PART ONE
LITERATURE SURVEY

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1. PHYSICO-CHEMICAL PROPERTIES OF OIL-FIELD WATERS

The oil-field waters generally have characteristic physico-chemical properties, including pH value, density or specific gravity, electrical conductivity or resistivity, temperature, dissolved solids, suspended solids, turbidity, alkalinity, acidity and hardness [1-6]

1.1. pH Value

The pH value of a water is the logarithm of the reciprocal of the hydrogen-ion activity. The determination of pH of water is an indication of its acidic or alkaline tendency; it is not a measure of acidity or alkalinity of a water sample. A pH value less than 7.0 shows a tendency toward acidity, while a value greater than 7.0 shows a tendency toward alkalinity. The pH measurement is an important factor in determining the corrosive action of water and assessing water treatment practices for industrial processes. It is also used to assess the extent of pollution in precipitation [1].

Most ground waters have pH values ranging from about 5.5 to slightly over 8, natural water with pH values lower than about 4.5 may contain free mineral acids added by volcanic gases or oxidation of sulphides, or may contain salts which on hydrolysis tend to give an acid reaction, ferric salts and aluminum salts are likely to make water acidic. Some waters containing organic matter may have rather low pH values owing to the presence of organic acids [4].

The pH of a water sample can be determined with a pH-meter which utilize the principle of measuring the electrical potential between an indicator electrode which assumes a potential dependent on the pH of the solution and a reference electrode which assumes a constant potential. Calomel electrode is widely used as reference electrode in water analysis [5].

A chemically modified electrode for pH measurement was constructed by electropolymerzing a poly (4,4'-diaminobiphenyl) coating onto a platinum electrode [7]. Microelectrodes for determining pH and pCO_2 were developed [8].

New automated marine pH sensor was described [9] for the determination of sea water pH using dual spectrophotometric measurements of thymol blue indicator in a semi-continuous sea water stream. In another study, an autonomous sensor for long-term in-situ pH measurements in natural water was described [10]. The system is based on spectrophotometric measurements of a mixture of sample and sulfonaphthalein indicator

The pH value can be determined with a pH-meter according to the ASTM D 1293 and D 5128 [1], APHA 4500-H^+ [2] and API [3] methods.

1.2. Density and Specific Gravity

Density is the mass (weight in vacuo) of liquid per unit volume at 15°C. When reporting results, explicitly states the density in units of mass (kilograms) and volume (litres)

together with the standard reference temperature, for example kilograms per litre at 15°C [1].

Specific gravity is a relative density, i.e. the ratio of the mass of a given volume of liquid at 15°C (or 60 °F) to the mass of an equal volume of pure water at the same temperature [1].

Pure water weighs 1 g/mL or 1000 kg/m^3. Thus, a specific gravity greater than 1.0 means that the water sample is more dense. Since petroleum-associated water contains dissolved matter (ions, compounds, gases), they are always more dense than pure water and therefore have a specific gravity greater than 1.0 [6].

The magnitude of the specific gravity is a direct indicator of the total amount of solids dissolved in the water. Therefore, comparison of the specific gravities of several waters give a rapid estimate of the relative amounts of solids dissolved in the waters [6].

Depending upon the accuracy desired, the specific gravity of a petroleum-associated water can be determined with a pycnometer, specific gravity balance, or hydrometer. Because any oil in or on the sample will interfere with the specific gravity determination, the sample should be filtered [5].

Fu et al. have studied the density of solutions of three types of inorganic salts, which are of ion structures of A(I)B(I), A(I)$_2$B(II), A(II)B(I)$_2$ [11]. The density of the solutions vs. mass concentration of salts (g/kg H_2O), has been evaluated. Based on their findings, a general equation on the density of the solution, which contains the variables temperature and mass concentrations of salts, has been established. These equations made it possible to calculate the density of formation water of oil or gas field.

Density correlations were proposed for a wide range of temperature T, pressure p and mass fraction expressed as sodium chloride X. Using experimental and calculated data, formulae which closely approximate the density were given in terms of variables T, p and X [12].

The density and specific gravity can be determined by the ASTM D 1429 [1], APHA 2710-F [2] and API [3] methods.

1.3. Electrical Conductivity and Resistivity

Electrical conductivity is the reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature [1].

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current, this ability depends on the presence of ions, their total concentration, mobility, valence, and relative concentrations, and on the temperature of measurement [2].

The resistivity of petroleum-associated water is used in electric log interpretations, and for such use the values must be adjusted to the formation temperature [13].

The conductivity of water is determined by the ASTM D 1125 and D 4159 [1], APHA 2510 [2].

1.4. Temperature

The temperature of the water affects the scaling tendency, the pH and the solubility of gases in water. The specific gravity of water is also a function of temperature [6].

Temperature readings are used in the calculation of various forms of alkalinity in studies of saturation and stability with respect to calcium carbonate, in the calculation of salinity, and in general laboratory operations. In limnological studies, water temperatures as a function of depth often are required. Elevated temperatures resulting from discharges of heated water may have significant ecological impact. Identification of a source of water supply, such as deep wells, is often possible by temperature measurements alone [2].

Temperature of water can be determined according to the APHA 2550 laboratory and field methods [2].

1.5. Turbidity

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample [1, 2]. It indicates the possibility of formation plugging in injection operations. It is often used to monitor filter performance [6].

The turbidity measurement was studied [14] by detecting the scattered light intensity in the direction perpendicular to the incident light beam. The linearity of scattered light intensity with turbidity is better than $\pm$ 3 %.

The turbidity is determined according to ASTM D1889 [1] and APHA 2130 [2] nephelometric methods.

1.6. Total solids

Total solids" is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids include " total suspended solids", the portion of total solids retained by a filter, and " total dissolved solids", the portion that passes through the filter [2].

1.6.1. Dissolved solids

The dissolved solids determination is used to estimate the accuracy of the resistivity determination. The specific gravity determination, and the evaporation method are used to double check the calculated total dissolved solids [5].

The residue method involves evaporating a filtered sample to dryness followed by drying the residue in an oven at 180°C for 1 hour. The cooled residue is weighed and the total dissolved solids are calculated. The evaporation method is subject to errors when

hygroscopic material such as calcium chloride is in the water, as is usually the case in oil-field waters [5].

Dissolved solids are determined by the ASTM D 1888 [1], APHA 2540 [2] methods.

1.6.2. Suspended solids

Suspended-sediment is the sediment (particles derived from rocks or biological materials) that is carried in suspension by the turbulent components of water or by Brownian movement [1]. It plays an important role in water quality management since it is related to total primary production and heavy metal and micro-pollutant fluxes. [15].

Filtration of a quantity of solids from a given volume of water using a membrane filter (a 0.45 μm pore size filter is commonly used) is one basis for estimating the plugging tendency of a water. It is possible to estimate the particle size distribution of the suspended solids in a water sample by various techniques. A knowledge of the particle size distribution is very helpful in determining the need for filtration and in filter selection. It is also useful in monitoring filter performance. Determination of particle shapes by visual or scanning electron microscopy is very helpful in the determination of filtration needs. It is usually used in conjunction with particle size distributions [6].

Determination of the composition of suspended solids is extremely important in determining their source and origin and what treatments are to be used to remove it or prevent it from reoccurring. [5, 6].

Suspended solids were determined photometrically in the range of 0.5 – 30 mg/L [16].

The water turbidity measured by optical methods (transmittance and backscattering) is usually expressed as beam attenuation coefficient (BAC) or formazin turbidity units (FTU). The transformation of these units to volumetric suspended sediment concentration (SSC) units is shown [17].

Suspended solid can be determined by the ASTM D3977 [1], APHA 2540 [2] and NACE TM-01 [18] methods.

1.7. Acidity

Acidity is defined as the quantitative capacity of aqueous media to react with a strong base, usually from below pH 4.5 to pH 7.0. Acidity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolyzing salts such as iron or aluminum sulfates may contribute to the measured acidity according to the method of determination [2].

The acidity of a petroleum-associated water may indicate a contaminant because of acid treatment of the well or it could indicate the presence of various dissolved gases and salts.

Most petroleum associated waters are of little or no acidity. If a water contains acidity, it does not contain alkalinity [5].

Acidity and alkalinity measurements are used to assist in establishing levels of chemical treatment to control scale, corrosion and other adverse chemical equilibria. Levels of acidity or alkalinity are critical in establishing solubilities of some metals, toxicity of some metals and the buffering capacity of some waters [1].

A spectrophotometric method, with flow injection analysis, was used to determine the free acidity and total acidity in water samples [19].

The acid neutralizing capacity of natural waters was determined by ion chromatography [20].

Acidity is determined by methods of ASTM D1067 [1], APHA 2310[2] and API [3].

1.8. Alkalinity

Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may be significantly with the end-point pH used, usually to a pH of 4.5. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known [2].

Alkalinity in water is usually attributed to the presence of bicarbonate, carbonate or hydroxyl ions [6]. Most oil-field waters contain no hydroxyl ions, and most of them contain no carbonate ions, but they contain bicarbonate ion [5]. Alkalinity as carbonate and bicarbonate of saline water is very important in chemical water flooding or tertiary recovery processes for recovering petroleum.

A combination of two methods using carefully determined titration end points, gives very good measurements of the alkalinity and the acid content of oil-field waters. The concept of alkalinity and alkalinity variations with addition of acids and bases are discussed [21].

A spectrophotometric method for the determination of sea water alkalinity was elaborated [22], based on the neutralization of all the basic species by a weak acid (formic acid) mixed with a pH sensitive dye, the Bromo-Phenol Blue. The neutralization reaction leads to a final mixture with an absorbance at 590 nm which is a function of the original alkalinity of the sample. Alkalinity measurements were compared with the results obtained by the classical Gran's potentiometric titration.

Alkalinity is determined by methods of ASTM D1067 and D 3875 [1], APHA 2320 [2], and API [3].

1.9. Hardness

Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per litre [2]. Hardness is caused by any polyvalent cations but those other than Ca and Mg are seldom present in more than trace amounts [1]. When hardness is numerically greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called "carbonate hardness", the amount of hardness in excess of this is called "non carbonate hardness" [2]. Hardness salts in water are the primary cause of tube and pipe scaling, which frequently causes failures and loss of process efficiency due to clogging or loss of heat transfer, or both [1].

Water hardness was determined by ion chromatography [23], spectrophotometry with chlorophosphonazo-1 [24], ion-selective electrode sensitive to Ca and Mg [25], flow injection analysis using a Cu-selective electrode [26], EDTA complexometric titration method with arsenazo III as indicator [27], and photometric method in which two complexes formed by EBT with Ca and Mg, where their absorbance maxima are at 520 nm [28].

A new potentiometic titration system has been developed for determination of the total Ca^{2+}, Mg^{2+} ions by hardness ion selective electrode, which consists of a designed simple and effective gradient mixing tube [29].

A FAAS method of hardness of underground water using La $(NO_3)_2$ as releasing agent for Ca and Mg was presented [30]. The results were consistent with those measured by EDTA method.

Hardness is determined by methods of ASTM D 1126 [1] and APHA 2340 B [2].

2. CHEMICAL ANALYSIS OF CATIONS IN OIL-FIELD WATERS

Various methods of analysis have been developed for the determination of cations in natural waters including atomic absorption and emission, inductively coupled plasma-atomic emission and -mass, and X-ray fluorescence spectrometry, molecular absorption, fluorescence and chemiluminescence, electrometric methods including potentiometry, coluometry and voltammetry, and separation methods including ion chromatography and capillary electrophoresis.

2.1. Atomic Absorption /Emission Spectrophotometry

K is determined by the standard method ASTM D 4192 (flame AAS), Ca and Mg are determined by ASTM D 511 B (AAS), Sr is determined by ASTM D 3920 (AAS), Ba is determined by ASTM D 4382 (GF-AAS), Mn is determined by ASTM D 858 (AAS), Fe is determined by ASTM D 1068 (AAS), Li, K and Na are determined by ASTM D 3561(standard additions method by AAS), and Sr is determined by ASTM D3352 (standard additions method by AAS [1].

Li, Na, K, Ca, Sr, Ba, Mn and Fe can be determined by AAS according to APHA 3500-B [2]

Li^+ was extracted with Sudan-1-methyltrioctylammonium chloride-*o*-dichlorobenzene, pyrolysis in a graphite tube, and determined by AAS using $Al(NO_3)_3$ as matrix modifier [31]. Also, the determination of Li in natural brines by a flame photometer was observed [32]. The highly concentrated elements may cause interference and affect the results. Standard additions method was used.

The potassium content of some natural waters was determined by flame AES using the methane-air flame [33]. Effects of the flame and of instrumental parameters on the emission of K was studied and optimized. The potassium content of waters was determined using both external calibration curve and standard additions method.

K, Na, Ca, and Mg were determined in water by flame AAS [34]. The sample was treated with La chloride releasing agent for the determination of Ca and Mg and then treated with CsCl solution to suppress ionization for the determination of K and Na.

Calcium was determined by flame AES using the methane–air flame [35]. The effect of flame and instrumental parameters was studied and optimized. The best results were obtained with the Ca line of 422.67 nm. In the presence of interferences the best results were obtained with the standard additions method. Also, trace amount of Ca was determined [36] by coprecipitation with a $SrCl_2$ solution and dissolving the precipitate with HNO_3 acid followed by flame AAS monitoring at 422.7 nm.

Magnesium, calcium and sodium were determined [37] by microwave plasma torch atomic emission spectrometry (MPT-AES). The microwave plasma torch is used as excitation light source, argon as support gas, and the sample solution was introduced into a pneumatic nebulization system by standard addition method.

A simple and reliable method was presented [38] for rapid and selective separation of trace amounts of Sr^{2+} ions from alkali and alkaline earth metal ions by octadecyl silica membrane disks modified with decyl-18-crown-6 in the presence of picric acid, and determination by flame AAS.

Barium was determined [39] in formation water associated with crude oil by AAS using matrix-matching procedure. Standards containing Na^{+} and Ca^{+2} in concentrations matching those of the sample matrix are used to avoid background interference. The sample was diluted with HCl before analysis at 553.4 nm in an air-acetylene flame. Also, barium was determined [40] using oxygen enriched air-acetylene flame in AAS and the effect of acetylene flow, oxygen flow and the ratio of O_2/C_2H_2 on the absorbance were compared.

Iron (II) and iron (III) were determined [41] in water samples by AAS after preconcentration using 2-mercaptobenzimidazole, loaded on silica gel (MBI-SG). A flow injection system was coupled with a UV-VIS and an atomic absorption spectrometer. Also, Fe (II) and Fe (III) were determined by flame AAS after their separation with Aspergillus niger immobilized on sepiolite as an adsorbent [42].

Fe (III) was preconcentrated using a strong base anion-exchange resin (Dowex 2X4) modified with feron and determined by AAS at 248.3 nm [43]. In another method Fe (III) was preconcentrated as $Fe(SCN)_6^{3-}$ by the phase-separation extraction using a mixture containing TritonX-100, *n*-octyl alcohol and water as phase-separation agent [44].

Manganese was determined [45] by a flow injection preconcentration coupled to electrothermal AAS. Manganese was complexed by1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid (Eriochrome black T), its complexes are retained onto an anion exchange resin, and eluted with HCl. In another method Mn (VII) / Mn (II) were separated and preconcentrated with crosslinked chitosan (CCTS) before determination by flame AAS [46].

A preconcentration method for the determination of dissolved Mn in environmental waters was developed [47] based on solid-phase extraction using a Sep-Pak C_{18} cartridge. Mn was converted into a stable complex with 4-(2-pyridylazo) resorcinol. The complex was eluted and Mn was determined by GF-AAS. In another method trace Mn was concentrated by on line extraction chromatography before its detection by AAS [48]. The chromatographic column was prepared using 2-mercaptobenzothiazole and 8-hydroxyquinoline as composite extractant and active silica gel as carrier.

Flow injection online-preconcentration and flame AAS determination of iron, cobalt, nickel, manganese and zinc in sea water was described [49], based upon on-line preconcentration on a micro column packed with C_{18} material. These metals were complexed with 5, 7-dichloro oxine in the flow system and adsorbed on the column. The preconcentrated elements were eluted and injected directly into the nebulizer.

A method was described [50] for the determination of Cu, Mn, Co, Cd, Pb, Ni, and Cr in water samples by flame AAS. Trace metals in water were sorbed as pyrocatechol violet complexes on activated carbon column. The effect of major cations and anions on the sorption of metal ions was investigated.

Trace metals Cu, Mn and Mo were determined [51] in seawater directly and simultaneously using a multielement electrothermal AAS equipped with a transversely heated graphite atomizer. A mixture of $Pd(NO_3)_2$ and $Mg(NO_3)_2$ with the special gas (5 % H_2 and 95 % Ar) was used as chemical modifier.

The addition of HF to a seawater sample in a graphite tube atomizer makes possible the removal of the major matrix components in an optimized pre-heating step, thus a near interference free determination of Cu and Mn trace metals was achieved [52].

The determination of Cu(II), Pb(II), Ni(II), Cd(II), Mn(II) and Fe(III) were determined [53] by flame AAS after preconcentration on Amberlite XAD-16 resin, using hexamethyleneammonium hexamethylenedithiocarbamate resin as a chelating agent.

The application of AAS determination of the Fe and Mn in underground H_2O with the standard concentration, standard additions method was studied [54].

The levels of some ions of heavy metals known to be associated with petroleum industry operations, including Pb, Ni, V, Cr, Cd, Zn and Fe were studied in untreated groundwater by AAS [55].

A sensitive and simple method for the separation/preconcentration of some trace metal ions as O-O-diethylphosphodithioic acid ammonium salt complexes on a mini chromatographic column filled with chromosorb-105 resin prior to flame AAS determination was established [56]. No influences were observed from the major ions of the natural water.

A study was carried out [57] on the preconcentration of ultratrace amounts of cadmium, lead, manganese, copper and iron from high-salinity aqueous samples and determined by AAS methods. To quantify the metals in the eluates, 2 AAS techniques were compared: electrothermal atomization AAS and inductively coupled plasma-optical emission spectrometry with simultaneous CCD detection system. Both techniques were found to be suitable.

A column solid-phase extraction method using diaion HP-2MG for the preconcentration and determination of cadmium(II), copper(II), cobalt(II), iron(III), lead(II), nickel (II) and Zn(II) dithizone chelates by flame AAS has been described. The method could be applied in natural waters [58].

Determination of boron by electrothermal AAS suffers from low efficiency of atomization. A variety of modifiers were examined [59], with the carbide-forming elements such as Zr, Ta, or V found to be best. The graphite tubes were pretreated by soaking in the metal solutions, drying, and slowly heating to > 1600°C to form the carbide. This increased the atomization efficiency for boron. Other types of matrix modifiers for the electrothermal AAS determination of B were investigated [60]. Combinatin such as Ca-Mg, Ca-La, and Sr-Mg were more efficient than single-element modifiers. $CaCl_2$ was used [61] as a modifier in natural waters.

An indirect AAS determination method of B in H_2O was described [62]. In pH 4.7, the complex formed by BF_4^- and $Ag(phen)_2^+$ was extracted by MIBK. Trace B was determined indirectly by AAS. More than ten ions such as K+, Na+, etc. have no interference with the determination.

2.2. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

ICP is an analytical technique that performs elemental analysis with excellent sensitivity and high sample throughput. The ICP instrument employs plasma as the ionization source and spectrometer analyzer to detect the ions produced. It can simultaneously measure most elements in the periodic table and determine analyte concentration down to the sub nanogram-per liter (ng/L) or part-per trillion (ppt) level. Interferences in ICP consist of the mass spectroscopic and non spectroscopic interferences resulting from the sample matrix. Minimization of non spectroscopic interferences can be achieved by standard additions and internal standard application.

Elements are determined by ASTM D 1976 (Direct Current Argon Plasma Atomic Emission Spectromrtry) [1].

Li, Na, K, Ca, Sr, Ba, Mn and Fe are determined by the standard method APHA 3500-C (Inductively Coupled Plasma Method), Ba is determined by ASTM D3986 (Direct-Current Argon Plasma Atomic Emission Spectroscopy) [1].

Specially designed multistage membrane filtration devices for the size fractionation of suspended particles and solutes were tested and used for speciation studies of metals Al, Fe, Zn, Mn, Ni, and Co, as well as Na, K, Mg, and Ca associated with natural water components [63]. The separated fractions were adapted to analysis by plasma source atomic emission and mass spectrometry.

The common analyte internal standardization (CAIS) technique was extended to correct for non spectroscopic matrix effects in ICP-AES measurements [64]. Experimental tests with four elements (Ba, La, Mg and Mn) in three matrixes (NaCl, H_2SO_4, HNO_3) were demonstrated.

The determination of K, Na, Ca, Mg, Si, Li, and B by Atom Scan 16 sequential ICP spectrometer was studied. Optima conditions had been researched [65].

An ICP-OEA instrument equipped with a dual-view plasma torch and a simultaneous detector was used [66] for determination of major elements in saline water using an internal standard to correct for interferences resulting from differences between the matrix composition of samples and standards

A flow injection analysis system incorporating a micro-column of ZrO_2 was used for the development of an online multi-element method [67] for the simultaneous preconcentration and determination of Al, Bi, Cd, Co, Cr, Cu, Fe, Ca, In, Mn, Mo, Ni, Pb, Tl, V, Sb, Sn, and Zn by ICP-AES

A method for the multi-elemental determination of ultratrace metals in seawater was developed based on column extraction using 8-hyroxyquinoline immobilized on fluorinated metal alkoxide glass (MAF-8HQ) and determination by ICP-AES or high-resolution ICP-mass spectrometry [68].

Sr and Ba were determined without preconcentration with ICP-AES in conjunction with an ultrasonic nebulizer [69]. The ultrasonic nebulizer, equipped with a desolvation system, enhanced the analytical sensitivity by ten to twenty fold compared to conventional pneumatic nebulizers.

Determination of Cd(II), Cu(II), Mn(II), Ni(II), Pb(II), and Zn(II) was made in natural waters by ICP-AES after preconcentration by solvent extraction with piperidine dithiocarbamate (pipDTC). On the other hand those metals in saline matrixes were preconcentrated on Amberlite XAD-4 resins coated with ammonium pyrrolidinedithiocarbamate (APDC) and piperidine dithiocarbamate (pipDTC). The results showed that Amberlite XAD-4 coated with APDC is more efficient in the recovery of metal ions compared with Amberlite XAD-4 coated with pipDTC [70, 71].

A flow injection analysis system for the preconcentration and simultaneous determination of Bi, Cd, Co, Cu, Fe, Ni, Pb and Zn in aqueous samples by ICP-AES with a charge coupled detector was described [72].

2.3. Inductively Coupled Plasma-Mass Spectrometry

Excellent sensitivity and high speed makes ICP-MS an excellent tool for the determination of trace elements in environmental samples

Two chelation ion-exchange columns, an in-house (xylenol orange) one and a commercial (Metpac CC-1) one, were used for matrix elimination and online pre-concentration of the analytes (the alkaline-earth and first–row transition metals) before their determination in brines by ICP-MS with a VG Plasmaquad II instrument [73].

Instrumental neutron activation analysis and ICP-MS techniques were used [74] to study the contributions of trace elements to oils from sources such as produced waters, formation water, drilling fluids, production equipment, storage container, biodegradation and migration, from which it was possible to identify contaminated samples.

Li, Na, Mg, K, Ca, and Fe were measured at nano gram per gram levels with ICP-MS using cold plasma conditions [75].

Isotope dilution-double-focusing ICP-MS has permitted high sensitivity and accuracy for determining iron in seawater [76]. The method used Mg $(OH)_2$ coprecipitation to preconcentrate iron in seawater. Another method [77] used on-line flow injection separation-preconcentration to speciation Fe(III) and Fe(II). Also, direct determination of trace concentration of Fe in natural waters by collision-cell ICP-MS was studied [78]. Possible polyatomic and isobaric interferences were reduced and optimal collision cell parameters were found.

On-line preconcentration performance characteristics of a commercially available iminodiacetate resin were applied [79] for the determination of Mn, Ni, Cu, Zn and Pb by ultrasonic nebulization ICP-MS.

A desolvating micronebulizer with sector field ICP-MS was used to determine V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in sea water with only a 50 μL sample and no reagents other than nitric acid were used [80].

A method for determination of traces of the transition metals Mn, Fe, Ni, Co, Cu, Zn, Cd, and Pb in saline samples was described [81] using batch preconcentration with subsequent ICP-MS analyses after direct sample insertion of the analyte loaded chelating resin.

A home-made column of commercially available iminodiacetic functional group resin, Muromac A-1, was used to separate and concentrate trace metals (Al, V, Mn, Co, Ni, Cu,

Zn, Mo, Cd, Pb and U) from seawater [82]. An automated low pressure flow analysis method with online column preconcentration-ICP-MS was described.

Trace elements were determined [83] with ICP-MS. Problems with interference can be minimized by standard additions and internal standard application.

Ultratrace elements in natural water samples were determined simultaneously by air-segmented flow-injection/inductively coupled plasma mass spectrometry [84, 85]. A small volume of the sample solution was introduced into a nebulizer by an air-segmented flow injection system. A chitosan-based chelating resin containing functional groups of iminodiacetate (IDA) was used to separate and enrich analyte metal ions. Another study [86] used a new online flow injection pre-treatment system using a disk-type chelating resin was developed for the simultaneous multi-element determination of trace metals in sea-water samples by ICP-MS. A chelating resin possessing an IDA functional group was used.

An ICP-MS with an octopole reaction/collision cell was used [87] for the multi-element determination of trace elements V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Pb, and U in seawater. The use of a reaction or collision gas, respectively, reduces serious spectral interferences from matrix elements.

The use of ICP-MS for direct seawater analysis was currently limited by spectral and non-spectral interferences caused by the seawater matrix so replaced by the use of double focusing ICP-MS instruments after preconcentration technique and matrix removal by using ammonium tetramethylene dithiocarbamate (APDC)/Methyl iso-Bu ketone (KIBK) solvent extraction [88].

A miniaturized column packed with a chelating resin Muromac A-1, was tested for the preconcentration of trace elements in seawater [89]. After preconcentration, the column was washed with ammonium acetate buffer to remove the major elements, such as Ca and Mg, and was then eluted with HNO_3. Twenty-six trace elements were determined by ICP-MS and ICP-ES.

ICP-MS and electrospray mass spectrometry (ES-MS) were used [90] not only for the analysis of trace elements, but also for identifying and characterizing the compounds within which each is present. They are usually coupled to a separation technique such as chromatography or capillary electrophoresis and applied to a large number of research problems.

Boron was determined by ICP-MS in fresh and seawater. Matrix effects were severe and cation exchange was necessary to allow accurate determination [91]

2.4. X-ray Spectrometry methods

Pre concentration of Cu, Co, Pb, Cd, Ni, Fe (III), Cr (III), and Zn using capric acid was described [92]. The metal complexes were extracted using n-octane and the elements determined by x-ray fluorescence spectrometry. Also total reflection x-ray fluorescence spectrometry was applied [93] to the analysis of trace elements in water. The method involves the irradiation at a grazing angle of a sample evaporated to dryness on an optically flat surface.

Energy-dispersive x-ray fluorescence was used to determine Cu, Pb, Fe, Hg, and Cr following concentration by precipitation [94]. In another method metals in water were precipitated with DDTC and then collected on a filter paper for x-ray fluorescence spectrometric determination [95]. Also, seven metal ions were preconcentrated by precipitation as chelates with piperazino-1, 4-bis-(dithiocarbamate) and then determined by energy-dispersive x-ray spectrometry [96].

Adsorption filters containing conformationally flexible aminocarboxylic groups were used to preconcentrate nine metals from sea water and river water for determination by x-ray fluorescence spectrometry [97].

A method for the determination of major and some minor ions (Cl^-, SO_4^{2-}, Br^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}) in brines by x-ray fluorescence spectrometry was presented [98]. X-ray fluorescence spectrometry provides the possibility of analyzing large numbers of samples within a short time interval using a simple sample preparation. Calibration graphs of standard solutions were compared with those of common titrimetric, colorimetric, and ion chromatographic methods.

Automated particle analysis of natural water samples by scanning electron microscopy and x-ray microanalysis was investigated [99]. A filtered water sample was analyzed automatically for 10 major elements (Si, Al, K, Ca, Mg, Fe, Mn, Ti, P, S).

The preconcentration of heavy metals (Cu, Co, Ni, Zn, Fe, Mn, Pb) on acetyl cellulose membranes by sorption of their complexes with 1-(2-thiazolylazo)-naphthol-2 coupled with direct x-ray fluorescence analysis of concentration was presented [100]. The results were compared with methods such as electrothermal-AAS, anodic stripping voltammetry and photometry.

Ten elements (V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb) were determined, by PIXE using 2.5 Me V proton beam. The relative detection efficiency for each x-ray of element and its recovery were studied in 2 methods: "drop and dry" and "concentration" methods [101].

An ion-exchange cellulose phosphate filter was used [102] to prepare in-line PIXE targets for long-term monitoring of heavy metal concentrations. Heavy metals (Mn, Fe, Cu, Zn, Pb and Hg) were detected by PIXE analysis with low detection limit of 0.5 – 1.0 ppb.

Trace elements (Al, Cr, Ni, Zn, Sr, Ba, Tl, and Pb) in water were determined [103] by sequential x-ray fluorescence spectrometer. The results of this method were compared with those obtained by AAS and ICP.

2.5. Molecular Absorption Spectrometry

Ultraviolet and visible methods are widely used for the determination of cations in waters.

Potasium was extracted from water sample with an ethanolic solution of dipicrylamine and a toluene solution of dibenzo-18-crown-6, followed by measuring the absorbance of the organic layer at 420 nm [104].

Na and K were determined using flow injection methods in which alkali metal crown ether complexes and an anionic dye were extracted into an organic phase and the absorbance of the organic liquid was measured at 615 nm [105, 106].

Magnesium was determined spectrophotometrically [107] by measuring the absorbance of the Mg complex formed with dibromophenylfluorone in the presence of cetyltrimethyl ammonium bromide. Beer's law was obeyed at 640 nm for 0 – 4 μg Mg/25 mL. Flow injection spectrophotometry at 635 nm was also used [108] to determine Mg in water using Eriochrome Azurol B and cetyltrimethyl ammonium chloride. The calibration curve was linear for 0.2 – 1.0 mg Mg/L.

Calcium was determined spectrophotometrically with *m*-bromoantipyrylazo [109], one of eight antipyrylazo color reagents tested. The complex absorbs at 630 nm in NaOH media. Amino G acid chlorophosphonazo was also used [110] which forms a complex with Ca which absorbs at 666 nm.

A method based on the reaction of Ca with chlorophosphonazo III was described [111].Also a kinetic method using chlorophosphonazo III which was oxidized to decoloration by potassium bromate, Ca ion decreased the reaction rate in diluted sulfuric acid media. The maximum absorption wavelength was at 550 nm. The results were in agreement with those using atomic absorption spectrophotometry [112].

Ca was determined [113] upon reaction with xylenol orange and cetylpyridium bromide in NH_3–Ni_4Cl buffer media at pH 10.8 producing a blue complex, which exhibited a maximum absorption at 610 nm. Also, Ca was determined using Kalces indicator in the presence of HOAc – NaOAc buffer solution medium (pH 5.2) forming blue complex which has maximum absorption at 620 nm [114].

Simultaneous spectrophotometric determination of Ca and Mg using 4-(2-pyridylazo)resorcinol and a multilinear regression program was used [115] to resolve the absorbance band and determine the concentration of each metal ion. A Flow injection method with the same reagent and a photometric diode array detector was reported [116].

Sinusoidal injection analysis was used for the determination of Ca and Mg complexed with arsenazo III [117]. In another study, a multivariate calibration method, Partial Least Squares Type 1, was proposed for simultaneous spectrophotometric determination of Ca and Mg as their complexes with Arsenazo III in buffer solution (Glycine 2 M – NaOH 0.2 M) in waters [118].

Strontium was determined at 671 nm after precipitation with ammonium carbonate and dissolution of the precipitate with dilute HCl. Correction for interference by calcium was made by a separate Ca determination [119].

Manganese in sea water was concentrated on 8-hydroxyquinoline immobilized on a vinyl polymergel, and determined by the reaction of leucomalachite green and KIO_4 with the Mn [120]. A similar method used p-amino-benzenesulfonic acid with KIO_4, and NTA as an accelerant [121].

A spectrophotometric method for the determination of manganese, based on the reaction of 2[(3,5-dibromo-2-pyridyl)azo-5-ethylamino-p-cresol]with manganous ions to form a bluish green complex with absorbance at 630 nm was described [122].

Decoloration of amaranth by oxidation with hydrogen peroxide in ammonium muriate medium using manganese as catalyst was investigated [123]. Also, the oxidation reaction of resplendency green with KIO_4 catalyzed by Mn(II) in HOAc– NaOAc buffers was used [124] for the determination of Mn(II).

A highly sensitive, selective method using N, N'-bis(2-hydroxy-5-bromo-benzyl)1,2–diamopopane which reacts with Mn (II) to produce a brownish complex [125].

Manganese was concentrated from natural and sea water on a palmitoyl quinolin-8-ol functionalized Amberlite XAD-2 copolymer resin (XAD-P.Ox), Mn in the eluate was determined by the formaldoxime spectrophotometric method [126].

Fe is determined by the standard methods ASTM D 1068(D) [1] and APHA 3500-B [2] (photometric bathophenanthroline method)

Fe (III) forms an anionic chelate of 2,2-dihydroxyazobenzene which is reacted with crystal violet and then adsorbed on the surface of a PVC film .The plating of the blue-violet ion pair allows for detection of Fe (III) at 592 nm [127].

A solvent-soluble stationary phase which is composed of nitrocellulose powder has been used for rapid pre-concentration of Fe (II). The separation was studied spectrophotometrically by using the complex of Fe(II)-1,10-phenanthroline (phen)-sodium

dodecyl sulfonate [128]. In another study Fe (II) ion reacts with 5-nitro-1,10-phenanthroline to form a stable complex compound, enriched on a cation exchange resin. The absorbance of resin-phase is at 520 nm [129].

Fe was determined spectrophotometry [130] with 6, 6"dimethyl-4'-phenyl-2,2':6',2"-terpyridyl as complexant in CH_3COONa-glacial CH_3COOH buffer solution of pH 4.5. The method showed high sensitivity and good accuracy.

A kinetic spectrophotometric method was developed [131], based on the discoloring reaction of bromophenol blue with potassium periodate catalyzed by Fe (III) in HAc–NaAc solution (pH 3.6). Another method based on the catalytic action of Fe (III) on the oxidation of indigo carmine by H_2O_2 in a dilute H_2SO_4 medium, Fe (III) was determined at 615 nm [132]. Also, the catalytic effect of Fe (III) on the oxidation rate of N, N-dimethyl-p-phenylenediammonium dichloride (DmPD) by H_2O_2 is monitored to determine Fe(III) at 554 nm [133].

Iron (II) reacts with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) in the presence of cationic surfactant CTMAB, to form a stable complex measured at 749 nm [134]. Also, 5-Br-PADAP was used for the simultaneous determination of iron and cobalt with in the presence of Tween-80 was studied [135].

Employing di-2-pyridyl ketone salicyloylhydrazone (DPKSH) as a colorimetric chelating agent for simultaneous spectrophotometric determination of Fe (II) and Fe (III) in natural waters was developed [136]. Both of the complex ions showed an absorbance max. at 375 nm, while that of Fe (II) showed a second absorbance max. at 644 nm.

A long liquid wave guide capillary flow cell was successfully adapted to a gas-segmented continuous flow auto-analyzer for trace analysis of iron in water [137]. It was made of Teflon AF-2400, with a refractive index (1.29) lower than water (1.33). Utilization of it enhances the sensitivity of automated colorimetric analysis of iron by the ferrozine method.

Fe (III) reacts with diantipyrylphenylethylenemethane in the presence of diluted HCl and Mn (II) to form a red complex measured at 540 nm [138].

By solid phase spectrophotometry, trace amounts of Fe^{2+} and Fe^{3+}can be determined , based on the fixation of Fe^{2+} as 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulfonic acid (5-Br-PAN-S) complex on a styrene-divinylbenzene anion-exchange resins. $Fe^{3+}$was determined by difference after reduction of Fe^{3+} to $Fe^{2+}$with hydroxylamine [139].

Ferrozine was used for the simultaneous determination of soluble Fe(II) and Fe(III) species in seawater [140]. Samples were heated and exposed to UV irradiation to eliminate the effect of organic matter in seawater.

By online coupling of spectrophotometry with flame atomic absorption spectrometry (FAAS), simultaneous determination of Fe (III) and Fe (II) in H_2O was carried out. The method involved cloud-point extraction (CPE) of both species with ammonium pyrrolidinecarbodithioate (APDC) under standard conditions, which facilitates the in – situ ferrozine complexation and extraction of both species. [141].

The strong base anion-exchange resin (Dowex 2X4) loaded with Ferron (7-iodo-8-hydroxyquinoline-5-sulfonicacid) was used for Fe (III) preconcentration, which was converted to Fe (II) and determined spectrophotometrically at 510 nm as Fe (II)-*o*-phenanthroline complex [142]. The accuracy of the method was verified by comparing the results with those using AAS with standard additions methods.

Spectrophotometric flow injection analysis method for the determination of iron, based on the control of the flow dissolution of the colorimetric reagent 1, 10-phenanthroline, was elaborated [143]. A comparison between the performance of this method and that of the conventional packed reactor was performed.

Cation exchangers of different nature could be used for the sorption preconcentration of iron (II) as phenanthrolinate and its determination in the adsorbent phase by diffuse reflectance spectrometry and chromaticity measurements [144].

Flow injection system with bead injection (BI) was developed for determination of low concentration (μmol L^{-1}) of iron in water samples. Chelex-100 chelating resin beads, trapped in a jet ring cell, were employed. The intensity of red complex of 1, 10-phenanthroline with Fe^{2+} was monitored using colorimetric detector with a LED green light source. Amount of total Fe (Fe^{2+} and Fe^{3+}) and Fe^{2+} can be determined with and without reduction of Fe^{3+} using ascorbic acid [145].

Determination of total iron by the *o*-phenanthroline photometry was modified [146]. The background colour of water sample was corrected with a test solution containing no *o*-phenanthroline. Hydroxylamine hydrochloride was added to reduce Fe^{3+} to $Fe^{2+}$to eliminate the interference of strong oxidation substances.

Anion-exchange solid phase extraction disks have been used [147] as solid phase for the determination of iron. Ammonium thiocyanate was used as chromogenic reagent for Fe (III), the complex is detected at 480 nm. Total iron can be determined by oxidizing Fe(II) to Fe(III) with hydrogen peroxide.

A simultaneous determination of Fe and Cu at sub–μg/L level by solid–phase third–derivative spectrophotometry was developed [148]. The compounds, TPTZ (2, 4, 6-tripyridyl-1, 3, 5-triazine) and Neocuproine (2, 9-dimethyl-1, 10-phenanthroline hydrochloride), were used as chromogenic reagents to form a blue Fe complex and an orange Cu complex, which were fixed and concentrated on a cation-exchange resin

Sephadex spC—25. Measurements were carried out at 622 and 477 nm for Fe and Cu, respectively.

Boron was determined by the standard method APHA 4500 [2] (B. Curcumin method and C. Carmine method).

Boron was determined by flow injection analysis coupled with indirect UV-visible spectrophotmetry, sample was mixed with a chromotropic acid reagent and the absorbance measured [149]. In another study flow injection analysis with spectrophotmetric detection at 415 nm using azomethine-H was developed [150].

The azomethine-H method was compared with the curcumin and carmine standard methods [151]. The azomethine–H method was the most sensitive and selective with a detection limit of 0.02 mg/L and no interference from ions commonly occurring in water.

A dual-wave length absorption photometric method gave a detection limit of 0.01 mg B/L was developed [152].

The classic curcumin method was improved [153] by using the microemulsion (SDS: OP: Bu alcohol: distilled H_2O 1.36: 13.64: 8.18: 76.82) to avoid the interference of salinity. The experimental results showed that the sensitivity of determination was enhanced greatly.

An improved JIS method was presented [154] in natural waters and waste water. The stability of the complex formed by B and azomethine-H was discussed. $CaCl_2$ was added for samples containing high concentration SO_4^{-2}. The measurement was made at 413 nm.An alternative method using methylene blue was reported [155], the results showed that it was a versatile method due to rapidity as well as good reproducibility.

Computer-controlled multi-syringe flow injection systems were developed [156] to perform the spectrophotometric determination of iron and boron in soil extracts. The method based on the formation of ferroin complex (for iron) and azomethine-H reaction (for boron). Both determinations were performed in manifolds with similar configurations by changing the reagents present in the different syringes.

2.6. Fluorescence and Chemiluminescence Spectrometry

Sodium was detected in water [157] using dual-pulse laser-induced breakdown spectroscopy. Laser-induced breakdown was formed by dual-pulse and crossed beam Nd:YAG lasers on a water film.

Potossium was immobilized with fluorogenic crown ether 4- (acryloylamido)benzo-18-crown-6 on nonionic polymeric resin Amberlite XAD-2. The fluorescence was measured by either a flow-through sensor or a new fiber-optic probe type sensor or "optrode" [158]

Magnesium was determined [159] using 7-[(8-hydroxy-5-sulfo-7-quinolyl)azo]-8-hydroxy-5-quinolylsulfonic acid with excitation at 546 nm and emission measured at 581 nm. Another method used 1,2,4-trihydroxy anthraquinone in ethylene glycol/water was described [160].

Catalytic Kinetic fluorometry was used [161, 162] to determine Mn using its catalytic effect on the oxidation of Rhodamine 6G with potassium periodate .

Fluorimetric determination of Mg and Al via pre-column and/or in-column derivatization with 8-hydroxyquinoline (oxine) in HPLC was developed [163]. The oxine complex of Al was selectively detected when the eluent contained no oxine, whereas the Al and Mg complexes could be simultaneously detected when the eluent contained oxine.

Chemiliuminescence detection of Mn separated by flow injection analysis was reported [164]. The Mn was concentrated on a column containing 8-hydroxyquinoline. The oxidation of 7,7,8,8-tetracyanoquinodimethane under alkaline conditions produces the photons which are detected.In another study a sodium bismuthate reactor was used for online oxidation of Mn(II) to produce MnO_4^- which react with luminol to generate chemiliuminescence signal [165].

Iron in sea water was determined by flow injection analysis and chemiliuminescence detection [166]. Another method was used [167] to determine ferric iron after immobilization by 8-quinolinol on a chelating resin, followed by elution with HCl. The Fe (III) content of the eluent was determined with luminol and H_2O_2.

The solid-phase reagent and chemiluminescent method coupled with membrane filtration, gel-permeation and ion-exchange chromatography were applied to the speciation of iron and cobalt in water [168].

Spectrofluorometry method for the determination of B with Alizarine Red S was described [169]. In another study flow injection and fluorescence detection was described [170]. The sample was mixed with a chromotropic acid and an alkaline solution simultaneously which reduced the background fluorescence of the chromotropic reagent.

First-derivative synchronous scanning spectrofluorometry was applied in natural waters [171]. B was compled with a chromotropic acid, and the excitation and emission wave lengths were separated by 24 nm. The detection limit was 0.4 μg of B/ L.

2.7. Electrometric Methods

2.7.1. Potentiometric methods

Sodium is determined by the standard method ASTM D2791 (ion selective electrode) [1].

The MnO_2 ionic sieve was used to separate Li ion from brine containing a large amount of K^+, Na^+, $Ca^{2+}$and Mg^{2+}. The separated Li was determined [172] using a fluoride selective electrode.

A sodium-selective membrane electrode based on 4'-tertbutylcyclohexano-12-crown-4 was reported to yield a detection limit of 5×10^{-5} mol of NaCl / L [173].

A capillary stream sensor for determining K was developed based on membrane solvent extraction using crown ether and microporous tubing. The sensor was applied to both continuous-flow analysis and flow injection analysis. The flow analysis procedure was used to analyze K in environmental waters [174]. Also, a valinomycin-based K-selective membrane electrode was developed for analysis of K in sea water [175].

The simultaneous determination of NH_4^+ and K^+ in water was studied using a potentiometric sensor array and multivariate calibration. The sensors used are rather non-specific and of all-solid-state type, using polymeric (PVC) membranes [176].

Flow injection analysis was used in the determination of Mg as the Mg-eriochrome black T complex at pH 11.5. The uncomplexed eriochrome black T was determined by amperometric measurement at +0.175 V on a glassy carbon electrode [177].

A Ca ion-selective electrode based on tetra (*o*-tolyl)-*o*-xylyldiphosphine dioxide was described which was highly selective for Ca and was used to measure Ca ion concentrations in the range of 10^{-1}-10^5 M [178, 179].

A BF_4-selective electrode was used to measure B in water [180].

2.7.2. Coulometric and voltammetric methods

Polarographic technique has the versatility for detecting and quantifying major and minor components in the same sample.

Barium was determined in water by stripping voltammetry after elimination of interference from magnesium by treating the water samples with 8-hydroxyquinoline [181].

Cathodic stripping voltammetry with adsorptive collection of Fe from seawater samples on 1-nitroso-2-naphthol was described [182]. The Fe is catalytically reoxidized with H_2O_2. A similar method used 1-nitroso-2-naphthol on a Hg drop electrode is developed for the determination of Fe (III) [183].

A preconcentration and voltammetric method was developed for the determination of total Fe by a chitosan-modified glassy carbon electrode. The measurements were carried out by cathodic stripping voltammetry [184].

Direct determination of Picomolar levels of Fe by cathodic stripping voltammetry (CSV) was preceded by adsorptive accumulation of the Fe(III) -2,3-dihydroxynaphthalene complex from seawater onto a static Hg drop electrode followed by reduction of the adsorbed species.The reduction current is catalytically enhanced by the presence of bromate [185].

Nafion-coated glassy carbon electrodes (NCE) were employed [186] for preconcentrating and detecting Fe^{2+} and Fe^{3+} cations from aquous solutions. By cyclic voltammetry, the ion-exchange voltammetric determination of iron in the μM concentration range was achieved.

A highly sensitive and selective voltammetric procedure was described [187] for the simultaneous determination of Cd, Pb, Cu, Sb, Bi, Se, Zn, Mn, Ni, Co and Fe in water samples.

The catalytic adsorptive striping voltammetry (CAdSV) was applied for the determination of the trace elements in water [188]. The CAdSV, coupling of very efficient adsorptive accumulation of the electroactive species on the electrode surface with the catalytic reaction, provides a significant amplification of the analysis response, and consequently a considerable decrease of the detection limit.

The cathodic stripping voltammetry (CSV) as a reliable electrochemical technique for analysis of very low concentration of dissolved metals present in an environment was given. [189]. The CSV is based on the cathodic voltammetric scan of the adsorbed (accumulated) metal complexes at the electrode surface from the bulk of the solution.

Square-wave adsorptive stripping voltammetry was used for the simultaneous determinination of zinc and manganese [190]. The sensitive adsorptive stripping peaks of Zinc(II) and Manganese(II)-Thiocyano complex were obtained by using square-wave adsorptive stripping voltammetry in the supporting electrolyte containing potassium thiocyanide.

The development of two voltammetric sensors [191] that allow real-time, in–situ monitoring of trace elements Cu (II), Pb (II), Cd (II), Zn (II), and Fe (II) in natural aquatic ecosystems was described. Both are based on agarose gel integrated Ir(Hg) microdisk arrays either interconnected or individually addressable.

The optimization and characterization of poly (sodium 4-styrenesulfonate)-coated thin mercury film electrodes was described [192] for the direct analysis of trace metals in estuarine waters by square-wave anodic stripping voltammetry. Ion exchange ability of poly (sodium 4-styrenesulfonate)-coatings onto glassy carbon was evaluated.

Oscillopolarography was used to determine B in sea water with a detection limit of 3 x 10^{-9} mol/L [193].

2.8. Cation Separation Methods

2.8.1. Ion chromatography(IC)

Ion chromatography was the method of choice for several metals determination; it is a well established and accepted technique in the separation of a variety of inorganic ions.

Li^+, Na^+, NH_4^+, and K^+ were determined [194] in brine, sea water or ground water by suppressed IC on a Dionex CG-2 column with a similar guard column and a Dionex Carbon Micro Mmbrane Suppressor column and conductivity detection.

Li^+, Na^+, NH_4^+, K^+, $MeNH_2$, $EtNH_2$ and $PrNH_2$ were determined [195] by non-suppressed IC using sulfamic acid as mobile phase and a cation-exchange column with conductometric detection

The electroinactive cations (Li^+, Na^+, k^+, Rb^+, Cs^+, NH_4^+)were determined [196] in single column IC using an amperometric detector based on the chemical modification of Nafion and indium (III) hexacyanoferrate (II,III) thin film onto a glassy carbon electrode.

Alkali metal ions were determined [197] in presence of alkaline earth ions by IC consisting of an eluent container, a HPLC pump, a fractionating pump, an auto sampler, two fractionating columns, a main separation column connected to conductivity detector, a waste container and two valves for controlling the solution path in the arrangement.

The common mono- and divalent cations including hydrogen ion were determined [198] by IC using a C_{30} column dynamically coated first with dodecylsulfate and then with 18-crown-6 ether to separate the cations by ion-exchange mechanism.

Ba^{2+}, Sr^{2+}, Mg^{2+} and Ca^{2+} were determined [199] in three oil-well brines using high-performance chelation ion chromatography using methylthymol blue-impregnated polystyrene divinylbenzene neutral hydrophobic resin column. Results are well compared with those obtained by ICP optical-emission spectrometry.

All alkali, alkaline earth and heavy metal ions were separated [200] in a single run with IC on a column of Nucleosil PBDMA; elution was effected with a variety of solution with detection by conductivity or at 205 nm. Various combinations of eluents were studied

Alkaline earth metals were separated and visible detected using a polystyrene–divinylbenzene reversed-phase column in conjunction with a mobile phase containing o-cresolphthalein complexone [201]. The retention order obtained was the reverse of that achieved with simple ion exchange, with Ba being eluted first followed by Sr, Ca and Mg. Visible detection at 575 nm is possible without the need of addition of post column reagents.

Two different separation columns (Ion pac CS10) and (CS12A) were tested [202] for the separation and determination of cations focused on alkali and alkaline earth ions, plus ammonium, in water produced with crude oil and natural gas.

IC behavior of alkali and alkaline earth metal cations and ammonium ion on various unmodified silica gel columns by elution with 2 mM HNO_3 was studied [203]. As a result one silica gel (Develosil 30-5) column acted as a cation exchange column under acidic eluent conditions and an excellent separation of these cations was achieved.

The application of laboratory-made aluminum-adsorbing silica gel (Al-silica) as a cation-exchange stationary phase to IC indirect photometric detection (IC-IPD) for common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} , and Ca^{2+}) was carried out with tyramine-containing crown ethers as eluent [204].In another study the application of laboratory-made zirconium-modified silica gels (Zr-silicas) as cation-exchange stationary phases to IC with conductimetric detection for common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{+2} and Ca^{2+} was carried [205].

Analysis of inorganic cations in brine solutions was developed, separation was carried out in a Dionex CG12A/CS12A with sulphuric acid as eluent, the optimum conditions for the determination of the cations with minimal dilution was investigated [206].

The cations Li^+, Na^+, NH_4^+, K^+, Mg^{+2}, $Ca^{+2,}$ Sr^{2+}, and Ba^{2+} were determined [207] by an ion chromatography using a Dionex DX-500 with Ion Pac CS12A as an analytical column, Ion Pac CG12A as a guard column, and aqueous methane sulfonate solution as eluent. The results obtained were compared with those obtained by conventional methods including flame emission spectrometry for Na^+ and K^+, AAS for Ca^{2+}, Mg^{2+}, Li^+ and Sr^{2+} and in addition NH_4^+ was directly determined by indophenol method.

Li^+, Na^+, NH_4^+, K^+, Mg^{+2}, Ca^{+2} were determined by IC in water. The optimum chromatographic conditions were studied. The results obtained were compared with other methods [208].

Determination of inorganic cations and ammonium by IC with a high capacity cation-exchange column (Ion Pac CS16), methanesulfonic acid eluent and suppressed conductivity detection was described [209].

Total acidity (H^+), Ba^{2+}, Ca^{2+}, and Mg^{2+}were determined in aqueous samples by IC with a standard ODS SiO_2 column modified by coating with n-hexadecylphosphocholine as the separation column, H_2O as the eluent, with conductimetric detection [210].

2.8.2. Capillary electrophoresis methods

Capillary electrophoresis (CE) has several advantages over HPLC: Simplicity, high efficiency, possibility of simultaneous determination of positively, neutral and negatively charged species, small samples, small volume of eluent and short analysis time. Currently, CE is growing rapidly in the region of inorganic ions and often compared to IC [211].

CE method was developed for the separation of some common alkali and alkaline-earth metal ions using EDTA as complexing agent using pyridine as a UV chromophore for indirect detection [212].

Na^+, K^+, Mg^{2+} and Ca^2 were determined in well water by CE. The factors affecting the separation were discussed; also the repeatabilities of the method, linearities and the detection limits were compared with those obtained by IC [213].

Some elements in sea water and formation water from oil wells were analyzed by CE on a fused–silica capillary with indirect UV-detection. The results obtained were compared with those obtained by an ICP-AES. The two methods agree very well for K^+, Mg^{2+} and Ca^{2+}, but less for Na^+ [214].

CE has been applied [215] to the separation and detection of Ba(II) and Sr(II) in the presence of excess levels of Ca and Mg using an electrolyte containing sulfonazo III. The analytes were separated as their anionic chelates and detected at 624 nm

Factors affecting the separation selectivity and electroosmotic flow (EOF) for the separation of alkali, alkaline earth cations, and ammonium ion in nonaqueous systems were evaluated [216]. The nature of electrolyte anion (chloride, perchlorate, and acetate) and solvent (methanol / acetonitrile) has important effects on the EOF in acidic conditions

The use of a quaternary amine-coated capillary in the separation of alkali and alkaline earth cations yielded a decisively better resolution than is possible with a conventional fused-silica capillary [217].

Three simple electrolyte systems were tested for determination of K^+, Na^+, Ca^{2+}, Mg^{2+} in natural waters by CE. The separation was achieved with indirect UV detection at 214 nm [218]

The application of CE to the separation and determination of metal ions after pre-column formation of negatively charged chelates has been described [220]. This kind of approach was applied to the determination of ferrous ions by using 1, 10-phenanthroline. The electrokinetic injection achieved low ppb concentration of Fe (II) using an iron (II)-1,10-phenathroline complexing system with CE, the detection of wavelength 270 nm instead of 508 nm [219].In another method iron was determined in water at trace level by on-line coupled capillary isotachophoresis and capillary zone electrophoresis (CZE) as the negatively charged complex with EDTA which is highly UV-absorbing at 254 nm.

CZE was applied [221] for the simultaneous determination of iron(II) and iron(III) selectively complexed with 1,10-phenamthroline and CDTA using a fused silica capillary filled with a borate buffer and with direct UV detection at 254 nm.

The application of CZE to the separation and determination of metal ions after the precolumn formation of negatively charged chelates was described [222]. Transition metals complexed with 8-hydroxyquinoline-5-sulphonic acid were separated in a fused-silica capillary column followed by direct UV detection.

CE with indirect detection using Cu (II) sulfate, 18-crown-6 and formic acid in background electrolyte was applied to the determination of the metal ions in water samples [223].

Determination of alkali, alkaline earth and transition metal ions in aqueous samples using CE could be accomplished [224] with indirect UV detection at 214 nm with a background electrolyte containing reagents with inherent absorbance in the UV range. Several electrolyte systems were studied.

CZE was applied [225] to the determination of inorganic ions in high saline natural waters. Emphasis was placed on advanced approaches utilized for securing separation performance from being degraded by the presence of matrix salts and for simultaneous separation of ions different in natural abundance.

A simple and fast method for simultaneous separation of nine metal cations Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, K^+, Na^+, Mg^{2+} and Ca^{2+}, and NH_4^+ in methanol was reported [226]. The separation was achieved by using 0.5 % acetic acid and 10 mM imidazole as electrolyte.

The separation of inorganic cations in CE was presented [227]. The method combines the use of certain crown ethers to form complexes with a specific cations in microemulsion electrokinetic chromatography.

The separation of transition metal Ni^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, and Fe^{3+} in methanol with CE was investigated [228] by using different types of organic acids as complexing agents. In pure methanol, the weaker and simpler acetic, propionic, butyric and valeric acids could enhance metal ions selectivity by increasing acid concentration, whereby metal ions could be separated with high efficiency.

CE-dynamic reaction cell inductively coupled plasma mass spectrometry for the speciation of iron (III, II), V (V, IV) and chromium (VI, III) was described [229]. Two different CE migration modes were employed for separating the six metal ions using pre-capillary complexation.

3. CHEMICAL ANALYSIS OF ANIONS IN OIL-FIELD WATERS

Various methods of analysis have been developed for the determination of anions in natural waters including molecular absorption, fluorescence and chemiluminescence spectrometry, separation methods including ion chromatography, high performance liquid chromatography and capillary electrophoresis, electrometric methods including potentiometry, coulometric and voltammetric and titration methods.

3.1. Molecular Absorption Spectrometry

I^- and Br^- are determined by the standard method ASTM D 3869 (B: Colorimetric for iodide 0.2 to 2000 mg/L and C: Colorimetric for bromide 40 to 6500 mg/L) [1].

F^- is determined by APHA 4500-F^-(D-SPADNS method, E-complexone method), Br^- is determined by standard method APHA 4500-Br^-(B-phenol red colorimetric method), I^- is determined by the standard method APHA 4500- I^- (B-leuco crystal violet method, C-catalytic reduction method), NO_3^- is determined by APHA 4500- NO_3^- (B-ultraviolet spectrophotometric screening method, E-cadmium reduction method, F-automated cadmium reduction method, H-automated hydrazine reduction method), SO_4^{2-} is determined by APHA 4500-SO_4^{2-}(F-automated methylthymol blue method) [2].

Halogens (F^-, Cl^-, Br^-, I^-) were determined as follows:

An extraction spectrophotometric method for the determination of fluoride in natural waters was presented [230] by use of octyl chemical bonded solid phase extraction (SPE) cartridge. First aluminum-oxinate chelate was adsorbed on SPE cartridge, then the water sample (containing fluoride) was passed through the SPE device. The excess of oxine on the sorbent was washed with acetate buffer and finally the residual of aluminum-oxinate chelate on the sorbent was eluted by ethanol and its absorbance was measured at 375 nm.

A simple method for estimation of fluoride in ground waters was developed based on the bleaching of a zirconium-xylenol orange complex [231].

Flow injection-spectrophotometric method based on the reaction of F^- ions to form stable complexes with Fe^{3+}, thus reducing the catalytic effect of Fe^{3+} on the oxidation reaction of 2, 4-diaminophenol with H_2O_2, and the reducing extent was linear with the concentration of fluoride [232].

A flow injection system using anion-exchange preconcentration and spectrophotometric detection by a mercury thiocyanate /iron nitrate method was developed for determining Cl^- in the range of 0.05 - 0.5 mg/L [233].Also a flow injection method for determining Cl^- was developed in which the sample was passed through a column packed with silver chloranilate, and the liberated chloranilate ion was monitored at 530nm [234].

A method for the simultaneous determination of Cl^- and residual Cl_2 was presented with $NH_4Fe\ (SO_4)_2$-$Hg\ (SCN)_2$ spectrophotometry. The determining wavelength was 460 nm, and the detection limit was 0.2 μg Cl^-/ mL [235].

Bromide was determined in seawater or brine by oxidation to Br_2 using H_2O_2 followed by CCl_4 extraction and spectrophotometry [236].

A catalytic spectrophotometric method [237] for the determination of Br^-, based on the diphenyl carbazide-chromium (VI)-iodate reaction in acid medium to give a violet complex, Br^- catalyzed oxidation of this violet complex, measuring the color change at λ 542 nm.

Iodide was determined in brines by membrane permeation flow injection analysis, iodide was oxidized to I_2. The I_2 permeates through the membrane into a collector stream containing iodide. The iodide reacts with iodine forming triiodide, measured spectrophotometrically in a flow cell at 350 nm [238].

A simple and sensitive method was described for the determination of iodine using leucocrystal violet as a reagent [239]. The method is based on the oxidation of iodine to iodate with bromine water and the liberation of free iodine from the iodate by addition of potassium iodide in acidic medium. This iodine oxidizes leucocrystal violet to form the crystal violet dye. The absorbance is measured at 592 nm.

A simple and high selective method for the determination of iodides was proposed, based on their oxidation with potassium iodate and subsequent interaction between I_2 and iodophenol red [240].

Iodide was determined in oil field water [241] by flow injection analysis, based on the developing reaction between iodide and starch. At first, iodide was oxidized by bromine water. Then excess bromine was removed and the developing reaction was finished on line.

A method for the catalytic photometric determination of micro amounts of iodides in natural water was presented, based on its strong catalytic action on the oxidation of thiocyanate by nitrite, the determining wavelength was 450 nm [242].

The halide can be oxidized with a suitable oxidizing agent to produce halogen gas that can be absorbed by CD-4 to form a colored compound. The absorbance of the compound can be measured at 510 nm and the halide can be determined [243].

Many spectrophotometric methods were applied for determining nitrate and nitrite, involved reduction of NO_3^- to NO_2^-, diazotization, coupling to form a stable dye, and measured [244-248].

Direct measurement of UV absorption of the untreated sample between 205 and 250 nm wavelength band offers a reliable, accurate and rapid methods for the detection of nitrate and evaluating for the correction of absorbance that organic matter might have contributed resulted in decreasing standard error [249, 250].

A comparison of UV spectrophotometry with the hydrazine method for the determination of nitrate shows that both methods provide reliable and reproducible results [251].

A catalytic spectrophotometric flow injection analysis method was proposed [252] for the determination of nitrite and nitrate based on the catalytic effect of nitrite on oxidation of naphthol green B (NGB) by potassium bromate in H_3PO_4 medium and nitrate being reduced to nitrite by a Cd-coated Zn reductor column. The redox reaction was monitored by measuring the decrease in the absorbance of NGB at 722 nm. Another catalytic spectrophotometric method is based on catalytic effect of nitrite on the oxidation of carminic acid with bromate in acidic media [253].

The standard technique for the analysis of NO_3^- in seawater and the interstitial waters of marine sediments is the Cd-Cu reduction method. The reduced sample is expelled and NO_2^- is determined colorimetrically [254].

A green analytical procedure was developed [255] for determination of nitrate in natural waters based on direct measurements in the ultraviolet region, using a flow injection system with an anion-exchange column for the separation of nitrate from interfering species.

A spectrophotometric method [256] for the determination of total carbonate, is based on the color change of an acid-base indicator in relation to the concentration of permeable gas substances through a membrane.

A method for determination of sulfate in water by UV spectrophotometry was presented [257].

The spectrophotometric determination of sulfate [258] is based upon the reaction of display color between dibromo-p-methyl-methylsulfonazo and barium ion. Known excess quantities of barium were added and sulfate precipitated as barium sulfate. The wavelength selected was 636 nm. On the other hand, barium chloranilate method [259]

was used, based on the precipitation of barium sulfate and the colored chloranilic ions was monitored at 528 nm.

A sequential injection analysis system was used to determine simultaneously NO_2^-, NO_3^-, SO_4^2 and phenolic compounds in wastewater. NO_2^-determination is based on Griess-Llosvay reaction. $NO_3^-$is previously reduced to NO_2^- in a copperized cadmium column and analyzed as NO_2^-. SO_4^{2-}determination is based on turbidimetric determination using barium chloride as reagent. Phenolic compound determination is based on oxidative coupling with 4-aminoantipyrine (4-AAP) in alkaline solution. The resulting products of each reaction were spectrophotometrically measured at 540 nm [260].

A multicommutated flow system was proposed [261] for the determination of anions in water samples. The flow set up was assembled with a set of computer-controlled three-way solenoid valves to manage the addition of different reagents by binary sampling. An optical-fiber CCD-array spectrophotometer with a tungsten-halogen lamp was employed for multidetection.

Inorganic anions were determined as triiodide by postcolumn reaction with iodide under an acidic condition with help of α-cyclodextrin in ion chromatography. Analytes reacting with iodide to produce iodine could be determined and detected at 287 or 355 nm. The presence of α-cyclodextrin caused an increase in the concentration of triiodide, leading to improvement of the sensitivity [262].

3.2. Fluorescence and Chemiluminescence Spectrometry

A fluorometric method for determining fluoride was developed [263], based on the fluorescence enhancement by F^- of the Al-salicylfluorone system. The linear range was 0-6 μg of F^-/25 mL.

Aluminum reacts with N-salicylidenethylenediamine in the presence of F^- to form fluorescent complexes and a flow injection analysis system based on the reaction was presented [264]. Also, a flow injection spectrofluorometric method [265] was based on the formation of a complex with Al(III) and eriochrome red B. The detection limit was 10 μg/L.

A method was developed [266] based on solvent extraction of fluoride into chloroform and fluorometric determination using an expanded porphyrin, sapphyrin in the presence of large excess of aluminium (III) and iron (III) and measurement of fluorescence intensity at 684 nm under excitation at 448 nm.

A fluorescence quenching method was elaborated [267] for determining chloride using 2,3,7-trihydroxy-9-(dibromohydroxy phenyl) fluorone as the fluorogenic reagent.

A chemiluminescence method for determining residual Cl in water was developed by treating the water sample with NaI, the liberated I was purged with air and trapped in an alkaline luminol solution, and the luminescence was measured [268]. Also the effect of Cl^- on the electrochemiluminescence of luminol in alkaline solution was used to determine Cl^- with a detection limit of 5.0×10^{-6} mol/L [269].

A method for determining bromide is based on the reaction of Br^- with Cl^- to form Br_2, which reacted with fluorescein, the excess fluorescein was sorbed on Sephadex DEAEA-25 resin and determined fluorometrically using a solid-surface attachment. [270]. Another spectrofluorometric method is based on oxidation of Br^- and bromination of fluorescein. The decrease in fluorescence was used to determine Br^- [271].

A fluorescence quenching method for determining iodide using dichlorofluorescein as the fluorogenic reagent was developed. The detection limit was 0.3 μg/25 mL [272].

A flow injection system for the determination of iodide was described [273], based on the chemiiluminescence (CL) reaction between iodine and luminol. Iodide is oxidized to iodine. Employment of a gas-diffusion unit allows for selective detection of the generated CL (425 nm).

A method for the determination of nitrite and nitrate [274] is based on the diazotization reaction between nitrite and a novel red region fluorescent dye, tetra-substituted amino Al phthalocyanine. Nitrate is determined as nitrite after reduction on a Cd column.

A method for the determination of nitrite and nitrate [275] is based on the quenching action of nitrite on the native fluorescence of murexide(ammonium purpurate) (λ_{ex}= 349.0 nm, λ_{em}= 444.5 nm) in acid range of 0.045-0.315 M H_2SO_4.

An analytical method for the determination of ammonia nitrogen and nitrates/nitrites nitrogen in water was provided [276]. Nitrates/nitrites N was first converted to ammonia gas by reduction in the presence of Devarda's Alloy, followed by catalytic oxidation of NH_3 to NO and the chemiluminescence determination of NO.

A flow injection analysis method for the determination of nitrite and nitrate was developed [277], based on their reduction to NO with hydrazine and/or ascorbic acid, followed by chemiluminescence detection.

A flow injection system was used for the simultaneous determination of nitrite and nitrate in water. The method combines online photolytic conversion of nitrate to nitrite, the

formed nitrite is determined after oxidation to peroxynitrous acid by the chemiluminescent reaction with luminol. Nitrate is reduced to nitrite by absorption of UV light at quartz capillaries and the sum of original and reduced nitrite was detected. Nitrate content was determined from the difference [278-280].

3.3. Anion Separation Methods

3.3.1. Ion chromatography

Anions can be determined by chemically suppressed ion chromatography according to ASTM D 4327 [1].

F^- is determined by the standard method APHA 4500- F^- (F- ion chromatographic method), Cl^- is determined by the standard method APHA 4500-Cl^-(F-ion chromatographic method), Br^- is determined by the standard method APHA 4500-Br^-(C-ion chromatographic method), NO_3^- is determined by the standard method APHA 4500-NO_3^- (C-ion chromatographic method), SO_4^{2-} is determined by the standard method APHA 4500-SO_4^{2-} (B-ion chromatographic method), and anions are determined by APHA 4110 (B-ion chromatography with chemical suppression of eluent conductivity, C-single-column ion chromatography with electronic suppression of eluent conductivity and conductimetric detection) [2].

An IC method was studied [281] for determining chloride and trace anions, such as F^-, Br^-, I^- and SO_4^{2-} in natural gas field H_2O with high chloride concentration. The separation was achieved on an IonPac AS11 column with NaOH as gradient eluent, and the detection was performed by a conductivity detection mode.

Iodide and iodate can be determined [282] by two new methods using anion-exchange chromatography with post-column reaction and UV/visible detection. Iodide was determined as IBr_2^- at 249 nm. Iodate was determined as I_3^- at 288 nm.

The use of a cetyltrimethylammonium-coated octadecyl-bonded silica column with a high anion exchange capacity and mobile phase containing $NaClO_4$ was studied for the highly sensitive detection of I^- in deep seawater [283].

An electrostatic IC method for rapid determination of iodide in seawater was reported [284] using a reversed-phase ODS packed column modified by coating with Zwittergent-3-14 micelles, with an eluent containing $NaClO_4$ and Zwittergent-3-14 and using UV detection at 210 nm.

An IC method for the rapid and direct determination of iodide in seawater was reported [285]. Separation was achieved using a laboratory-made C_{30} packed column modified with

poly (ethylene glycol). Effects of eluent composition on retention behavior of inorganic anions have been investigated.

NO_3^- and NO_2^- were determined [286] using reversed-phase chromatography and UV photometer monitored at 210 nm. A methanol/water mixture was used as mobile phase, and tetra ethyl ammonium bromide as the ion-pair reagent.

Inorganic N-containing species (NO_3^-, NO_2^-, NH_4^+) were simultaneously determined by micro-column IC. NO_3^- and NO_2^- were determined by UV detection at 206 nm; NH_4^+ was determined by fluorescence detection [287].

The nitrate-selective copperised-cadmium (Cu-Cd) reduction reaction coupled directly to a highly sensitive nitrite IC detection, produced a more precise method [288] for the determination of nitrate than either the conventional colorimetric method or the conventional IC method.

A method for determining HCO_3^- using ion-exclusion chromatography and conductimetric detection had a linear range of 2-20 μg/mL [289].

Sulfate was determined [290] by suppressed IC in deep subsurface oil field brines, which were diluted and analyzed on an AS-4 column protected by an AG-4 guard column and operated with an anion micro membrane suppressor with H_2SO_4 as suppressant and $NaHCO_3$-Na_2CO_3 as eluent and conductivity detection.

The effects of parameters such as eluent conductivity, working ranges, peak integration and sample dilution were evaluated for the determination of sulfate in sea and oil-well waters by IC [291].

For the characterization of oil field waters, the minor components bromide, iodide and sulfate are very important among the major components chloride and hydrogen carbonate. The chloride content of these water samples are higher than1 %, whereas the concentration of the minor components is in the lower ppm rang. The proposed method [292] permits the determination of bromide, iodide and sulfate in one IC run using an Ion Pac AS9-SC analytical column with sodium carbonate as eluent and detection by suppressed conductivity. Chloride is titrated because of its high concentration and it is also possible to determine chloride by IC if the sample is diluted.

A new post column chemiluminescence (CL) detection method was developed [293] for the determination of the anions. Several inorganic anions such as chloride, bromide, nitrite, nitrate and sulfate were separated by anion-exchange chromatography using a potassium hydroxide solution as eluent.

The use of IC with a hydroxide-selective Ion pac AS17 column, automated eluent generation and potassium hydroxide gradient represents a new approach, which is a modification of US Environmental Protection Agency Method 300.0 for the determination of inorganic anions in environmental waters [294].

Trace amounts of Br^-, NO_3^- and SO_4^{2-}were determined [295] in sea water by IC. Electrolysis by Ag electrodes was used to minimize the disturbance of Cl^-.

Analytical potential of some eluents absorbing in UV region derived from pyridyl sulfonic acid was evaluated [296] for IC analysis of anionic species. The eluent 2-pyridylhydroxymethanesulfonate offers best conditions for separation and quantification of mono and divalent analyte ions.

Inorganic anion samples were analyzed by capillary ion analysis. Eight inorganic anions (bromide, chloride, sulfate, nitrite, nitrate, fluoride, phosphate and carbonate) were determined with indirect UV detection using automatic hydrostatic sample injection [297]

The major inorganic anions (chloride, fluoride, nitrite, nitrate, sulfate and phosphate) in the environmental samples were studied by IC. Their contamination levels and sources were also evaluated [298].

Simultaneous determination of F^-, Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-} ions on trace level by using preliminary concentration and water removal from concentrating column was proposed [299].

A method for the determination of inorganic ions in oil field water by a single-column IC was presented. On an anion-bonded column, using a mixture of sodium benzoate and sodium citrate as eluent, Cl^-, NO_3^- and SO_4^{2-} in oil-field water can be determined [300], on a cation-bonded column, using a mixture of oxalic acid and ethylenediamine as the eluent, then Mg^{2+}, Ca^{2+}, Sr^{2+} and $Ba^{2+}$are determined.

Indirect photometric detection ion chromatography (IPD, IC), using trimellitic acid (1, 2, 4-benzenetricarboxylic acid)-EDTA as the eluent, was investigated [301] for the simultaneous determination of common inorganic anions (Cl^-, NO_2^-, NO_3^-, and SO_3^{-2}), bicarbonate (HCO_3^-), Mg^{2+} and Ca^{2+} in various environmental water samples.

Low pressure IC was developed [302] and used to analyze inorganic anions and cations in H_2O such as Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-}. The analytical results have a good agreement with the results obtained using the general results.

The simultaneous ion-exclusion/cation-exchange separation column packed with a polymethacrylate-based weakly acidic cation-exchange resin was used [303] to achieve the

simultaneous high-speed separation of anions and cations (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}), the high-speed separation was based on a combination of the ion-exclusion mechanism for the anions and the cation-exchange mechanism for cations.

Suppressed conductometric detection IC method was investigated [304] for the separation and detection of inorganic anions, calcium and magnesium by anion-exchange chromatography using a sodium carbonate-EDTA mobile phase. The formation of anionic Ca^{2+}-EDTA and Mg^{2+}-EDTA complexes allowed its separation from other inorganic anions opening the way for their simultaneous determination in a single chromatographic run.

3.3.2. High performance liquid chromatography

Fluoride was determined [305] by HPLC using an anion-exchange resin including post column derivatization with La and alizarin. Another method [306] has used a post column reaction detection system based on decolorization of the zirconyl xylenol orange complex. The detection limit was 0.05 μg/L.

F^- was determined by a reversed-phase HPLC. The detection limit was 0.10 mg/L and injected amount of 25 μL. The method has a good repeatability and stability [307].

Chlorine was separated by HPLC and determined by UV spectrophotometry following precolumn reaction to form 4-bromoacetanilide [308].

Iodide was derivatized to form 4-iodo-2, 6-dimethyl phenol and determined by HPLC with UV detection. The detection limit was 0.5 ng of I^- for a 100 μL injection [309].

Iodine in natural water was reduced to iodide with excess $NaHSO_3$, and the solution diluted with H_2O and analyzed by HPLC on a Diones AG7 column with HNO_3 as mobile phase and amperometric detection at Ag/AgCl [310].

HPLC method was developed [311] for the determination of iodine species. Iodide was determined by combining anion exchange chromatography and spectrophotometry. Iodate and the total organic iodine species are determined as iodide.

Both NO_2^- and NO_3^- were determined by anion–exchange HPLC with UV detection at 215 nm. Detection limits were 31 μg of NO_3^-/L and 23 μg of NO_2^-/L [312].

Reversed-phase ion-pair LC with tetrabutylammonium bromide as the counterion was used to determine NO_2^- and NO_3^- with a detection limit of 0.3 ng [313].

Determination of nitrate in environmental water samples was made [314] by conversion into nitrophenols and solid phase extraction-spectrometry, liquid chromatography or gas

chromatography-mass spectrometry. Conversion of nitrate into nitrophenols by reaction with 2-methylphenol or 2,6-dimethylphenol allowed at least 100-fold enrichment of the derivative on Lichrolut EN polymeric cartridge. The derivative was eluted with ammonia-methanol mixture. This reaction has permitted a choice of final measurement by UV-Vis spectrophotometry, liquid chromatography or gas chromatography-mass spectrometry.

Reversed-phase columns permanently coated with cetylpyridinium ion or hexadecyltrimethylammonium ion were used to separate SO_4^{2-}, $S_2O_3^{2-}$, and SCN^- by HPLC with indirect UV detection [315].

Chromatographic retention and separation of NO_2^- , Br^-, NO_3^-, and I^- anions on a column packed with Nucleosil 100-5C_{18}, dynamically modified with trimethyloctadecyl ammonium bromide (TMODAB), was studied using direct UV detection [316].

A monolithic column was used [317] to perform ultrafast separations of common inorganic anions using ion-interaction chromatography with tetrabutylammonium-phthalate as the ion-interaction reagent and were monitored using either direct conductometric or indirect absorbance detection.

3.3.3. Capillary electrophoresis methods (CE)

A capillary zone electrophoresis (CZE) method was developed [318] for the determination of bromide ion in sea water. A tenfold-diluted artificial seawater was adopted as the buffer solution to prevent interference from high concentrations of chloride ion in sea water. No electro osmotic flow reverser was used to shorten the analysis time. The results obtained agreed with those obtained by the standard addition method.

A CZE with transient isotachophoresis (ITP) method as an on-line concentration procedure was developed [319] for the simultaneous determination of iodide and iodate in seawater using artificial seawater as a background electrolyte. Limits of detection for iodide and iodate were 4.0 and 5.0 µg/L (as iodine).

Direct determination of NO_2^- and NO_3^- in water by high performance capillary electrophoresis was described [320]. Separation conditions are optimized using a statistic orthogonal design.

Rapid analysis of nitrate and nitrite by CE has been limited by ions of very similar electrophoretic mobilities. The mobility of nitrate can selectivity be reduced using a low pH buffer in CE. With this method nitrate and nitrite are separated [321] faster than current separation methods. Direct UV detection at 214 nm was employed and offered sub µM detection limits.

The use of transient isotachophoresis (ITP) to improve the limit of detection in CZE in determining Low concentrations of NO_3^- and NO_2^- in environmental water was described [322]. Another study [323] described a combination of selected ions as a terminating ion which is useful for transient isotachophoresis (ITP) in CZE for the determination NO_3^- and NO_2^- in sea water.

A highly sensitive capillary zone electrophoresis with artificial seawater as the background electrolyte and transient isotachophoresis as the on-line concentration procedure for the simultaneous determination of nitrite and nitrate in seawater was described [324].

A flow injection-CE method was developed [325] by sample automatic introduction with FI-CE interface. The experimental parameters such as detection wavelength, concentration of electroosmotic flow modifier and Na tetraborate in carrier, pH of the carrier, carrier flow-rate and sample loop volume were optimized.

The petroleum tracers nitrate and thiocyanate in subterranean waters were determined [326] by CE using UV detection. The effect of high concentrations of salts in samples was examined.

Sulfur-containing species ($S_2O_3^{2-}$, SO_4^{2-}, $S_4O_6^{2-}$, S^{2-}) have been determined [327] by CE with indirect UV detection. The optimization of the method was particularly focused on S^{2-} since this species rapidly yields $S_2O_3^{2-}$ and SO_4^{2-} in the presence of oxidizing agents. There fore, it could not be analyzed by CE with chromate as the back ground electrolyte. Pyromellitate and naphthalenetrisulfonate, the mobilities of which are close to that of S^{2-} give the best sensitivity for this species, with good resolution and sensitivity for all species.

A method was validated [328] for the determination of anions (fluoride, chloride, bromide, sulphate, nitrate, nitrite, thiosulphate and phosphate) with CE in combination with indirect UV detection. The method was compared with another buffer system.

A new interface for coupling flow injection analysis and CE has been developed [329]. A FIA system is connected to a flow-through channel of the interface. One end of a capillary is positioned in a flow-through channel inside the interface together with a platinum electrode. The other end and a second platinum electrode are immersed in a liquid reservoir situated outside the interface.

CE with conductometric detection was used [330] to separate and detect chloride (Cl^-), nitrate (NO_3^-), bicarbonate (HCO_3^-) and dihydric phosphate ($H_2PO_4^-$) ions by using citric acid and sodium citrate as buffer solution.

The CZE was used [331] for the determination of small ions-especially inorganic anions and cations. The use of CZE for anions analysis was compared with IC. The CZE and IC analysis techniques are found complementary rather than competitive.

CE with reversal electroosmotic flow (EOF) was used [332] for the determination of inorganic anions with methanol-water buffer. Highly stable and reversed EOF were achieved by the addition of small amounts of the cationic surfactants cetyltrimethyl-ammonium bromide or didodecyldimethylammonium bromide to the electrophoretic buffer.

A CE system for the simultaneous determination of small cations and anions has been developed [333]. They are separated in one single electrophoretic run using one capillary and just one detector. The sample is injected into the first end of the separation capillary and subsequently into the second end. When the high voltage is applied, the cations and the anions in the two injected sample portions start to migrate against each other toward the center of the capillary. The detection window is placed approximately in the middle of the capillary.

Simultaneous separation of small inorganic and organic anions and metal cations by CE after complexation with EDTA was demonstrated [334]. Metal cations, in the form of their chelates with EDTA, are separated together with the anions using an anionic separation mode.

CZE was applied to the determination of inorganic ions in high saline waters [335]. Emphasis was placed on advanced approaches utilized for securing separation performance from being degraded by the presence of matrix salts and for simultaneous separation of ions different in natural abundance.

Simultaneous analysis of cations and anions by CE in conjunction with indirect fluorescence detecting using a blue light diode (LED), was developed [336] based on the displacement of fluorescein with anionic EDTA-metal complexes and anions.

3.4. Electrometric Methods

3.4.1. Potentiometric methods

F^- is determined by ASTM D 3868 and D 1179 (fluoride selective electrode) [1], and 4500-F^- (C-ion-selective electrode) [2], Cl^- is determined by the standard methods ASTM D 512, D 4327 [1], and APHA 4500-Cl^- (D-potentiometric method), Br^- is determined by ASTM

D1246 [1] (ion-selective electrode) and NO_3^- is determined by APHA 4500- NO_3^- (D-nitrate electrode method, G-titanous chloride reduction method).

Fluorides in waters, brines, and common salt were determined [337] potentiometrically with ion-selective electrodes using ultrasonic sample preparation, which extends the range of sample types and makes analysis more rapid, sensitive and precise.

A comparative analysis of metrological characteristics of potentiometric and photometric methods for fluoride-ion determination in H_2O was performed [338]. A potentiometric method appeared advantageous.

Choice of appropriate TISAB (total ionic strength adjusting buffer) plays a crucial role in fluoride analysis in H_2O samples by ion selective electrode. The efficiency of ten different TISAB for fluoride estimation in water samples in presence of F^- binding cations e.g. $Al^{3+}$and Fe^{3+} was studied [339].

Trace fluoride in seawater was determined [340] with fluouide ion selective electrode by addition of sodium citrate and EDTA to eliminate the effects of interfering ions, such as AL^{3+}, Fe^{3+}, etc., by the standard addition method to eliminate the effects of salt.

Determination of chloride by multisyringe flow injection analysis with potentiometric detection was reported [341]. The results achieved were compared with those obtained by a potentiometric sequential injection analysis (SIA) method reported in the literature. When Mohr titration was carried out for validating the results offered by both techniques, no significant differences were found.

An automatic potentiometric titrator was explored and provided basis for developing a method for determining low levels of chloride in water [342].

Sequential injection with lab-at-valve (LAV) approach was demonstrated [343] for potentiometric determination of chloride, the LAV flow-through electrode system consists of two Ag/Ag Cl electrodes: One as a reference electrode, and the other as a working electrode placed in a flow channel. The results agree with IC and titrimetric methods.

A Br^- ion-selective electrode was used [344] in a flow injection system for the analysis of sea water. The matrix effect of Cl^- was removed by calibrating the electrode in NaCl solution.

The performance of two kinds of silver working electrode was compared [345] in electrochemical detector, the disposable and conventional electrode for the determination of iodide using high performance anion-exchange chromatography hyphenated with pulsed amperometric detection. Results showed that disposable working electrode manifested

equal or better results than conventional working electrode and could be used for iodide analysis.

A direct potentiometric method for the analysis of nitrates was presented [346] using an ion-selective electrode. The method was shown to give more precise measurements of nitrates than methods using other electrodes.

Ion-selective electrodes (ISE) based on polymeric membranes for in-situ determination of nitrate and ammonium contents in ground water have been developed [347]. The ISE are integrated in a multisensor module for monitoring these ions. The receptor is a PVC-membrane with tridodecylammonium nitrate for nitrate.

Automatic monitoring of nitrate using a novel ion-selective electrode was performed [348]. The ISEs did not require re-calibration and no deterioration in performance of the membrane surface was observed.

A nitrate-selective electrode based on a tris(2-aminoethyl)amine triamide derivative receptor was developed for the determination of nitrate [349].

Bicarbonate in water was determined using a solid-membrane pb(II)-sensitive electrode [350].

Sulfate was determined by an indirect FIA method in which lead perchlorate was added to the carrier stream and a lead-selective electrode was used to determine the amount of lead remaining in solution. The system was used to determine sulfate in the range of 50 - 10 000 mg/L [351].

A solid membrane, sulfate ion-selective electrode was developed using barium chloranilate and poly (vinyl chloride). The electrode was used in the range of 10^{-1} - 10^{-4}mol of SO_4^{2-}/mL [352].

Sulfate was determined by potentionetric titration of excess Ba^{2+} following precipitation of $BaSO_4$. A Hg electrode was used in the titration with EGTA [353].Also a potentiometric titration of SO_4^{2-} with $pb(NO_3)_2$ using a pb-selective electrode was studied [354]. In another study sulfate was reduced to S^{2-} and then determined by potentiometric titration with $pb(NO_3)_2$ using a S^{2-}-selective electrode [355].

Anion-selective light-addressable potentiometric sensors (LAPS) for the determination of nitrate and sulphate ions by using a solid-state microelectronic device integrated with an ion-recognition membrane has been elaborated [356].

An amperometric detector with 2 working electrodes modified with poly diphenylamine (PDPA) and polydiphenylamine dodecyl sulfate (PDPA-DS) was successfully [357] used

for the simultaneous determination of electroinactive anions (SO_4^{2-}, Cl^-, NO_3^-) and cations (Na^+, $NH_4^+$and K^+) in single-column ion exclusion chromatography-cation exchange chromatography. In another study [358] a single working electrode for simultaneous determination of those cations and anions was designed as a detector in ion chromatography.

3.4.2. Coulometric and voltammetric methods

The complex Ce(III)-Alizarine complexone-F^- was determined by [359] adsorptive polorography over the range of 8 x 10^{-8} - 5 x 10^{-6} M F^-. Also a procedure was described [360] in which the complex La (III)-ALizarine complexone-F^- was adsorbed at a hanging Hg drop electrode and the reduction current was measured by a linear sweep voltammetry.

An automated system for coulometric measurements was developed and applied to the determination of Cl^- with electrogenerated Ag [361].

The Ag electrode used in the stripping voltammetric determination of Cl^- was renewed [362] between analyses by cutting off a thin layer of the metol. Also a flow injection cathodic potentiometric stripping method [363] was developed for determining Cl^-. The linear range was 1 x10^{-6} - 8 x10^{-3} mol/L.

An indirect kinetic method for determining Br^- in water was based on its catalytic effect on the oxidation of methyl orange by potassium bromate with poloragraphic detection, which gave a detection limit of 0.2 μg /mL [364].

Catalysis by I^- of the oxidation of malachite green by $KClO_4$ was the basis of a kinetic polarographic method [365] for determining I^-. Also, a cathodic stripping voltammetry method [366] was used to determine I^- with a detection limit of 0.1 ng/mL.

Friedel's salt, a mineral anion exchanger, was synthesized and used as a novel electrode modifier for the accumulation of iodide species and their subsequent voltammetric determination at carbon paste [367].

Voltammetric determination of iodide was developed [368] by use of an interdigitated microelectrode array (IDA) sensor based on reversible charge transfer in the redox system I_2 /$2I^-$ at a platinum microelectrode.

A voltammetric method for determining NO_3^- based on its catalytic effect on the oxidation of Ti(0) to Ti(I) was described [369]. The linear range was 0.5 - 60 μg of NO_3^- /mL.

Nitrite and nitrate were determined at trace levels in natural waters by differential pulse polarography. Limits of determination were of 0.10 μg/mL and 0.003 μg/mL for nitrate and nitrite, respectively [370].

A method was presented [371] using the adsorptive complex wave of pb (II)-tetrakis [4-(trimethylammonio)phenyl] porphyrin in an indirect voltammetric determination of SO_4^{2-}. Also, sulfate was precipitated with Ba and then determined [372] by ac oscillopolorogrophic titration with potassium chromate as the titrant.

Determination of dissolved inorganic C (DIC) in natural H_2O was established. A complete analysis procedure using nonaqueous coulometric titration was studied and optimized to get the finest color switch-point [373].

Simultaneous coulometric titration method was described [374] for the determination of iodide, bromide, and chloride using an electronic circuit for automatic switching of three-electrode constant current chronopotentiometric operation to the three-electrode square wave voltammetric (SWV) operation using the same electrochemical device.

3.5. Titrimetric Methods

Cl^- is determined by the standard methods ASTM D 512 [1] and APHA 4500-Cl^- (mercuric nitrate titration, silver nitrate titration) [2] and ASTM D 4458 (mohr method with silver nitrate) [1], $Br^-$and I^- are determined by the standard methods ASTM D 3869 (volumetric method from 0.2 to 2000 mg/L iodide and from 5 to 6500 mg/L bromide) [1].

Rapid method for the quantitative determination of iodide in water involving acidification of the sample and oxidation of I^- with calcium hypochlorite followed by extraction with benzene or toluene and titration of the extract with sodium thiosulfate [375].

A titrimetric method for determining HCO_3^- was reported in which the sample was titrated to pH 4 - 4.5, CO_2 was removed and the sample was back-titrated to its initial pH [376].

Sulfate was preconcentrated by anion exchange and determined by titration with $BaCl_2$ in the presence of arsenazo III [377].

The effects of standing time after adding precipitating agent in water on experimental results of EDTA volumetric determination of sulphate in water were studied [378].

4. ANALYSIS OF ORGANIC CONSTITUENTS IN OIL-FIELD WATERS

The amount, kind, and state (dissolved, suspended or colloial) of organic matter in petroleum–associated waters was important in determining the origin and migration of petroleum and in problems concerning pollution of fresh waters by petroleum–associated waters [5].

Dissolved organic matter include hydrocarbons (saturates and aromatics), organic acids (fatty acids, naphthenic acids and humic acids) and phenols [5].

Different techniques have been developed for the analysis of organic constituents in natural waters, including spectrometry and chromatography

4.1. Spectrometric Methods

Petroleum products concentrations in industrial and natural waters were determined in the range 5 – 60 mg/L. The absorbance was measured with a photoelectric colorimetric with blue filter [379].

A method was described [380] for the determination of total organic carbon in an aqueous sample by trapping the organic matter on a sorbent which is carbon free and analyzing the sorbent by combustion and determination of total CO_2 by IR.

A direct aqueous supercritical fluid extraction (SFE) system was developed [381] which can be directly interfaced to an IR spectrometer to determine oil in water. The method involves minimum sample handling stages.

The performance indices and testing results of an IR spectroscopic oil analyzer and a FTIR spectrometer were compared [382] in the determination of mineral oil in water. The results showed that the performance indices of both methods meet the international requirements for environmental monitoring.

The solid phase extraction as a solvent-free method for the analysis of oil and grease in waters was studied [383]. The use of a PTFE surface as a solid phase allows the retention of the volatile fraction of oil and grease, and further analysis of C-H bonds using IR spectroscopy could be done. The method is fast, and allows reproducible measurements of oil and grease in water that do not require the use of a solvent.

IR transmitting silver halide fibers were used [384] as internal reflection elements for the spectroscopic detection of hydrocarbons that are dissolved in water. The fibers were partly flattened by pressing and coated with an analyte-enriching organic polymer to increase the sensor sensitivity.

Total hydrocarbons were determined in water [385] and sediment samples by the standard methods and IR spectrophotometry.

Computer–assisted IR spectrometry was proposed [386] for the separate determination of aliphatic and aromatic petroleum products in water samples. The integral intensities of absorption bands was measured with a Fourier-transform IR spectrophotometric complex. Individual hydrocarbons and their mixtures were studied, and water samples were then analyzed.

An IR reflection–absorption method was developed [387] to detect aromatic organic compounds in aqueous solutions. Two aluminum plates were used to form the sampling cell for the detection of small amount of aqueous samples.

Using near infrared (NIR) evanescent field absorption (EFA) measurements in quartz glass fibers coated with a hydrophobic silicone membrane, it is possible to design and construct sensors for monitoring hydrocarbons in aqueous matrixes [388]. A fiber-optic sensor system for the determination of aromatic hydrocarbons in ground water or industrial waste water was presented.

4.2. Chromatographic Methods

Headspace solvent microextraction (HSME) was shown [389] to be an efficient preconcentration method for extraction of some polycyclic aromatic hydrocarbons in different water samples, which were then analyzed by gas chromatography.

A solid-phase microextraction–gas chromatography–mass spectrometry (GC-MS) analytical method for the simultaneous separation and determination of 16 polycyclic aromatic hydrocarbons from aqueous samples has been developed [390], based on the sorption of target analytes on a selectively sorptive fibre and subsequent desorption of analytes directly into GC-MS.

The resin and fatty acids in pulp mill effluents were extracted, concentrated and methylated. The methylated products were determined by gas chromatography on a fused-silica column using a flame ionization detector [391].

Traces of 15 naphthenic acids occurring in the high-salinity waters of Karachi Lake were identified and determined [392] by GC on a glass column, packed with 15% of poly ethanediol adipate on Chromosorb R (pre-modified with 10% H_3PO_4). The concentration of individual acids ranged from 1 to19 μg/L in the lake brine.

Naphthenic acids in water sources [393] were extracted with CH_2Cl_2, where the organic phase was dried and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and treated with trimethylchlorosilane. Portions of the mixture were analyzed for naphthenic

acids by GC on a glass column packed with 5 % OV–17 on Chromosorb WAW DMCS operated isothermally at 110°C with N_2 as carrier gas and FID.

Lower fatty acids were determined [394] in sediment pore water by direct injection GC, with column of FFAP–CB wax and FID or mass selective detection.

Short-chain (C_2 – C_5) carboxylic acids were determined in oil-field water [395] by evaporation to small bulk and the distillate was concentrated on a rotary evaporator. Portions were analyzed by GC on a capillary column coated with AT 1000 and FID detection.

Fatty acids in water were determined [396] by combined solid-phase micro extraction (SPME) and GC-FID. The SPME apparatus contained a syringe with a 1 cm long fiber, the fiber was coated with poly (dimethylsiloxane), poly (acrylate), or Carboxen. Detection of short-chain acids was enhanced by derivatization in situ by immersing the coated fiber in 5 mg/L of 1-pyrenyldiazomethane in hexane for 1h before use.

The isolation and concentration of fatty acids from water was achieved [397] by continuous steam-distillation /liquid-liquid extraction. The extracts were then analyzed by GC on glass capillary column coated with OV-210 or with DEGS plus H_3PO_4 and operated with N_2 as carrier gas and FID.

Organic compounds in waters [398] were concentrated on a column of LiChroprep RP-18, with methanol and CH_2Cl_2 as eluents or by extraction with $CHCl_3$ (before and after acidification with HCl to pH 2). Subsequent liquid chromatography on a column of Spherosil XOA allowed separation in chemical classes of increasing polarity. Alkanes, alcohols and fatty acid methyl esters were analyzed by gas chromatography and identified by comparison of their retention times with those of authentic standards. Identities of all compounds were confirmed by MS.

Gas chromatography–electron impact mass spectrometry was used [399] to characterize organic acids in water produced during the extraction of bitumen from oil sands. These acids are a complex mixture of substituted acyclic and cycloaliphatic carboxylic acids, with the general chemical formula $C_nH_{2n+Z}O_2$, where n is the carbon number and Z specifies a homologous family.

Naphthenic acids (NAs), found in hydrocarbon deposits (petroleum, oil sands bitumen, and crude oils), are not well characterized and comprise a large group of saturated aliphatic and alicyclic carboxylic acids. These acids were determined [400] in natural waters by using negative–ion electrospray ionization mass spectrometry (ES-MS) of extracts. Preconcentration was achieved by a solid-phase extraction procedure utilizing a cross

linked polystyrene-based polymer with acetonitrile elution. This procedure proved to be a fast and sensitive method for the recovery and detection of NAs in natural waters.

A comprehensive analysis procedure was developed [401] for analyzing organic compounds in oil field produced water. Adsorbable organic compounds were extracted by soxhlet extractor and concentrated, then analyzed by GC-MS. They included aromatics, phenols and acids. Short chain fatty acids, C_2 to C_5, were determined by ion chromatography with a UV detector.

Oil-produced water samples in the North Sea were analyzed [402] for PAHs and phenols by GC-MS. Analysis of organic acids was done by isotachophoresis, metal determinations by atomic absorption spectrometry, and radioactivity measurements by high resolution gamma spectroscopy.

A polysiloxane-based extraction method combined with liquid chromatography was applied [403] to determine polycyclic aromatic hydrocarbons in water samples.

The abundance of alkylphenols in the system of water, oil and rock is of great geochemistry significance. The analysis of alkyl phenols in an oil field water using micellar electrokinetic chromatography with UV detection is described and showed that there are phenol, *o*-, *m*- and *p*- cresol in this water sample [404].

Short chain organic acids in oil-field water were analyzed by isotachophoresis. Formic acid, acetic acid, propionic acid, butyric acid, lactic acid and benzoic acid were determined [405].

Short-chain carboxylic acids in oil-field water were determined [406] by high-performance capillary zone electrophoresis using indirect UV detection. Quantization was made by the internal-addition method. Acetic, propionic, butyric and valeric acids were well separated.

5. CLASSIFICATION OF OIL–FIELD WATERS

Classification systems for waters are devised in an effort to facilitate comparison of water analyses and to demonstrate some relations between waters and their sources or environments. Most systems of classifying water depend on relations between carbonate, bicarbonate, sulphate, chloride, calcium, magnesium and sodium ions; the reason being that these ions are the only ones determined in many routine water analyses [4, 5].

Waters from various geological formations are classified by the systems of Palmer [407], Sulin [408], Chebotarev [409], Schoeller [410] and Bojarski modification of Sulin system [411, 412]. These classifications are useful in exploration and production problems.

5.1. Palmer Classification System

Palmer [407] stated that the fundamental character of natural waters depends on the general properties of salinity and alkalinity. The salinity, defined as the property given by the non-hydrolyzable salts of strong acids, is obtained by doubling the total reaction values (in milliequivalents) of the strong acid anions. These values are doubled because any cations in combination with these anions would also be considered as contributing to salinity. The alkalinity is a property attributed to free alkaline bases produced by easily hydrolyzable salts of weak acids. The alkalinity is obtained by doubling the reaction values of the bases in excess of the strong acid anions. The reaction value of each radical is determined by multiplying its concentration (mg/L) by its reaction coefficient, which is the valence of the radical divided by its atomic or molecular weight.

Ions determined in water analysis are arranged in three groups:

Group (a): Alkalis (sodium and potassium),

Group (b): Alkaline earths (calcium and magnesium), and

Group (d): Hydrogen (strong acid anions).

Palmer designated five properties according to the predominance of reaction values of the contained ions as follows:

Primary (alkali) salinity: The salinity is not to exceed twice the sum of the reaction values of the alkali ions.

Secondary salinity (permanent hardness): The excess of salinity over primary salinity is not to exceed twice the reaction values of the ions of the alkaline earths.

Tertiary salinity (acidity): This is any salinity in excess of the primary and secondary salinity.

Primary (permanent) alkalinity: The excess of twice the sum of the reaction values of the alkalis over salinity.

Secondary (temporary) alkalinity: This is the excess of twice the sum of the reaction values of the ions of the alkaline earths over secondary salinity.

Waters are classified by numerical values of the relationships of the anions to the cations, where a, b, and d represent the percentage reaction values of the alkalis, alkaline earths, and strong acid anions, respectively. Any one of the following five conditions may

exist: d may be less than a, equal to a, greater than a, less than a + b, equal to a + b, or greater than a + b. According to these conditions, waters may be divided into five classes:

Class 1: d < a.

2 d = primary salinity, 2 (a – d) = primary alkalinity, and 2 b = secondary alkalinity.

Class 2: d = a.

2 a = 2 d = primary salinity, and 2 b = secondary alkalinity.

Class 3: d > a; d < a + b.

2 a = primary salinity, 2 (d – a) = secondary salinity, and 2 (a + b – d) = secondary alkalinity.

Class 4: d = a + b.

2 a = primary salinity, and 2 b = secondary salinity.

Class 5: d > a + b.

2 a = primary salinity, 2 b = secondary salinity, and 2 (d – a – b) = tertiary salinity.

These five classes of waters are found in nature. Examples of the first three classes are various surface waters; sea water and brines represent class 4, while mine drainage waters and waters of volcanic origin fall in class 5.

5.2. Sulin Classification System

Sulin [408] proposed a classification system based upon various combinations of dissolved salts in the waters. The waters are described according to chemical types, subdivided into groups, subgroups and classes.

He found four basic environments of natural water distribution:

Continental (terrestrial) conditions which promote the formation of "sulphate- sodium" type of waters.

Continental conditions which promote the formation of "bicarbonate-sodium" type of waters.

Marine conditions with formation of "chloride-magnesium" type of waters.

Deep subsurface conditions within the earth's crust, with the formation of "chloride- calcium" type of waters.

The first two types are characteristic of meteoric and/or artesian waters, the third of marine environments and evaporite sequences, and the fourth of deep stagnant conditions.

Water composition is expressed in milligram-equivalents of separate ions, and the composition is calculated per 100 g of water. The percent of the sum of the equivalents is used to exclude the degree of water mineralization, and to compare waters containing different amounts of dissolved solids.

The ratio Na/Cl, expressed in the percent equivalent form, determines the genetic water type. If the value is greater than one, sodium predominates over chloride and the excess sodium can be combined with sulphate or bicarbonate. Therefore, waters with a Na/Cl ratio greater than one belong to the bicarbonate-sodium or sulphate-sodium types, while if it is less than one, they belong to the chloride-calcium or chloride-magnesium types.

The ratio (Na – Cl)/SO_4 if greater than one indicates that the water is the bicarbonate-sodium type, while if it is less than one it is the sulphate-sodium type. Similarly, the ratio (Cl – Na)/Mg if less than one indicates the chloride-magnesium type, but if greater than one it indicates the chloride-calcium type.

Subdivision of the groups of water is made using the Palmer characteristics, because these characteristics express the dissolved constituents in the waters a generalized format. For example, the sum of the alkali chlorides and sulphates corresponds to primary salinity, and the sum of the alkaline earth chlorides and sulphates corresponds to secondary salinity and the sodium bicarbonate-calcium stage.

No sodium bicarbonate is present in sulphate-sodium, chloride-magnesium, or chloride-calcium types of waters, while bicarbonate-sodium type waters contain sodium bicarbonate. These types are classified into the bicarbonate, sulphate and chloride groups. The groups are subdivided into the following classes:

Class A_1: Primary alkalinity predominates (alkali carbonates and bicarbonates).

Class A_2: Secondary alkalinity predominates (alkaline earth carbonates and bicarbonates).

Class S_1: Primary salinity predominates (alkali sulphates and chlorides).

Class S_2: Secondary salinity predominates (alkaline earth sulphates and chlorides).

Class S_3: Tertiary salinity predominates (iron and aluminium sulphates and chlorides and free strong acids).

The classes are subdivided into subclasses, e.g. class S_1 can include: S_1 S_2 A_2, $S_1A_2S_2$, S_1S_2, and S_1. The water classification is thus expressed by use of a formula representing decreasing values of the Palmer characteristics. For example, S_1 S_2 A_2 indicates that primary salinity is predominant, then followed by secondary salinity and secondary alkalinity.

The Palmer characteristics do not account for the interrelations between chloride and sulphate and between calcium and magnesium. Therefore, the ratio SO_4/Cl and Ca/Mg are calculated to establish additional subgroups. The complete water characterization includes the following:

Water formula given in Palmer characteristics,

Coefficients in percent equivalents for SO_4/Cl and Ca/Mg,

Sum of milligram equivalents per 100 g of water ($\sum$ r) to illustrate the degree of water mineralization, and

The genetic coefficients (Na – Cl)/SO_4, (Cl – Na)/Mg and Na/Cl to determine genetic types of water.

Sulin [408] noted that certain properties of subsurface waters are favourable indicators for hydrocarbon accumulations, most commonly related to water types in this order:

chloride-calcium > bicarbonate-sodium > chloride-magnesium > sulphate-sodium.

Most oil field waters of the chloride-calcium type belong to the S_1 S_2 A_2 class with a few in the S_2 S_1 A_2 class, while most oil field bicarbonate-sodium waters belong to the S_1 A_1 A_2 and A_1 S_1 A_2 classes.

Sulin grouped other significant indicators; none of them can assure the existence of hydrocarbons, and certainly cannot provide definite evidence of the size of their accumulation. The groups are as follows:

Group I: direct hydrocarbon indicators; for example, naphthenic acid salts and iodide, as well as dissolved gases and absence of oxygen. The naphthenic acids are more soluble in bicarbonate-sodium type waters and are related to the composition of the hydrocarbon accumulation. Iodide is related to oil because it must have an organic origin.

Group II: highly mineralized chloride-calcium or bicarbonate-sodium types of water containing reduced forms of sulphur are important indirect indicators of oil. The sulphate content should be low to indicate interaction with bituminous constituents and/or sulphate-reducing bacteria.

Group III: constituents which have no genetic relationship to hydrocarbons, but appear to be characteristic of waters that are related to hydrocarbon accumulations. The constituents are bromide, boron, barium, strontium, radium, and possibly fluoride.

5.3. Bojarski Modification of Sulin System

Bojarski [411] studied 400 water analyses and differentiated hydrochemical zones within basins in Poland that appear suitable for preservation of hydrocarbon deposits. He distinguished the waters as follows:

(1) Waters of the bicarbonate-sodium type, with $(Na - Cl)/SO_4 > 1$. A ratio which indicates an excess of sodium with respect to both chloride and sulphate. Such waters occur in the upper zone of a sedimentation basin, with "intense water exchange", that is a hydrodynamic situation where the waters are moving at a relatively fast geological rate, which promotes unfavourable conditions for the preservation of petroleum and natural gas deposits.

(2) Waters of the sulphate-sodium type, with $(Na - Cl)/SO_4 < 1$. This ratio indicates that all of the sodium will react with the chloride or sulphate.

(3) Waters of the chloride-magnesium type, with $(Cl - Na)/Mg < 1$. This ratio indicates that all of the chloride will react with the sodium and magnesium. Such a water is characteristic of the transition zone between a hydrodynamic area which is becoming more hydrostatic in the deeper part of the basin, and the amount of dissolved bromide increases directly with the (Cl – Na)/Mg ratio.

(4) Waters of the chloride-calcium type, with $(Cl - Na)/Mg > 1$. This ratio indicates an excess of chloride with respect to sodium and magnesium, and the excess will react with calcium. This type of water occurs in deeper zones which are isolated from the influence of infiltrated waters and are hydrostatic or almost hydrostatic.

Bojarski observed a large variation in the chemical composition in the chloride-calcium type of water, and subdivided this type into five classes as follows:

Class I, with Na/Cl > 0.85, characterizes an active hydrodynamic zone with considerable water movement. It is considered a zone of little prospect for the preservation of hydrocarbon deposits.

Class II, with Na/Cl = 0.85-0.75, characterizes the transition zone between an active hydrodynamic zone and a more stable hydrostatic zone of the sedimentation basin, which is generally considered as a poor zone for hydrocarbon preservation.

Class III, with Na/Cl = 0.75-0.65, characterizes favorable conditions for the preservation of hydrocarbon deposits. It is designated as a fairly favorable environment for the preservation of hydrocarbons.

Class IV, with Na/Cl = 0.65-0.50, is characterized by complete isolation of the hydrocarbon accumulations as well as by the presence of residual waters. It is considered as a good zone for the preservation of hydrocarbons.

Class V, with Na/Cl < 0.50, is characterized by the presence of ancient residual sea water which has been highly altered since original deposition, both in the concentration of dissolved solids and in the ratios of the dissolved constituents. A zone of this type is one of the most likely areas where hydrocarbons are accumulated.

Additional characteristics of water associated with hydrocarbon accumulations are as follows:

(1) iodide > 1 mg/L, (2) bromide > 300 mg/L (increasing iodide and bromide concentration may point to a bitumen accumulation), (3) ratio Cl/Br < 350, and (4) $(SO_4 \times 100)/Cl < 1$.

5.4. Chebotarev Classification System

Chebotarev [409] classified waters on the basis of dissolved bicarbonate, sulphate, and chloride, and the assumption that anions are independent variables while the cations are dependent. The geochemical types of waters are related to the products of weathering because, although the concentration of dissolved solids in subsurface waters may vary substantially, the types of soluble salts remain largely unchangeable.

The waters are classified into three major geochemical groups: bicarbonate, sulphate and chloride, which are divided into genetic types (classes), and are determined from the absolute concentrations of the dissolved constituents, expressed in percent reaction values. The amounts of bicarbonate plus carbonate and chloride plus sulphate determine the genetic types (classes). The classification is as follows:

The bicarbonate group contains three genetic types (classes):

(a) bicarbonate (I), (b) bicarbonate-chloride (II), and (c) chloride-bicarbonate (III).

The sulphate group is subdivided into two genetic types (classes):

(a) sulphate-chloride (IV), and (b) sulphate.

The chloride group includes three genetic types (classes):

(a) chloride-bicarbonate (III), (b) chloride-sulphate (IV), and (c) chloride (V).

The water classes are related to the products of weathering, rain fall, and drainage conditions:

Class I waters correspond to soluble products from the weathering of orthoeluvium or igneous and highly metamorphosed rocks and their silicate compounds.

Class II waters are related to products of weathering from the same silicates and calcareous accumulations.

Class III waters primarily are related to weathered products from calcareous accumulations.

Class IV waters are related to weathering of alluvial, detrial, and gypsum deposits.

Class V waters are related to marine deposits plus weathering of the products that is derived from class IV waters.

The equilibrium of the chemical systems (those typical of the major geochemical groups of waters) is a criterion called the coefficient of water exchange (K_e) and is computed as:

$$K_e = \frac{Na(K)HCO_3 + (Ca, Mg)(HCO3)_2}{Na(K)Cl + (Ca,Mg)Cl_2 + Na_2SO_4 + (Ca,Mg)SO_4}$$

The absolute and relative coefficients of water exchange for the three major groups of waters, derived from assumed chemical compositions of their typical waters, are as follows:

Water major group	K_e(absolute)	K_e(relative)
Bicarbonate	1.55	96.9
Sulphate	0.11	6.9
Chloride	0.016	1.0

The highly concentrated chloride waters are primarily associated with oil occurrence; however, this is not always true.

Chebotarev [409] applied his classification to 917 subsurface waters in oil fields in the world, and indicated that 73.7, 23.0 and 3.3 % of the waters are of the chloride, bicarbonate, and sulphate types, respectively. Most of the bicarbonate and sulphate types are found in the Rocky Mountain areas of the United States and probably are mixtures containing infiltrated meteoric water.

5.5. Schoeller Classification System [557]

Schoeller [410] proposed the principal characteristics for classifying the different chemical types of waters in petroleum reservoirs, with their order of importance; which are as follows:

1. Chloride concentration (in epm): Six types are distinguished:

Hyperchlorinated waters, with Cl > 700,

Marine-chlorinated waters, with Cl 700-420,

Strong-chlorinated waters, with Cl 420-140,

Medium-chlorinated waters, with Cl 140-40,

Oligochlorinated waters, with Cl 40-10, and

Normal-chlorinated waters, with Cl < 10.

2. Sulphate concentration (in epm): Four groups are distinguished:

Hypersulphated waters, with $SO_4 > 58$,

Sulphated waters, with SO_4: 58-24,

Oligosulphated waters, with SO_4 24-6, and

Normal-sulphated waters, with $SO_4 < 6$.

When the $\sqrt{(SO_4)(Ca)}$ is greater than 70, the waters are near saturation with $CaSO_4$, and when it is less than 70, the waters are under saturation.

3. Bicarbonate plus carbonate concentration (in epm): Three groups are distinguished:

Hypercarbonated waters, with $HCO_3 + CO_3 > 7$,

Normal-carbonated waters, with $HCO_3 + CO_3 = 7 - 2$, and

Hypocarbonated waters, with $HCO_3 + CO_3 < 2$.

It is preferable to use the $\sqrt[3]{(HCO_3 + CO_3)^2(Ca)}$, rather than using the $(HCO_3 + CO_3)$, which is proportional to the pressure of gaseous CO_2 in equilibrium with $CaCO_3$ in water.

4. Index of base exchange (IBE):

If Cl > Na, then IBE = (Cl – Na)/Cl, and it will be positive.

If Cl < Na, then IBE = (Cl – Na)/($SO_4 + HCO_3 + CO_3$), and it will be negative.

Schoeller [557] found that the waters of petroleum reservoirs have more positive IBE as the chloride increases, and more negative IBE as the chloride decreases.

5. Importance of anions and cations: In the petroleum reservoir waters, the following sequences are practically found:

(a) $Cl > SO_4 > CO_3$, (b) $Cl > CO_3 > SO_4$, (c) $CO_3 > Cl > SO_4$, (d) $CO_3 > SO_4 > Cl$

(e) $Na > Mg > Ca$, and (f) $Na > Ca > Mg$.