# A Technical Review on Determination of Chemical Contaminants for Marine Environment

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#### ABSTRACT

Marine environment has a huge biodiversity in so many living creatures such as microorganisms, invertebrates, plants, fish, sharks, and whales. Chemical contamination can easily break down the weak balance of the marine environment. Recently, organic and inorganic chemicals are the main detecting contaminants in the marine samples involving fish and seawater. Oil, hydrocarbons (C<sub>x</sub>H<sub>v</sub>), and heavy metals can be detected qualitatively and measured quantitatively using the modern instrumental analysis tools. Infrared (IR), Ultraviolet/Visible (UV/Visb.), Proton Nuclear Magnetic Resonance (<sup>1</sup>HNMR) and Mass Spectrophotometer (MS) are the most usable and reliable tools to investigate the structure elucidation of organic contaminants whereas Flame Photometer (FP), Atomic Absorption (AA) spectrometer, and Inductively Coupled Plasma (ICP) are the common spectroscopic tools for the detection and determination of light (Li, Na, K, Ca, Ba, Sr) and heavy (Pb, Cd, Hg, As, Sn, Ag, Zn) elements in seawater and marine samples. These modern instrumental tools have been provided as a result of developments of marine science, chemistry, pollution science, and engineering. Our present review provides a scientific detail about the available and reliable modern tools that can be used for determination of organic and inorganic contaminants in marine samples. The main sources of contaminants, the mutual relationship between contaminants and ecosystem, and the chemical aspects in marine environments have been outlined.

Keywords: Organic & inorganic contaminants, Marine Environment, Heavy metals, Spectroscopic tools

#### Introduction

Marine ecosystems are the major and largest part of the Earth's aquatic ecosystems. They include so many creatures deep inside the sea like Mangroves and Coral reefs as biotic components. Oceans, Estuaries, Lagoons, and the Sea floor are involved in Marine ecosystems. These are the gigantic reservoirs of water covering approximately 71% of the Earth's surface. These ecosystems are different from freshwater ecosystems mainly because of its salty water. The world's oceans have, on average, a salinity level of about  $\approx 3.5$  %, i.e., 35 grams of dissolved salts per liter of water [1]. Sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>), and magnesium (Mg<sup>2+</sup>) are the major cations, whereas chloride (Cl<sup>-</sup>) and sulphate (SO<sub>4</sub><sup>2-</sup>) are the major anions [2], both naturally occurring cations and anions are present permanently in the

marine ecosystems as abiotic components in a certain fixed concentration. Any undesired increase in the amount of any cation or anion in marine environment was considered as unfavorable contamination. Additions of new inorganic elements such as heavy metals or organic compounds to the marine environment are also a new type of contamination or pollution because the marine ecosystem does not contain inorganic and organic contaminants. Prevention of these chemical pollutants to reach the environment must be done now and in the future generation to save the genetic and species biodiversity in the marine ecosystem. The world need to know what is the chemical contaminants or pollutants (organic or inorganic) that can be reached through different pathways to the marine environment as a result of human activities in the see. Recently, it was estimated that about  $\approx$ 35 to 40 % of the developing countries are aware of environmental issues but they do not bother about it because they does not have the facilities to detect and determine pollutants qualitatively and quantitatively. In fact, each chemical pollutant has a suitable conventional instrument for detection and determination of that pollutant, especially in aquatic samples. In the current article, we aimed to review the analytical instrumental tools of inorganic and organic contaminants. Several techniques have been presented for the determination of metal concentrations in marine samples such as flame atomic absorption spectrometry [3, 4], graphite furnace atomic absorption spectrometry [5, 6], electro-thermal atomic absorption spectrometry [7], and inductive coupled plasma [8]. The most of inorganic contaminants like Zinc (Zn), Manganese (Mn), Mercury (Hg), Copper (Cu), Nickel (Ni), Aluminum (Al), Arsenic (As), Cadmium (Cd), and Lead (Pb) were successfully determined using these tools in samples from marine environment [9-11]. So many organic contaminants like hydrocarbons, organic acids, alcohols, aldehydes and ketones can easily detected and hence, the chemical identity were elucidated using Infrared (IR), Ultraviolet/Visible (UV/Visb.), Proton Nuclear Magnetic Resonance (<sup>1</sup>HNMR) and Mass Spectrophotometer (MS) techniques [12, 13].

# Sources of marine pollution

The main sources of marine pollution can be classified into the following [14]:

- 1) Chemical wastes: Toxic chemicals (inorganic or organic) produced from industrial and agricultural activities are the most common form of sources of marine pollution that are directly discharged into the environment, resulting in seawater pollution.
- 2) Illegal sewage pipelines: Contamination/pollution can enter the seawater and ocean directly by illegal sewage system. Polluting substances flow through sewage, rivers, or drainages directly into the marine ecosystem easily by water stream. This is often how minerals and chemical substances from mining camps find their way into the environment.
- 3) Land runoff is another source of pollution in the ocean. This occurs when water infiltrates the soil to its maximum extent and the excess water from rain, flooding or melting flows over the land and into the ocean.
- 4) Ship pollution is considered as a huge source of ocean pollution, the most devastating effect of which is oil spills.
- 5) Ocean mining in the deep sea is yet another source of ocean pollution. Ocean mining sites drilling for silver, gold, copper, cobalt and zinc create sulphide deposits up to three and a half thousand meters down in to the ocean.

## Probable impacts of marine chemical contamination

Marine pollution occurs when harmful, or potentially harmful, effects result from the entry of chemicals, particles, industrial, agricultural, and residential waste into the marine ecosystem.

The effects of marine pollution are very diverse because there are many different types of marine pollution. The impact of contamination can change marine ecosystems lives forever and finally reach to humans too. The following impacts can probably occur in common cases with a short lifespan [15]:

- 1) Disturbing the balance of ecosystems as a result of failure in the reproductive system of sea animals.
- 2) Damage to living creatures and loss of fauna by toxicity.
- 3) Potential damage and acute/delayed risk on public health of humans.
- 4) Bio-magnification of undesirable material.
- 5) Aesthetic degradation of beach life.
- 6) Reduction of marine resources due to cut-off the food chains.
- 7) Accelerated Corrosion with depression of oxygen content in seawater.
- 8) Disruption to the cycle of Coral Reefs.
- 9) Shortcut of O<sub>2</sub> gas and CO<sub>2</sub> gas cycles in marine environments.
- 10) Incomplete Nitrogen (N) and Phosphorous (P) cycles in marine environments.

#### Theoretical aspects on spectroscopic techniques

The focus of this part is on the interaction of different radiations with matter to determine the concentration. Because spectroscopic techniques use optical phenomena to disperse and focus the radiation, they often are identified as optical spectroscopies and the simpler term spectroscopy. Despite the difference in instrumentation, all spectroscopic techniques share several common features and it depends on the same principle. A spectroscopic measurement is possible only if the interaction of photons with the sample leads to a change in one or more of properties of the electromagnetic radiation like energy, velocity, amplitude, frequency, phase angle, polarization, and/or direction of propagation. When the measurable material absorbs electromagnetic radiation, the number of photons passing through a sample decreases. The measurement of this decrease in photons, which we call absorbance, is a useful analytical signal to determine concentration. Spectroscopy can be divided into two broad classes of techniques absorption and emission. It depends on transfer of energy between the photon and the sample as shown in Figure (1) and (2) [16]. Spectroscopic techniques use instruments that have several common basic components, including a source of energy, a wavelength selector, a detector for measuring the signal, and a signal processor that displays the signal in a form convenient for the analyst. Transmittance (T), percentage transmittance, and absorbance (A) were defined as shown in the following equations:

$$T = \left(\frac{I_T}{I_0}\right)$$

$$\% T = \left(\frac{I_T}{I_0}\right) \times 100$$

$$A = -Log_{10} (T) = -Log_{10} \left(\frac{I_T}{I_0}\right) = \varepsilon \times L \times C_M$$

Where  $\left(\frac{I_T}{I_0}\right)$  is the ratio between transmitted radiation intensity ( $I_T$ ) and the initial intensity of incident light ( $I_0$ ), and  $\varepsilon$ , L, and  $C_M$  are molar absorptivity (L/mol.cm), the pass length (cm) and the concentration (mole/L) respectively. The last equation is well-known as Beer – Lambert law which is the relationship between the absorbance and the concentration of the measurable material.





Fig (1): Absorption and emission of radiation



## Ultraviolet/Visible (UV/Visb.) and Infrared (IR)

Quantitative analysis of the contaminant's concentration in marine samples using absorption of infrared (IR), ultraviolet (UV) or/and visible (Vis.) techniques is one of the most frequently instrumental analytical methods. One reason for its popularity is that so many organic and inorganic compounds have strong absorption bands in the IR and UV/Vis regions of the electromagnetic spectrum. If the substance does not exhibit absorption of UV/Vis radiation or if its absorbance is too weak, it easily reacts with another strongly absorbing compound. For example, a dilute solution of ferrous ion Fe<sup>2+</sup> does not absorb visible light and therefore the reaction of Fe<sup>2+</sup> with *o*-phenanthroline forms an orange–red complex of [Fe(o-phen)<sub>3</sub>]<sup>2+</sup> that has a strong and broad absorption band near 500 nm. Table (1) shows typical examples of the determination of heavy metals using UV techniques. In a same manner, saponins as naturally occurring bioactive organic compounds have absorption band between 250-350 nm, while heavy metal-saponin complexes for Mn, Co, Ni, Cd, Zn, and Pb exhibit major absorption peaks in the narrow wavelength range of ~ 320 to 400 nm with absorbance value in the range of 0.2 to 1.2 due the red shift towards the shorter wavelength of the complexes [17].

Infrared spectroscopy (IR) is routinely used to analyze gas, liquid, and solid samples. Transparent solid samples can be analyzed directly by placing them in the IR beam. Most solid samples, however, are opaque, and must be dispersed in a more transparent medium before recording the IR spectrum. Solid sample cells are made from compacted NaCl and KBr that are transparent to infrared radiation. Gases are analyzed using a cell with a path length of approximately 10 cm. Longer path lengths are obtained by using mirrors to pass the beam of radiation through the sample several times. A liquid samples may be analyzed using a variety of different sample cells. For non-volatile liquids a suitable sample can be prepared by placing a drop of the liquid between two NaCl plates, forming a thin film that typically is less than 0.01 mm thick. Volatile liquids must be placed in a sealed cell to prevent their evaporation. Figures (3) and (4) represent different forms of the IR-samples and IR-spectrum of dioxane as a contaminant.

Heavy metal ion	Ligand nucleus	Product (measurable form)	λ (nm)
Fe <sup>2+</sup>	1, 10- phenanthroline	$R_{4}$ $R_{4$	500
Cu <sup>2+</sup>	$H_3C$ $CH_3$ Neocuprine	Yellow Bis neocuprine copper complex	457
Cd <sup>2+</sup> , Pb <sup>2+</sup> , Hg <sup>2+</sup>	Dithiazone	N N N N N N N N N N N N N N N N N N N	518 510 492
		Bis dithiazone lead complex (Orange to red)	
Cr <sup>6+</sup>	HN NH O I, 5- diphenylcarbazide		540

Table (1): Determination of heavy metals using UV/Vis. Absorption



Fig. (3): Forms of samples in IR instrument [16]

(A) NaCl salts plates.

(B) Fixed path length (0.5 mm) sample cell with NaCl windows.

(C) Disposable card with a polyethylene window.

# Table (2): Functional groups and their IR peaks

No.	Peak	Function Group	Notes
1	4000 -670 cm <sup>-1</sup>	Wave number scale	The whole absorption scale
2	4000-1400 cm <sup>-1</sup>	High frequency region	Fingerprint regions
	1400-600 cm <sup>-1</sup>	Low frequency region	
3	2800-3300 cm <sup>-1</sup>	С-Н	
	2800-3000 cm <sup>-1</sup>	sp <sup>3</sup> (-C-H)	Alkanes or alkyl group
	3000-3300 cm <sup>-1</sup>	sp <sup>2</sup> (=C-H)	Alkenes
	~ 3300 cm <sup>-1</sup>	sp (≡C-H)	Alkynes
	1360-1385 cm <sup>-1</sup>	sp <sup>3</sup> [C (CH <sub>3</sub> ) <sub>2</sub> ]	Germinal or gem dimethyl
4	Weak bands	sp <sup>3</sup> (C-C) (Aliphatic)	σ - bond
	1450-1600 cm <sup>-1</sup>	sp <sup>2</sup> (C-C) (Aromatic, Aryl)	π - bond
	1600-1700 cm <sup>-1</sup>	sp <sup>2</sup> (C=C) (Olefins)	π - bond
	2100-2250 cm <sup>-1</sup>	sp (C $\equiv$ C) (Acetylenes)	
5	500-1430 cm <sup>-1</sup>	C – X	Halo-alkanes
	~ 760 cm <sup>-1</sup>	C-Cl	
6	3000-3700 cm <sup>-1</sup>	C – OH (broad spectrum)	Alcohols (H-bonding)
	(the left of C –H)	N –H	Amines (sharp peak):
	900-1300 cm <sup>-1</sup>	C-O or C-N	R -NH <sub>2</sub> (double peak)
	~ 3000 cm <sup>-1</sup>	OH of carboxylic acid	R <sub>2</sub> -NH (single peak)
		(overlaps with the C-H stretch)	R <sub>3</sub> -N (no peak)
7	1720-1740 cm <sup>-1</sup>	RCHO	Aldehyde
	1705-1750 cm <sup>-1</sup>	RCOR	Ketone
	1700-1725 cm <sup>-1</sup>	RCOOH	Carboxylic acid
	1735-1750 cm <sup>-1</sup>	RCOOR	ester



Fig. (4): Typical example for IR-spectrum of 1, 4-Dioxine [18]

As shown in Table (2), IR spectrum depends on the nature of functional groups present in the organic compounds and the main chemical structure of any marine contaminants can be determined using IR-technique.

## Atomic Absorption (AA) Spectroscopy

Atomic absorption spectrophotometers use a single or double-beam optical system for the determination of unknown concentrations of over 62 different metals in liquid form. To analyze the sample it must convert the substance into free atoms by atomization process and the target analyte must be in solution form. If the sample is a solid, then it must bring it into solution before the analysis. Atomization process aimed to convert the substance to free gaseous atoms and there are two common atomization methods: flame atomization and electro-thermal atomization, although a few elements are atomized using other methods. Efficiency of the atomization process was greatly affected by the flame temperature and hence the type of fuel-oxidant mixture. The (acetylene - air) and the (acetylene - nitrous oxide) flames are the most popular that provide the desired temperature range of (2100-2400°C) and (2600-2800°C) respectively. The atomization flame itself has three different zones or regions: the first is the ignition zone, the second is the atomization or combustion zone (hottest region), and the third is the waste release zone. Liquid samples were introduced to the flame atomizer by means of a continuous aspiration or a flame micro-sampling, and each method has some advantages and disadvantages. A great improvement was done by using an electro-thermal atomizer (graphite furnace) where a graphite tube was used instead of the flame that led to significant enhancement of sensitivity. Inside the graphite furnace, the sample goes through three sequential steps: drying, ashing, and atomization and the temperature will rise from 110°C to 1200°C and finally to 3000°C within about ~ 70 seconds during the three stages. So many factors affect the net result of analysis among of these factors are choosing the method of atomization, selecting the wavelength and slit width, preparing the sample for analysis, minimizing spectral and chemical interferences, and selecting a method of standardization. Figure (5) shows the light source of atomic absorption which is a multi-elemental hollow cathode lamp consisting of a cathode and anode enclosed within a glass tube filled with a low pressure of neon (Ne) or argon (Ar) gas. Solid samples are brought into solution by dissolving in an appropriate solvent or may be digested on hydrochloric acid HCl, nitric acid HNO<sub>3</sub>, sulphoric acid H<sub>2</sub>SO<sub>4</sub>, perchloric acid HClO<sub>4</sub>, or aqua regia solution (3 volume HCl:1 volume HNO<sub>3</sub>). Alternatively, we can extract the substance using a Soxhlet extractor. Liquid samples may be analyzed directly or a liquid–liquid extraction using an organic solvent and a chelating agent is frequently used to concentrate the substance. Dilute solutions of Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup>, for example, can be concentrated by extracting with a solution of ammonium pyrrolidine dithiocarbamate, Figure (6), in methyl isobutyl ketone. Due to the narrow width of absorption lines, atomic absorption provides excellent selectivity and can be used for the analysis of over 60 elements at concentrations at or below the level of  $\mu$ g/L [19].





Fig. (6): Ammonium pyrrolidine dithiocarbamate

# Fig. (5): A multi-elemental hollow cathode lamp [16]

## Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) is one of the most common techniques for elemental analysis used for samples of marine environment. Atomic emission technique is an analytical method that uses the intensity of light emitted from atoms excited by a proper source at a particular wavelength to determine the quantity of an element in a sample. The wavelength of the atomic spectral line gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element. At thermal equilibrium, the intensity of an atomic emission line,  $(I_e)$ , is proportional to the total number of excited atoms,  $(N^*)$  with the proportionality constant (k) as shown in the equation:

$$I_e = k \cdot N^*$$

The number of excited atoms  $(N^*)$  and the total concentrations of the original atoms (N) are in a relation by Boltzmann approximation equation:

$$N^* = N \times \left(\frac{g_i}{g_0}\right) \times e^{-E_i/kT}$$
[19]

Where  $g_i$  and  $g_0$  are statistical factors that account for the number of equivalent energy levels for the excited state and the ground state,  $E_i$  is the energy of the excited state relative to a ground state energy,  $E_0$ , and k is Boltzmann's constant (1.3807×10<sup>-23</sup> J/K), and T is the temperature in kelvin. (ICP-AES) can perform qualitative, semi quantitative, and quantitative analysis and the instrument detection limits are at or below ppt  $(1 \times 10^{-9})$  concentration level. Plasma is an electrical conducting gaseous mixture containing a significant concentration of cations and electrons. It is used to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. As shown in Figure (7), the ICP torch (the source of plasma) consists of three concentric quartz tubes, surrounded at the top by a radio-frequency (RF) induction coil. The sample is mixed with a stream of Argon gas using a nebulizer, and is carried to the plasma through the torch's central capillary tube. Plasma formation is initiated by a spark from a Tesla coil. An alternating radio-frequency current in the induction coils creates a fluctuating magnetic field that induces the argon ions and the electrons to move in a circular path. The resulting collisions with the abundant unionized gas give rise to resistive heating, providing temperatures as high as 10000 °K at the base of the plasma, and between 6000 and 8000 °K at a height of 15–20 mm above the coil, where emission is usually measured. At these high temperatures the outer quartz tube must be thermally isolated from the plasma. A wide range of elements in the periodic table (alkali, alkaline and transition metals, non-metals, most of lanthanides, few of actinides) can be detected and analysed by (ICP-AES) with high sensitive/efficient performance, stable and reproducible signal.



#### Fig. (7): Schematic diagram of an inductively coupled plasma torch [16]

#### Flame Photometer (FP)

The estimation of the alkali and alkaline earth metals by flame photometry is the most important application in routine chemical analysis of marine samples. Low temperature flame photometry provides the most reliable and convenient procedure available for so many samples in the laboratory. The basis of FP is the same as that of the simple quantitative analytical flame test. Compounds of the alkali (Li, Na, K, Rb, & Cs) and alkaline earth metals (Mg, Ca, Sr, & Ba) are thermally dissociated into atoms at the temperature of a Bunsen burner flame and that some of these atoms produced are further excited to a higher energy level. When these 'excited' atoms return to the ground state, they emit radiation, which for the elements of these two groups lies mainly in the visible region of the electromagnetic spectrum. The wavelength of the light emitted from the flame is characteristic of the particular element. The intensity of this light is, in most cases, proportional to the absolute quantity of the species present in the flame at any moment, i.e. the number of atoms returning to the ground state is proportional to the number of atoms excited, i.e. the concentration of the sample. The emitted radiation is isolated by an optical filter and then converted to an electrical signal by the photo detector. The analysis of group I & II elements are typically determined at 1500-2000°C, therefore suitable mixtures are propane/air, butane/air and natural gas/ air. Table (3) shows the values of the emitted wave length and the associated color of different metals.

property	Group (I) elements				Group (II) elements				
	Alkali metals				Alkaline earth metals				
	Li	Na	К	Rb	Cs	Mg	Са	Sr	Ва
Wave length	670	589	766	780	852	285	622	461	554
(λ, nm)									
color	Red	Yellow	Violet	Violet			Orange	Scarlet	green

Table (3): Characteristic wavelength and color of group (I) & (II) elements [20]

#### Proton Nuclear Magnetic Resonance (<sup>1</sup>HNMR)

<sup>1</sup>HNMR spectroscopy is one of the most powerful techniques available to study the structure of organic molecules. <sup>1</sup>HNMR spectrometers use magnetic fields between 1 and 20 T. Even so, the energy separation is small and radiofrequency radiation is enough to excite the nucleus and change its spin orientation with the field. <sup>1</sup>HNMR includes the absorption of radio-waves by the nuclei of some combined atoms in an organic molecule located in a magnetic field. Not unlike UV/Vis. radiation, radio-waves are of low energy electromagnetic radiation and their frequency is on the order of 10<sup>7</sup> Hz. In analytical chemistry <sup>1</sup>HNMR is a technique that can be used to study the shape and structure of molecules. Also it provides information on the spatial orientation of atoms in the molecule. The chemical shift ( $\delta$ ) is the key to structure determination by NMR. To explain the <sup>1</sup>HNMR spectrum, we can use the de-shielded (higher  $\delta$ ) or shielded (lower  $\delta$ ) proton terms. The chemically identical nuclei are shifted from the chemically different nuclei. De-shielded nuclei would be moved to the left on the <sup>1</sup>HNMR spectrum. As a result, we are able to distinguish between different functional groups in a molecule as shown in the ethanol spectrum, Figure (8). In both <sup>1</sup>HNMR and <sup>13</sup>CNMR, the same reference compound is used, tetra-methyl silane (TMS), Si(CH<sub>3</sub>)<sub>4</sub>. TMS thus shows only one peak at  $\delta = 0$  in the spectrum. In benzene molecule, all 6 H-atoms are in exactly the same environment and hence have the same value of chemical shift. Also, the 6 C-atoms in benzene are identical. In the <sup>1</sup>HNMR spectrum, all six <sup>1</sup>H nuclei will absorb at exactly the same frequency as each other and in the <sup>13</sup>CNMR spectrum, all six <sup>13</sup>C nuclei will similarly absorb at exactly the same frequency as each other. So, there is one singlet sharp peak at  $\delta \approx 7.4 \, ppm$  in the <sup>1</sup>HNMR spectrum of benzene ring and one peak in the <sup>13</sup>CNMR spectrum. Therefore, <sup>1</sup>HNMR and <sup>13</sup>CNMR can be used for the determination of the chemical structure of aliphatic and aromatic contaminants in marine samples.

# **Mass Spectrometry (MS)**

The molecular mass of a compound can be determined by the mass spectrometer. The process starts by vaporization of a small solid sample of the compound in a mass spectrometer under a reduced vacuum and becomes a target for a beam of high-energy electrons. The ejection of an electron from the molecule will occur to form a positively charged ion called the molecular ion or parent ion ( $M^{+*}$ ). Any formed ion is characterized by its mass-to-charge ratio, (m/z).

 $M + e^- \rightarrow M^{+*} + 2e^-$  (Ejection of an electron and formation of molecular ion)

The positively charged ions are accelerated by the action of an electric field before passing through a magnetic field. The ions will travel in a curved motion according to its (m/z) ratio. Lighter ions have higher energy to move and are deflected more strongly than heavier ions. When the molecular ion arrives at the detector, it produces a peak in the mass spectrum. The peak height is proportional to the number of ions arriving in a given time. During the ionization process, molecular ions  $(M^{**})$  with high energy may go through break down to produce fragment ions or daughter ions  $(m^{*})$  as shown in the equation:

 $M^{**} \rightarrow m^{+}$  + neutral fragment (Fragmentation of the molecular ion)

Each fragment again appears in the mass spectrum at the corresponding mass value on the scale. The height of the peak due to the fragment depends on the amount formed. The peak with the highest (m/z) value usually corresponds to the parent ion and so can usually be used to measure the molar mass of the molecule. Sometimes, a fragment ion is the most abundant ion and so produces the tallest peak in the spectrum. Whether the tallest peak is due to the parent or a fragment, it is called the base peak and is arbitrarily assigned a relative height of 100%. Heights of all of the other peaks are then expressed as percentages of the base peak. Actually, the mass spectrum is a table or a plot of the ratio (m/z) of detected ions on x-axes versus their relative abundance (relative concentration) on y-axes. Figure (9) represents the mass spectrum of the benzene molecule that shows the main peak of molecular ion at m/z = 78 with about  $\approx 100$  % relative intensity.



Fig. (8): <sup>1</sup>HNMR spectrum of ethanol [21]



Fig. (9): MS spectrum of benzene [22]

#### **Complete determination of marine samples**

Actually, we cannot use one technique for complete identification and determination of contaminants in marine samples either organic or inorganic. We need to use more than one technique to identify all elements, all compounds in a sample qualitatively and quantitatively. For example, to obtain a complete identification and structure elucidation of organic contaminants, we need to use mass spectrometer to know the molecular mass of the compound, need to use IR instrument to know what is the functional groups are present in the compound, need to use <sup>1</sup>HNMR to know how many types of hydrogen and carbon atoms are present? Also, we need to use UV/Vis. technique to know the presence of aromaticity or conjugated polyene's (multi-double bonds). However, identification/determination of elements using one technique seems to be more available than molecular determination, but still insufficient for complete analysis for all elements. Table (4) shows a comparison between the above mentioned techniques. It was noticed that most instruments used for the determination of inorganic compounds need a calibration curve for enhanced performance and it can be used for qualitative and quantitative analysis. Instrumental analysis of organic contaminants does not need a calibration curve for performance and the most of them were used for qualitative molecular identifications.

Technique	Mode of	Calibration curve		Qualitative		Quantitative	
	analysis	Organic	Inorganic	Elemental	Molecular	Elemental	Molecular
UV/Vis.	Non-	No	Yes	Yes	Yes	Yes	Yes
	destructive						
IR	Non-	No	No	No	Yes	No	No
	destructive						
AA	Destructive	N.A	Yes	No	No	Yes	No
ICP-AES	Destructive	N.A	Yes	Yes	No	Yes	No
FP	Destructive	N.A	Yes	Yes	No	Yes	No
<sup>1</sup> HNMR	Non-	No	N.A	No	Yes	No	No
	destructive						
MS	Destructive	No	N.A	No	Yes	No	Yes

Table (4): Comparison between analytical tools for marine samples

N.A: not available

#### Conclusions

Marine environment has a dynamic diversity in marine creatures that contains so many solid and liquid organic and inorganic contaminants. Many techniques and many instruments are proposed for the analysis of these chemical contaminants such as IR, UV, 1HNMR, and MS for identification of organic compounds, while UV, FP, ICP, and AA can be used for the analysis of inorganic contaminants. The present article provides the basic principles of the instrumental analysis that can be used for identification and determination of organic and inorganic contaminants in marine samples. Brief information about the mathematical forms controlled some practical performance of these instruments. Terminology, examples, pictures, chemical structures, tables, and figures also provided to highlight the scientific knowledge for marine laboratories.

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	Abbreviations	Notations		Unites	
IR	Infra-red	Т	Transmittance	cm	Centimeter
UV/Vis.	Ultraviolet/Visible	А	Absorbance	mm	Millimeter
<sup>1</sup> HNMR	Proton nuclear magnetic resonance	I <sub>T</sub>	Intensity of transmitted light	μm	Micrometer
<sup>13</sup> CNMR	Carbon nuclear magnetic resonance	Io	Intensity of incident light	nm	Nanometer
MS	Mass Spectrometer	8	Absorptivity Coefficient	mol.	Mole
AA	Atomic absorption	L	Pass length	L	Litter
(ICP-AES)	Inductively Coupled Plasma Atomic Emission Spectrometer	См	Molar concentration (molarity)	°C	Degree centigrade
RF	radio-frequency	h	Planck's constant	°K	Kelvin degree
FP	Flame photometer	ν	Frequency	μg	Microgram
TMS	tetra-methyl silane	$\Delta E$	Energy gap	ppm	Part per million
		λ	Wave length	ppt	Part per trillion
		Ie	intensity of an atomic emission line	Hz	Hertz
		N*	number of excited atoms	Т	Tesla
		Ν	Original number of atoms		
		$E_i$	Excited state energy		
		$E_0$	ground state energy		
		k	Boltzmann's constant		
		$(\delta)$	chemical shift		
		(m/z)	mass-to-charge ratio		

# Appendix: Abbreviations, Notations, and Unites