 3869 Method: Test Method D-Colorimetric.

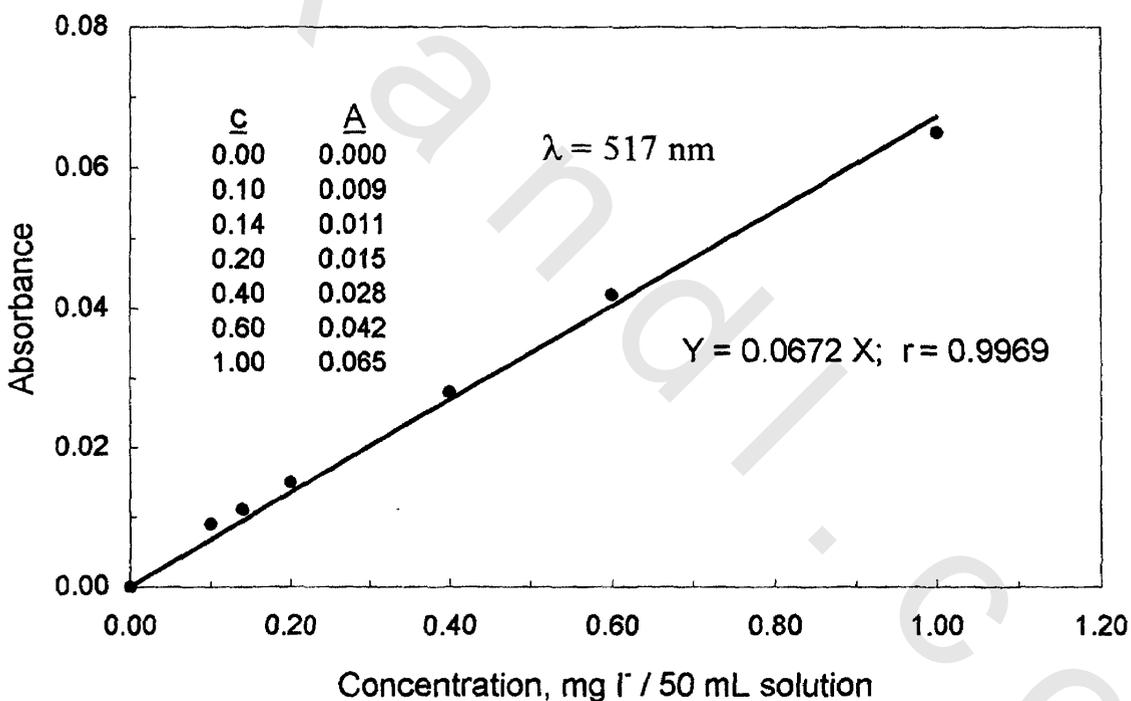


Fig.5. Calibration curve of the standard iodide solutions according to ASTM D 3869 Method: Test Method B-Colorimetric.

2.6.5. Gravimetric method for sulphate

Sulphate was determined with the gravimetric method according to the ASTM D516 [1] APHA 4500-SO₄²⁻ [2], API [3] and Collins [5] methods.

In this method, the sulphate ions are precipitated and weighed as barium sulphate after removal of silica and other insoluble matter.

A suitable aliquot of the water sample acidified with hydrochloric acid using methyl orange as indicator and excess acid is added. The solution is heated to boiling and barium chloride added slowly with stirring. The suspension of barium sulphate is filtered on ashless filter paper, washed with hot distilled water, ignited at 800°C, cooled in a desiccator and weighed.

2.6.6. Ultraviolet spectrophotometric method for nitrate

Nitrate was determined by the ultraviolet spectrophotometric screening method according to the APHA 4500-NO₃⁻ B [2] method.

The apparatus used was an UV-VIS spectrometer, ATI Unicam model 8625, equipped with quartz cells.

Procedure: In an aliquot of the water sample, 1 mL hydrochloric acid is added and mixed thoroughly. The absorbance is read against redistilled water set at zero absorbance at wavelength 220 nm to obtain nitrate reading and at wavelength 275 nm to determine interference due to dissolved organic matter. For the samples and standards, two times the absorbance reading at 275 nm are subtracted from the reading at 220 nm to obtain absorbance due to nitrate, $A_{\text{NO}_3^-} = A_{220} - 2 A_{275}$.

The sample concentration was obtained directly from the prepared concentration-absorbance calibration curve of standard solutions, or from its equation estimated by the linear regression analysis, as shown in Fig. 6.

2.6.7. Calculation of borate from boron

Borate ion was calculated from the boron determined previously in (2.5.1).

2.7. Calculation of Parameters for the Water Classification

Parameters used in the water classification systems were calculated as follows.

2.7.1. Reaction values in milliequivalent/litre (me/L)

The reaction value, in me/L, of an ion is calculated by multiplying its concentration in mg/L by its reaction coefficient, which is its valence divided by its relative atomic or molecular mass.

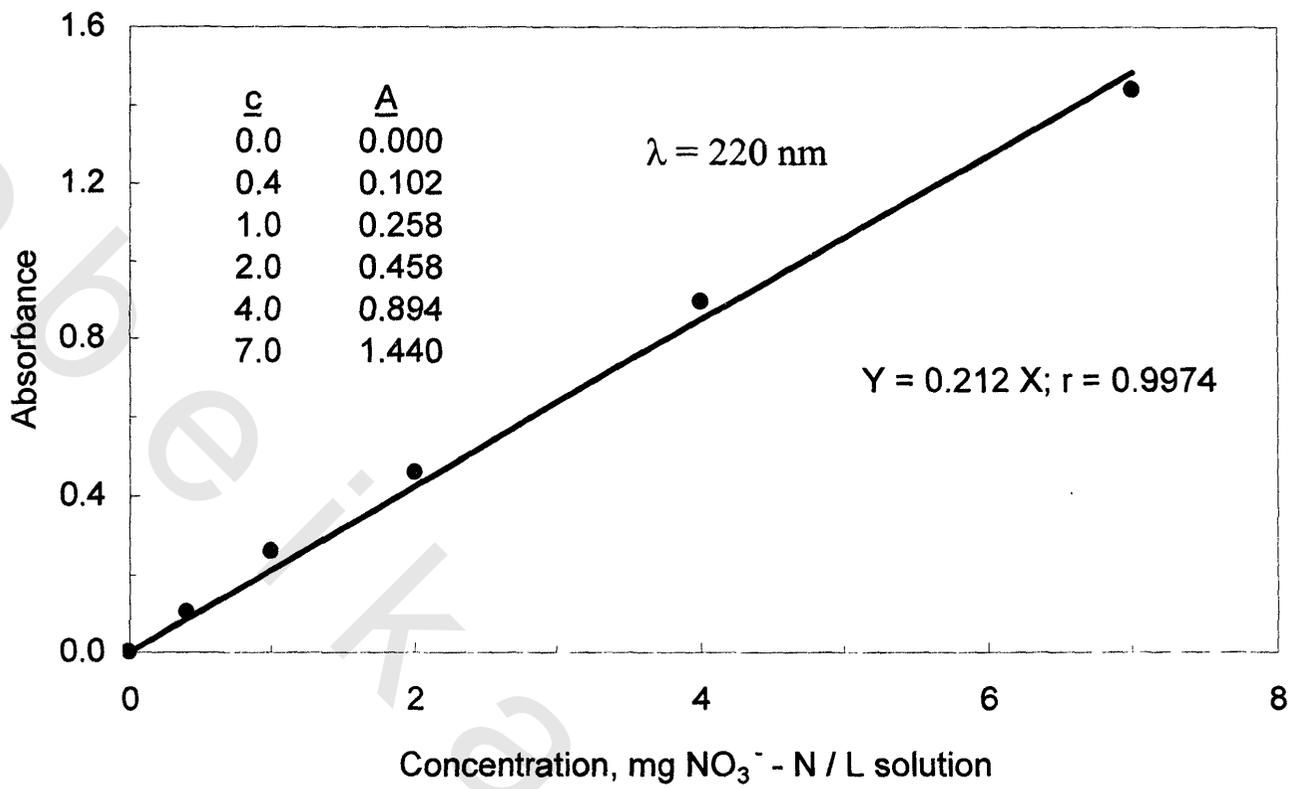


Fig. 6. Calibration curve of the standard nitrate-nitrogen solutions according to APHA 4500-NO₃⁻, B: Ultraviolet Method.

2.7.2. Reaction values in equivalent per million (epm)

The reaction value, in epm, of an ion is calculated by dividing its reaction value in me/L by the density of the water sample.

2.7.3. Probable compounds from the hypothetical combinations of ions

The hypothetical combinations of dissolved compounds in the water were calculated by combining the cations (strontium, calcium, magnesium, iron, potassium, sodium, lithium) and anions (bicarbonate, sulphate, borate and chloride). Strontium was first combined with bicarbonate, then with sulphate, borate and chloride until it is exhausted. Calcium was combined with the remaining anions in the same order, and followed by magnesium, iron, potassium, sodium, and finally with lithium. The hypothetical combinations were then estimated by multiplying their reaction values by their combination factors [5].

2.7.4. Reaction values in equivalent percent (e %)

The reaction value, in e %, of an ion is calculated by dividing its reaction value in me/L by the total reaction values, in me/L, of total ions and multiplying by a hundred.

2.7.4.1. Reaction groups

The reaction groups of the ions (alkali cations, alkaline earth cations and strong acid anions) were calculated.

2.7.4.2. Reaction properties

The reaction properties of the ions, primary (alkali) salinity, secondary(alkaline earth)salinity, tertiary salinity, primary (alkali) alkalinity, and secondary (alkaline earth) alkalinity, were calculated using the procedure of Palmer [407].

2.7.5. Coefficient of exchange

The coefficient of exchange (K_e) of waters is calculated using the hypothetical combinations from the relation:

$$K_e = \frac{\text{Na(K)HCO}_3 + (\text{Ca, Mg})(\text{HCO}^-)_2}{\text{Na(K)Cl} + (\text{Ca, Mg})\text{Cl}_2 + \text{Na}_2\text{SO}_4 + (\text{Ca, Mg})\text{SO}_4}$$

The absolute and relative values for each water sample were calculated [5, 409].

2.8. Genetic coefficients

Genetic coefficients of: Cl/Na, Cl/Mg, Cl/Ca, Cl/(Ca + Mg), (Cl - Na)/Mg, (Na - Cl)/SO₄, Na/Cl, Na/Mg, Na/Ca, Na/(Ca + Mg), Na/ $\sqrt{(\text{Ca} + \text{Mg})/2}$, Ca/Mg, (Ca + Mg)/Mg, Cl/SO₄,

(SO₄ x 100)/Cl and Cl/Br were calculated from their corresponding reaction values [5, 408, 410].

2.9. Statistical Correlations

The correlations between the physico-chemical properties, concentrations of major and minor ions, and some genetic coefficients of the studied oil-field waters, as well as their depths of the producing zones, were statistically carried out using the following linear regression equations [423, 424]:

$$Y = m X + c \quad (1)$$

$$m = \frac{\sum (X - \bar{X})(Y - \bar{Y})}{\sum (X - \bar{X})^2} \quad (2)$$

$$c = \frac{\bar{Y} \sum X^2 - \bar{X} \sum XY}{\sum (X - \bar{X})^2} \quad (3)$$

$$r = \frac{\sum (X - \bar{X})(Y - \bar{Y})}{\sqrt{\sum (X - \bar{X})^2 \sum (Y - \bar{Y})^2}} \quad (4)$$

$$-1 \leq r \leq 1 \quad (5)$$

where:

X = independent variable,

Y = dependent variable,

$\bar{X} = \sum X / n$,

$\bar{Y} = \sum Y / n$,

n = number of samples,

m = the slope of the line,

c = the intercept of the line, and

r = correlation coefficient.

These statistical correlations were calculated by the linear regression analysis program present in Microsoft Excel 2000.

2.10. Determination of Organic Constituents in the Oil-Field Waters

Organic constituents of the oil-field water samples were analyzed as follows:

- Extraction of fatty acids from the water samples by aqueous sodium carbonate solution,
- Extraction of oils from the water samples by methylene chloride,
- Fractionation of the extracted oils to their components, i.e. 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.

2.10.1. Extraction of fatty acids from the water samples by sodium carbonate

Fatty acids were extracted from the water samples according to Fatoki and Vernon method [425].

Procedure: Volumes (2 - 5 L) of the water samples were acidified with HCl solution to pH 2. Water samples of low salinity were saturated with solid NaCl. Each water sample was then extracted three times with 60 mL of chloroform. The chloroform extracts were combined, and the free fatty acids were then extracted three times with 30 - 50 mL of 0.1 M Na₂CO₃ solution. The combined extracts were acidified to pH 2 with 2 M HCl solution and then extracted three times with 20 mL of diethyl ether. The extracted fatty acids were pooled together and dried over anhydrous sodium sulphate. The diethyl ether extract was evaporated to dryness, and the fatty acids were dried in an oven to constant weight.

2.10.2. Extraction of oils by methylene chloride

Extraction of the oils from the water samples was performed and determined by the gravimetric method according to the ASTM D 4281 [1] and APHA 5520 B [2] standard methods.

Procedure: One litre of the water sample was acidified by HCl solution to pH < 2, and poured into a separating funnel, then extracted with 30 mL methylene chloride (instead of fluorocarbon) as a solvent for 15 min. Solid NaCl was added to water samples that form emulsions to enhance solvent separation. The solvent layer was drained through a filter paper moistened with the solvent and contained anhydrous sodium sulphate. The extracting step was repeated twice more. The extracts were combined in a clean, dry weighing flask, and the filter paper was washed with 10-20 mL of the solvent. The extracted oil was dried in an oven at 50°C, cooled in a desiccator to constant weight.

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

The extracted oils were fractionated into their components, i.e. saturates, aromatics, and resins, on silica gel column chromatography [426].

Procedure: A glass column (70 x 1 cm.) was packed with 25 g of silica gel (100-200 mesh, Merck) activated at 180°C in an oven for 4 hours. The three components were eluted by *n*-hexane, benzene, and methanol-methylene chloride mixture (1:1), respectively. The solvents were evaporated on a water-bath and the separated components were dried in an oven and cooled in a desiccator to constant weight.

2.10.4. Determination of the extracted fatty acids by gas chromatography

The extracted fatty acids were first methylated, to be analyzed by the gas chromatography, as follows:

Procedure: 1 mL of absolute methanol and 2 mL of concentrated sulphuric acid were added to the extracted fatty acids. This mixture was refluxed for 30 min on a water-bath,

cooled, then the formed esters were extracted by shaking with diethyl ether in a separating funnel. The ether layer was separated, washed with distilled water, then dried on anhydrous sodium sulphate, and finally concentrated in 1 mL-glass ampoule.

Apparatus used: A gas chromatograph, Perkin-Elmer 8700; capillary column: HP-50 plus (30 m length and 0.53 mm internal diameter), packed with poly (dimethyl siloxane) as stationary phase; detector: flame ionization.

1 μL of the methyl esters was injected into the injector heated at 200°C , the column temperature was programmed from 60 to 250°C at ramp rate of $3^{\circ}\text{C min}^{-1}$, and nitrogen was used as a carrier gas with flow rate of 3 mL min^{-1} .

The peak retention times and areas of the separated methyl esters of the extracted fatty acids were determined, qualitatively and quantitatively, by comparing with those of standards of methyl esters of fatty acids.

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

The *n*-paraffins in the separated saturates were determined by gas chromatography [427, 428].

Apparatus used: A gas chromatograph, model Agilent 6890 plus, equipped with a flame ionization detector, a fused silica (HP-1) capillary column (30 m x 250 μm), packed with poly(dimethylsiloxane) as stationary phase, and an integrated data handling system.

Procedure: $1\mu\text{L}$ of the saturates dissolved in methylene chloride was injected into the injector heated at 300°C . The column temperature was programmed from 80 to 300°C at ramp rate of $3^{\circ}\text{C min}^{-1}$, and nitrogen was used as a carrier gas with a flow rate of 3 mL min^{-1} . Retention times and areas of separated peaks in the chromatogram of the saturates were determined by comparing with those of a reference sample of *n*-paraffins.

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

Polyaromatics in the separated aromatics were determined by high performance liquid chromatography (HPLC) according to the ASTM D 4657 standard method [1].

Apparatus used: A HPLC machine, model Waters 600E, equipped with an autosampler Waters 717 plus, a dual wavelength absorbance detector Waters 2487 set at 254 nm and a column of Supelcosil LC-PAH, 15 x 4.6 mm ID, 5 μm particles size.

Procedure: $1\mu\text{L}$ of the aromatics dissolved in acetonitrile was injected into the column, and a gradient elution was carried out with an acetonitrile-water (HPLC grades) mixture from 50 : 50 to 100 : 0, with a flow rate of 0.2 mL/min for the first 2 min, then 1.0 mL/min for other 43 min [429]. The retention times and areas of the resulting peaks were recorded. A reference sample of polyaromatics (Supelco) was injected under the same conditions. The retention times and areas of its peaks were used to determine, qualitatively and quantitatively, each of the polyaromatics in the separated aromatics.

2.10.7. Determination of functional groups of the extracted oils by infrared absorption spectrometry

Infrared spectra of the extracted oils were carried out using a FT-IR Spectrometer, model 960M000g, ATI Mattson Infinity Series. The infrared spectra of the oils were measured in the range of 4000-400 cm^{-1} using the KBr disc technique.