TRACE ELEMENT CONTAMINANTS IN THE KUWAIT WATER PRODUCTION SYSTEM

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by

LAILA AL ANQAH

DEPARTMENT OF CHEMISTRY
BRUNEL UNIVERSITY
UNITED KINGDOM

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ABSTRACT

Fresh water in Kuwait is produced by non-conventional methods. About 95% of this water comes from desalinated seawater using multi-stage flash distillation technique and the remainder comes from underground brackish water. The blended water containes organic, inorganic and trace metal impurities within the recommended international standard limits.

The purpose of this work is to identify the source of selected trace metals present in the drinking water in Kuwait. Chromium, copper, iron, lead, manganese, nickel, vanadium and zinc have been analysed using atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectroscopy (ICP-MS).

Efforts were made to improve the preconcentration of the selected metals and their separation from the high concentration of salts in seawater which affect the accuracy and cause major interference in the analysis.

Solid-liquid extraction (chelex-100 resin) and liquid-liquid extraction (methyl iso-butyl ketone and freon) with and without back-extraction into nitric acid were investigated. Liquid-liquid extraction without back-extraction proved to give optimum recovery of the selected metals.

Results confirmed that both AAS and ICP-MS are suitable for the analysis of trace metals in Kuwait's waters. Although AAS technique proved to be more accurate in analysing the selected metals than ICP-MS, the latter was adopted since its accuracy is acceptable (1.1-4.4%) and it is easier and faster than the former technique.

The study revealed that the source of copper, iron, nickel and zinc is the construction materials of the distillation plants, while the source of lead and vanadium is the brackish water. Manganese and chromium concentrations are very low in all sources. No direct relationship between the metal concentration in the seawater and the distillate could be deduced.

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TO MY FAMILY

I wish to dedicate this thesis

for their support and

encouragement

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CHAPTER 1

INTRODUCTION

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INTRODUCTION.

Kuwait is an independent Arab State, situated at the north western corner of the Arabian Gulf between Latitudes 28° 45′, 30° 05′ north and Longitudes 46° 30′, 48° 30′ east of Greenwich.

Water is Kuwait's most critical resource. This stems from the fact that Kuwait is located in a coastal desert and lacks natural occurrence of fresh water. This has severely hindered the development of Kuwait for many years in the past. When the funds from oil revenues became available, Kuwait turned to the sea for its fresh water supplies.

The phenomenal social and economic growth witnessed in Kuwait during the past forty years has depended on the fresh water supply from desalination plants that utilize seawater as a feed.

The first Kuwaiti desalination plant came into operation as early as 1953, by 1990 Kuwait had developed six desalination costal sites.

Kuwait's current total installed multi-stage flash "MSF" distillation capacity exceeds 250 million imperial gallons per day (MIGPD) and the current consumption amounts to 120-140 MIGPD. Since the operational capacity of the MSF plants very rarely exceed 70-80%, the present available desalination capacity is just enough to meet the need for daily fresh water supplies.

Distilled water (D.W.) is obtained from seawater of very high salinity using multi-stage flash evaporators (MSF). Table 1 shows the chemical characteristics of the seawater of Kuwait [Al Awadi and Abdel-Jawad, (1987)]. The distillate is very soft water of low buffer capacity and is considered quite aggressive to the materials that come into contact with it.

Distilled water in Kuwait is blended with brackish water (B.W.) (2500 - 10000 μg/ml), pumped out from ground aquifers, to improve its palatability. Chemical chracteristics of B.W. used for blending are shown in table (2) [MEW, (1992)]. The

blending is based on a 4 to 12% blending ratio of brackish to distilled water, depending on the availablity of B.W. and on the need of the quantity of product water.

The blended water (potable water P.W.) is disinfected by the addition of chlorine. Caustic soda is added to maintain the pH value between 7.5 and 8.5. Chemical analysis and physical properties of the drinking water as shown in table (2), indicate that it complies with the desirable limits of the international drinking water standards (Appendix I). Chemical analysis indicates a deficiency in carbonate and bicarbonate ions, and the sulphates and chlorides exceed the concentration of the carbonate and bicarbonate. These criteria give the potable water its aggressiveness towards the material which comes into contact with it.

Dealing with such types of aggressive waters (sea, distilled, brackish and potable water) which may cause leaching of trace metals during production and distribution encouraged this study. Its aim is to identify the source of certain trace metals that enter the water production process.

Table (1)

Chemical analysis and physical properties of seawater.

PARAMETER	CONCENTRATION mg/l*	
Total Dissolved Solids (180·C)	47000	± 2000
pH	8.2	± 0.1
Total Alkalinity (as $CaCO_3$)	175	± 15
Carbonate	14	± 8
Bicarbonate	185	± 18
Carbon dioxide	14	± 4
Sulphate	3400	± 300
Chloride	24000	± 700
Calcium	570	± 45
Magnesium	1700	± 150
Sodium	12300	± 20
Potassium	470	± 20
Total Iron	0.08	± 0.008

*** Average concentration of 12 samples collected monthly during 1985.**

Standard deviation indicates variation in seawater concentration rather than experimental error.

[Al Awadi and Abdel-Jawad (1987)]

Table (2)

Chemical analysis and physical properties of distilled (D.W.) brackish (B.W.)and potable water (P.W.).

PARAMETER	CONCENTRATION mg/l		
	D.W.	B.W.	P.W.
Conductivity (μS)	8.5	-	-
TDS	-	3201	241
pH	6.2	7.74	7.8
Carbonate	0.0	0.02	0.0
Bicarbonate	1.15	149	13.2
Total Alkalinity (as $CaCO_3$)	0.94	122	11.5
Chloride	<0.2	734	56
Sulphate	<5.0	1182	80
Sodium	0.73	448	39
Potassium	<0.1	15	1.2
Total Hardness (as $CaCO_3$)	-	1384	118
Total Iron	0.01	0.19	0.019
Fluoride	-	2.10	0.15

[Ministry of Electricity and Water, Water Resources Development Center, Kuwait (1992)].

1.I. Multi-Stage Flash Distillation of Seawater.

Kuwait has been fully dependent for its fresh water supplies on seawater distillation plants for the last 39 years. Multi Stage Flash Distillation Plants (MSF) have been successfully used for about 30 years and during this period Kuwait has gained wide experience in the design, commissioning, operation and maintenance of constructed MSF Plants. Figure (1) shows the locations of these MSF stations.

Process Description.

It is useful to state the principle of MSF distillation of seawater with the help of the simplified block diagram of a typical MSF evaporator shown in figure (2).

A liquid at a given pressure has its own saturation temperature. This temperature decreases as the pressure drops. Therefore, a liquid under such saturated condition contains maximum amount of heat energy and will boil or vaporize if either additional heat is supplied or pressure is reduced.

When a liquid at saturation temperature is introduced into an unheated chamber in which the vapour pressure is maintained at such a level that the boiling point of the resident liquid is below its incoming temperature, it immediately boils or vaporizes. This phenomenon is called "flash evaporation", and high purity distillate is then obtained by condensing this flashed vapour.

MSF distillation plants take full advantage of this fact to produce distilled water from seawater feed. The MSF evaporator is divided into a number of stages each at successively lower pressures. All or almost all stages are operated under near vacuum (low pressure) conditions. These pressures are maintained by the air ejectors. Usually, the last three stages constitute the heat recovery sections.

Recirculating brine flows into the tube side of the heat recovery section, where it is gradually heated by flashed

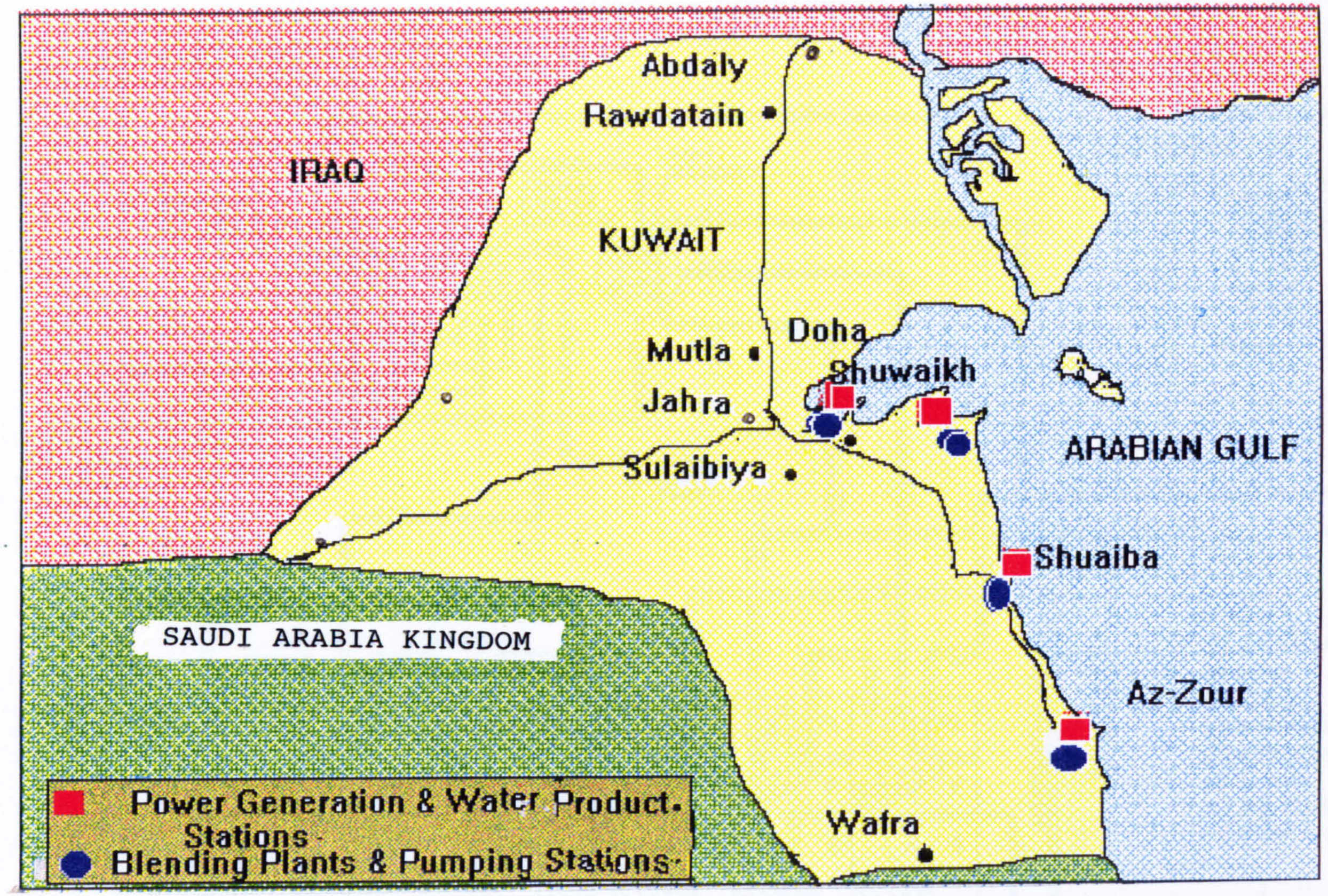

Fig. (1) POWER GENERATION AND WATER PRODUCTION STATIONS
BLENDING PLANTS AND PUMPING STATION

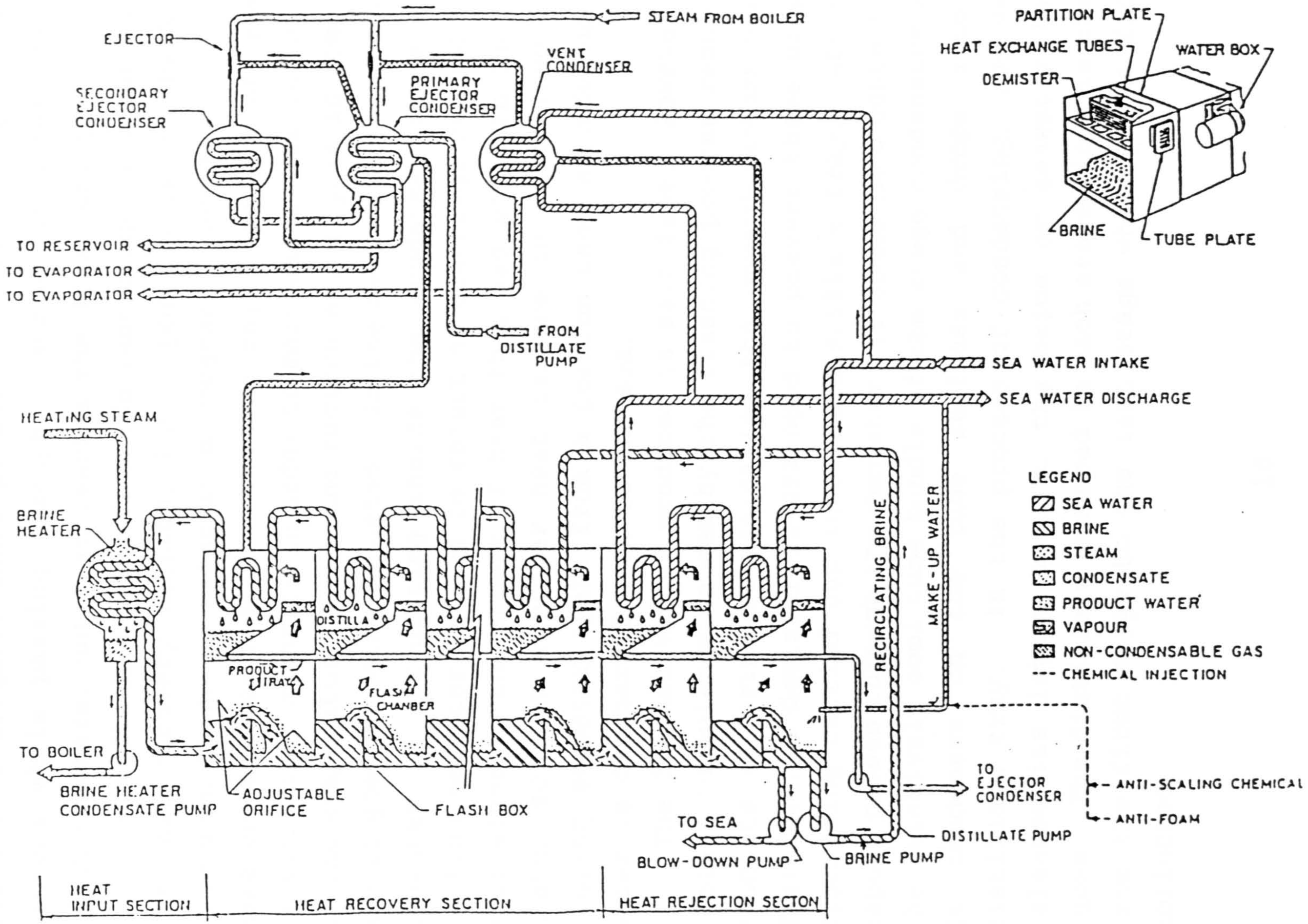

Figure (2) Simplified Block Diagram of a Typical M. S. F. Plant.

vapour at each stage condenser. The brine is finally heated to its terminal temperature by the heating steam in the brine heater, it then flows through a pressure reducing orifice into the first stage chamber of the evaporator and initial flash evaporation occurs. As the brine is still hot enough to boil again at a slightly lower pressure, it repeats the flashing process while passing through a series of inter-connected flash chambers, until it reaches the final stage.

The unflashed brine from the last stage is returned into the heat recovery section, but a portion is discharged as blow-down brine to maintain a constant concentration level. Make-up seawater feed from the heat rejection section is added in sufficient quantity in order to maintain a material balance in the evaporator. The brine recirculating cycle is completed and it goes on being repeated. In the heat rejection section, seawater is circulating inside the condenser tubes. The cooling seawater is used to reject or discharge heat which is equivalent to the amount of heat that was added in the brine heater so that a proper heat balance is maintained. The cooling seawater apart from a portion used as make-up feed water is discharged back to the sea.

The flashed vapour produced is salt free. However, the violent turbulence caused by the flashing process results in droplets of brine contaminating the upward moving vapour. Therefore, a demister is arranged to prevent these droplets from being carried out into the distillate tray. After the vapour passes through the demister, it comes into contact with the relatively cool tube bundle of the stage condensers where it condenses on the tube surfaces and drops into the distillate tray. In the process of condensing, the vapour releases its latent heat to the brine or seawater in the tubes. The distillate produced in each stage flows in cascade from the first stage to the last stage where it is finally collected.

Chlorination of the seawater is carried out at the intake system, this operation consists of both continuous dosing of 2 mg/l free chlorine in addition to frequent high rate shock dosing for short intervals. Chlorination is carried out in order to prevent marine fouling of the seawater intake system and the condenser tubes of the heat rejection section where seawater is flowing.

Before the introduction of the make-up feed into the flash chamber of the last stage, two different chemicals are injected. Firstly, about 1.5-2.5 mg/l of an anti-scalant additive is added in order to control the formation of scaling compounds (i.e $CaCO_3$ and $Mg(OH)_2$) inside the condenser tubes especially at the higher temperature end of the plant. The second addition constitutes the injection of about 0.07 mg/l of an anti-foaming agent in order to suppress foaming tendencies of seawater inside the flash chambers. Both these additives are organic compounds.

1.II. Distillate Blending and Treatment.

The production of the seawater distillation constitutes the first phase of potable water production in Kuwait.

The distilled water as produced has a dissolved solids content within the range of 3 to 30 mg/l depending on the design and performance of the plant. The distilled water is usually slightly acidic due to dissolved carbon dioxide, devoid of dissolved oxygen, insipid in taste, and tends to be aggressive. The pH of the distilled water is adjusted by injecting sodium hydroxide. This treatment gives the distillate a pH value of 8.0, but the water is still extremely low in solids content and tends to be tasteless and insipid.

The second phase involves the blending of the distillation product with about 4-12% by volume brackish water in order to make the water palatable and acceptable for human consumption. From a health point of view, blending distillate

with brackish water has certain limits. The international standards for drinking water state that the highest desirable level of chloride in potable water is 200 mg/l, and sulphate is also 200 mg/l. From the corrosion point of view, it is desirable to keep these constituents as low as possible.

The pH adjustment is carried out by the addition of sodium hydroxide, which is supplied in a liquid form of 50% concentration and stored in a concrete reservoir lined with stainless steel, and is diluted to 10% concentration before it is added to the distilled water. The dilution of sodium hydroxide is carried out in a concrete reservoir lined with stainless steel equipped with automatic pumps.

Chlorination is carried out by injecting chlorine gas, to prevent any biological activity inside the water distribution system. All of these processes are performed at the water blending plants, located in four locations:

- Shuwaikh.
- Doha (figure 3).
- Shuaiba (figure 4).
- Az-Zour (figure 5).

Corrosivity of the potable water produced by this process has been studied extensively by Abdel-Jawad *et. al.* 1981. Table (3) shows the corrosivity parameters of Kuwait's potable water. It can be seen that the concentrations of the carbonate and bicarbonate are low while of the sulphate is high. Due to this chemical unstability, the corrosion saturation index, known as Langelier Index, is negative and the Ryznar Stability Index is higher than 7. There is no initial excess of calcium carbonate to form scale protecting the inner layers of the water containers and the ratio of [chloride + sulphate]/alkalinity indicates a very corrosive quality of water.

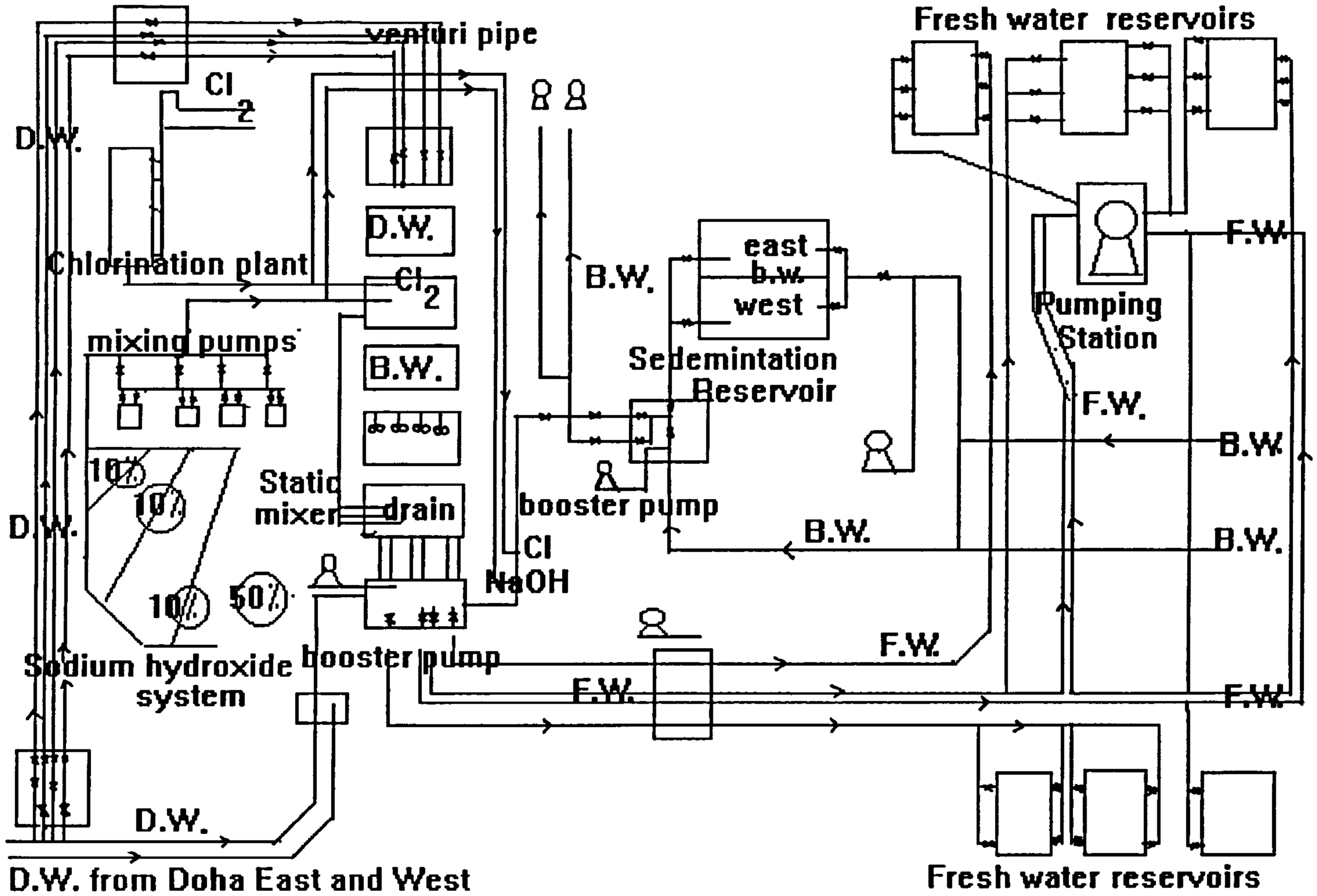

Fig. (3) Doha Blending Plant

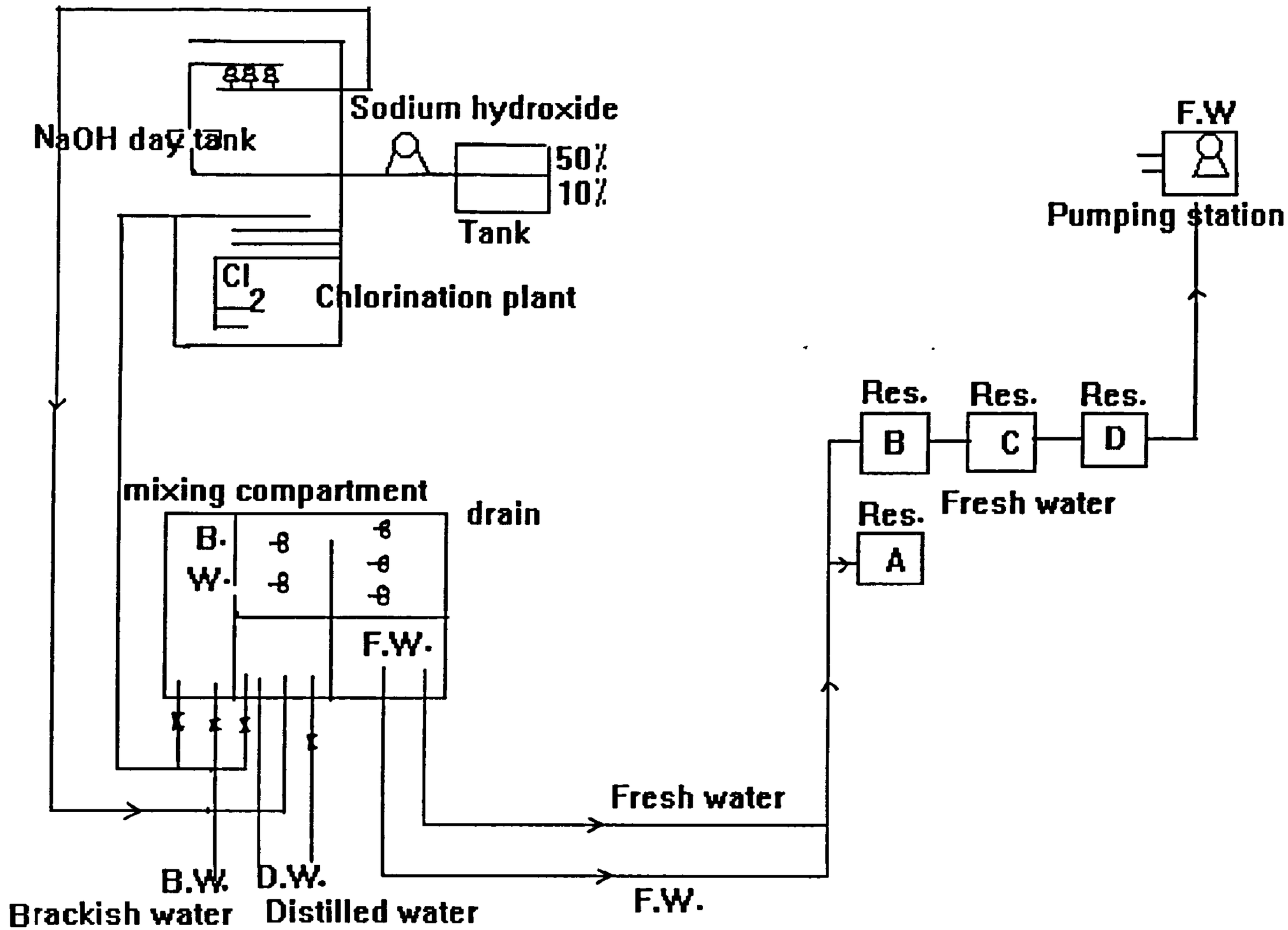

Fig. (4) Shuaiba Blending Plant

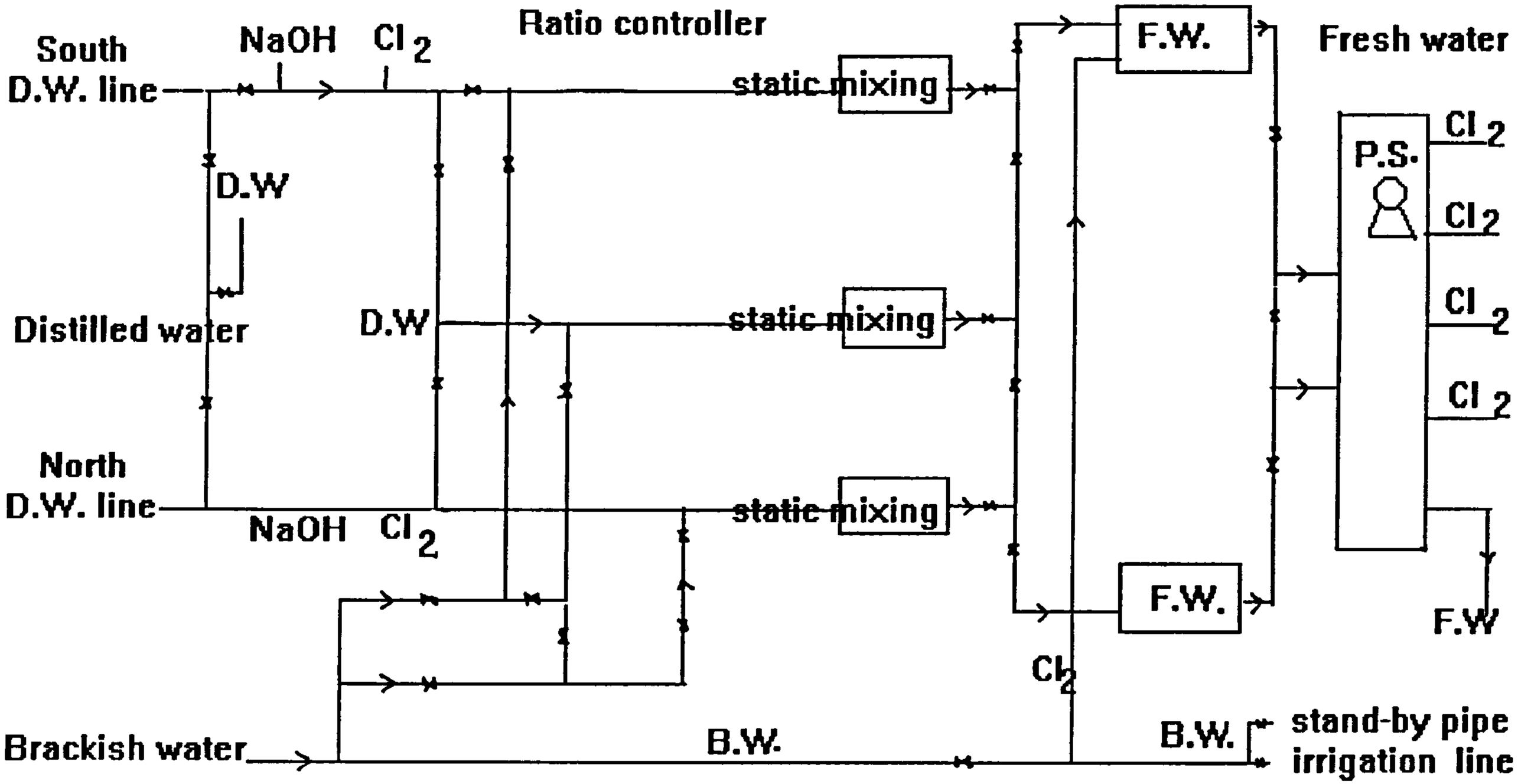

Fig. (5) AzZour Blending Plant.

Table (3)

Corrosivity of the potable water produced in Kuwait. *

Parameter	Actual Value	Recommended Value**
Ca, as $CaCO_3$ μg/ml	80	80
Alkalinity, as $CaCO_3$ μg/ml	20	60-100
Cl, μg/ml	70	<100
SO_4, μg/ml	124	<100
pH	8.1	8.2
pHs	8.29	-
Saturation Index	-0.18	>0.1
Ryznar Index	8.5	<7.0
Initial excess of $CaCO_3$, μg/ml	no excess	1-2
[Cl + SO_4] / Alk. μg/ml	11.4	0.1

* Results are based on 219 samples.

Abdel-Jawad, M. *et al*. (1981).

pHs = pH of saturation.

** Recommended value for scale formation and prevention of corrosion.

1.III. Power Generation and Distillation Production Stations.

Before 1990, there were six dual-purpose stations in Kuwait for the generation of power and production of distilled water. These stations are fully established and operational, while a seventh station is still in the planning stage.

These stations are:

1.III.1. Shuwaikh Power Generation and Water Production Station. Shuwaikh power generation and water production station was the first dual purpose plant (built in 1953), with a total installed distillation capacity of 32 MIGPD (MEW 1982).

1.III.2. Shuaiba North Power Generation and Water Production Station. 7 distillation units were commissioned as follows:
3 during 1965-1966, another 3 in 1968 and finally one unit commissioned in 1971. The total installed distillation capacity is 14 MIGPD.

After the Iraqi invasion of Kuwait (Aug 1990), the Shuwaikh and Shuaiba North power generation and water production stations are no longer in operation.

1.III.3. Shuaiba South Power Generation and Water Production Station. 6 distillation units commissioned during 1971-1975. The total installed distillation capacity is 30 MIGPD.

1.III.4. Doha East Power Generation and Water Production Station. 7 distillation units commissioned during 1978-1979. The total installed distillation capacity is 43 MIGPD (MEW 1985).

1.III.5. Doha West Power Generation and Water Production Station. The distillation plants were installed over two stages.
Stage I: 4 distillation units commissioned during 1983-1984.
Stage II: 12 distillation units commissioned during 1984-1985.
The total installed distillation capacity is 96 MIGPD.

1.III.6. Az-Zour South Power Generation and Water Production Station. 8 distillation units commissioned during 1988. The total installed distillation capacity is 48 MIGPD.

1.III.7. Sabiya Power Generation and Water Production Station. The new Sabyia station was designed to satisfy the increased demand for power and water in the 1990's, but is still in the preliminary and preparatory planning stage.

All these power generation and distillation stations are constructed near the sea for securing the necessary quantities of cooling water and feed water for distillate water production.

1.IV. Chemical Composition of Distillation Plant Components.

1.IV.1. Heat Exchanger Tubes. All tubes are made of a cupro-nickel alloy, with a chemical analysis of 66% copper, 30% nickel, 2% iron and 2% manganese. (The heat input section, heat rejection section, and in the first and second stages of heat recovery section). The condenser tubes in the remaining stages of the heat recovery section are made of aluminium brass with an analysis of 76% copper, 22% zinc and 2% aluminium (ASM 1979).

1.IV.2. Heat Exchanger Tube Plates and Supports. Tube plates of the brine heater are made of Naval Brass with chemical composition 60.5% copper, 1.0% tin, 0.2% lead, 38.7% zinc, 0.1% iron (ASM 1979).

1.IV.3. Distillation Ducts, Trays and Condenser Shell. The distillate ducts and trays, distillate transfer ducts and the condenser are made of 316L stainless steel with a chemical composition of 0.03% carbon, 17% chromium, 12% nickel, 2.5% molybdenum and iron as remainder (ASM 1979).

1.IV.4. Brine and Distillate Orifices and Weirs. The material used for the brine entry box in stage No.1 is carbon steel lined with 316L stainless steel or is wholly made of 316L stainless steel . The carbon steel chemical composition is <1.65% manganese, 0.06% silicon, 0.6% copper and iron as remainder.

1.IV.5. Demisters. The demister mesh and the supporting frames are manufactured from 316L stainless steel.

1.IV.6. Venting and Splashing Baffle Plates. Splashing baffle plates are made from 316L stainless steel.

1.IV.7. Flash Chambers. The evaporator shell and heat exchanger plates are made of low carbon steel having not more than 0.15% carbon content.

1.IV.8. Deaerator. The deaerator is made of steel material lined internally with 316 stainless steel with chemical composition 0.08% carbon, 17% chromium, 12% nickel, 2.5% molybdenum and iron as remainder (ASM 1979), and painted with a protective coating and is cathodically protected to guard against corrosion. The packing used is made from corrosion resistant material. The packing support structure

is made from 316L stainless steel and painted.

The make-up feed spray nozzles and the perforated cross pipe assembly used to inject the stripping steam is made from 316L stainless steel.

1.IV.9. Water Boxes. The water boxes are made of mild steel, the typical compositions are 0.05-0.1% carbon, 0.25-0.5% manganese, 0.035% phosphorus and 0.04% sulphur (ASM 1979).

1.IV.10. Brine Heater. The heater shell is made from mild steel, venting baffle plates are made of 316L stainless steel.

1.IV.11. Vent and Ejector Condensers. The shell of the condenser is made from 316L stainless steel. The tube plates are made of 70/30 copper.nickel, the chemical composition is 65-69% copper, 28-32% nickel, 0.5-1.5 niobium, 0.25-1.5% iron, 1.5% manganese, 0.5% silicon, 0.15% carbon and 0.03% lead (ASM 1979).

The water boxes are made from carbon steel clad with 90/10 copper.nickel, the chemical composition is 0.05% lead, 1-1.8% iron, 1.0% zinc, 1% manganese, 9-11% nickel and 88-92% copper (ASM 1979).

1.IV.12. Pumps. All parts of the seawater supply and recirculating pumps, brine recirculating and brine blow down pumps including casings, shafts, impellers... etc. are made from 316L stainless steel.

The brine recirculating pump barrel is made from mild steel(low carbon steel).

The casing of the distillate pump and heater condensate pump is made from zinc-free bronze and the shaft impeller and barrels...etc. are made from stainless steel. The chemical composition of bronze is 71% min copper, 11.0-14% manganese,

7.0-8.5% aluminium, 2.0-4.0% iron, 1.5-3.0% nickel and 0.1% max silicon. Any strainers are made from 316L stainless steel.

The bearings in pumps have 70/30 copper.nickel cooling coils and fittings.

1.IV.13. Piping. Seawater carrying pipes are made from carbon steel. Sections near the evaporator are made from 90/10 copper.nickel. Pipes with diameters of 50 mm and less are made from 90/10 copper.nickel.

Pipes carrying brine to/or from the unit are made from mild steel, piping for distillate service is made from 316L stainless steel.

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CHAPTER 2

TRACE METALS UNDER STUDY

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2. Trace Metals Under Study.

Although Kuwait lacks natural fresh water resources, it managed to meet almost all sectorial demands through the seawater desalination. Seawater, from the Gulf has the highest salinity in the world. Hence, it is expected to be more corrosive than other seawater. Its aggressivness is aggravated by the very high seawater temperature of around 35 °C, which yearly persists for six months. The product of distillation process, known as distillate, is even more corrosive than the seawater itself. It is very hungry water and has the tendency to dissolve/leach out ions from materials in contact with this type of water. Moreover, blending this water with brackish water, to produce potable water, does not satisfy the chemical balance required to render the blended water non-corrosive.

Knowing the characteristics of the water resources in Kuwait, materials of construction of the production, transmission, storage and distribution facilities and presence of oil near the ground water aquifers, the seawater feed to distillation plants, indicate potential presence of certain trace metals in Kuwait's fresh water supplies. Therefore, chromium, copper, iron, lead, manganese, nickel, vanadium and zinc are selected for this investigation.

2.1 CHROMIUM

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INTRODUCTION.

Elemental chromium does not occur in nature. The chief ore of chromium is chromite $FeOCr_2O_3$, a spinel with chromium (III) in tetrahedral sites [Cotton (1980)]. The naturally occurring ore is usually found with a certain percentage of the FeO replaced with MgO [N.A.Sc. (1974)]. The average concentration of chromium is 100 mg/l in crustal rock, 0.03 mg/l in seawater. Other references state the background chromium level in seawater to be less than 1 μg/l or in the range between 0.2-0.7 μg/l, 1.0 μg/l in stream waters, 0.23 μg/l in land plants and 1.0 μg in marine plants [Mason (1982)]. Drinking water contains 0.3-0.45 μg/l. Virtually all foods and beverages contain chromium in varying amounts (30-100 ng Cr/g wet weight). The U.S. Food and Nutrition Board has recommended a safe and adequate dietary intake of 50-200 μg chromium/day, based on epidemiological data of average intake among populations lacking any signs of chromium deficiency [N.R.C. (1980)].

I. CHEMICAL PROPERTIES.

Chromium can exist in formal oxidation states -2 to +6 [Cotton (1980)]. The low formal oxidation states (-2 to 0) are found mainly in carbonyl and organometallic compounds.

The most stable oxidation states of chromium are +2, +3, and +6 [Cotton (1980)]. Chromium (II) is a strong reducing agent in aqueous solution and is not stable in aerobic systems since it is labile and rapidly oxidized to chromium (III) by air. Thus, chromium (III) and chromium VI) are the oxidation states found in nature. Chromium (V) and chromium (IV) species are generally unstable due to their reactivity and kinetic lability [Mitewa (1985), Beattie (1972)]. Although chromium is soluble in non-oxidizing acids such as hydrochloric and sulphuric acids, it is passivated by nitric acid and aqua regia [Cotton (1980), N.A.Sc. (1974)].

I.1. Chromium (VI).

Chromium (VI) exists only in oxo species such as chromium (VI) oxide (chromic acid CrO_3), chromyl chloride (CrO_2Cl_2), chlorochromate (CrO_3Cl^-), chromate (CrO_4^{2-}). Chromyl chloride and chlorochromate are hydrolyzed by water to chromate and hydrochloric acid. In aqueous solution the form of chromium (VI) depends on the concentration and pH of the solution, subject to the following equilibria [Cotton (1980)]:

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Thus, at physiological pH chromium (VI) exists mainly as the tetrahedral chromate ion.

Chromium (VI) compounds are strongly oxidizing under acidic (pH = 0) conditions [Cotton (1980)]:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$$

Chromium (VI) is much less oxidizing under basic (pH = 14) conditions where it exists as chromate [Cotton (1980)]:

$$CrO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Cr(OH)_3(s) + 5OH^-$$

I.2. Chromium (III).

Chromium (III) forms six-coordinate octahedral complexes with a variety of ligands and can exist as cationic and anionic complexes. Depending on the number and charge of ligands attached, these complexes are relatively inert to substitution [Cotton (1980)].

II. TECHNOLOGY.

The major industries producing occupational exposure to chromium are stainless steel welding, chromate production, chrome plating, ferrochrome production, leather tanning, and industries concerned with printing, dyes, pigments, primer paints, wood preservatives, bleaches, detergents and many others. The average airborne concentration of chromium (VI) in fumes and dust in these industries ranges from 5 to 1000 μg/l [Stern (1982)].

Chromium has been used extensively in research and medicine. Chromium (VI) is readily taken up by erythrocytes, where it becomes specially bonded to haemoglobin. This has allowed researchers to measure total blood volume, erythrocyte turnover, and splenic function, and labelled cells have been used to detect gastrointestinal bleeding. In addition, labelling of other specific cell populations, (e.g., leucocytes, blood platelets, liver cells, and parasitic micro organisms), has enabled researchers to study the distribution and function of these cells *invivo* [Sanderson (1982)]. Chromium alloys are used in joint replacement prostheses.

III. PHYSIOLOGY.

III.1. Uptake and Distribution.

Chromium is distributed approximately equally among human tissue. The three principal routes of exposure are through the lungs, gastrointestinal tract, and skin. In the absence of industrial exposure, the main uptake of chromium is absorption from food and water by the gastrointestinal tract. It has been estimated that 1% of the chromium content of the diet is absorbed [Guthrie (1982), Langard (1982)]. The experimental studies found that chromium (VI) is taken up much more readily than chromium (III). By oral administration approximately 10% of the dose of chromium (VI) is absorbed, whereas less than 0.5% of the chromium (III) dose is absorbed [Langard (1982)], and both are distributed throughout the body

with highest concentrations in liver, kidney, and lungs.

III.2. Metabolism.

Metabolism of chromium (VI) involves cellular reduction of chromium (VI) by small molecules and enzyme systems, a process which generates reactive intermediates and chromium (III) [Connett (1983)]. The metabolites ultimately bind to cellular constituents and may result in impairment of their normal function in the cell.

III.3. Excretion.

In oral and intravenous uptake chromium is excreted principally in urine and the studies found that 80% of the chromium (VI) dose was recovered in urine in 4 days [Langard (1982), Love (1983)]. Long exposure or high concentrations of chromium (VI) cause tabular necrosis. Normal urinary loss of chromium is approximately 0.5-2.0 μg/day, with an average urine concentration of 1 ng/ml [Guthrie (1982)].

IV. TOXICITY.

IV.1. Mutagenicity and Genotoxicity.

Chromium (III) has been shown to interact with DNA and can inhibit DNA and RNA transcription *invitro* systems, while chromium (VI) was in active *invitro* in the absence of a reduction system. The genotoxicity data all support the hypothesis that chromium (VI) is not genotoxic per se but that chromium genotoxicity is mediated by the intracellular reduction of chromium (VI) to chromium (III), which is the ultimate genotoxic form of chromium. Chromium (III) does not induce DNA damage even through it binds to DNA *invitro* and *invivo*. It has therefore been suggested that reactive intermediates, for example chromium (V) or chromium (IV), mediate chromium induced DNA damage during the reduction of chromium (VI) to chromium (III) [Cupo (1985), Wetterhahn *et al*. (1984)].

IV.2. Teratogenicity.

Teratogenicity means tending to cause developmental mal production of monstrous growths or foetuses formation and monstrosities. There are several studies which indicate that chromium is teratogenic in animals. Chromium (VI) compounds have been shown to cross the placenta [Langard (1982)] and to induce neural tube defects and lethality in mice [Iijima (1983)], cleft palates and lethality in hamsters [Gale (1979)], and a variety of abnormalities in chick embryos [Ridgeway (1952), Gilani (1979)]. Chromium compounds may therefore pose a teratogenic hazard to women of childbearing age who are occupationally exposed.

IV.3. Carcinogenicity.

Chromium (VI) compounds induce cancer in experimental animals at the site of exposure, while chromium (III) compounds are inactive. There is no evidence for an increased risk of skin cancer in humans.

IV.4. Skin Lesion and Contact Dermatitis.

Exposure to chromium through inhalation can lead to nasal ulcers and perforation of the nasal septum. Topical exposure of exposed skin can lead to lesions which can develop into deep ulcers "**chrome holes**" without treatment [Pederson (1982), Burrows (1983)]. Chromium in such diverse products as leather, cement, brewery yeast, wood preservatives, priming paint, glue, and paint pigments my cause contact dermatitis [Pederson (1982), Polak (1983)].

IV.5. Organ Toxicity.

In animal studies, chronic exposures to chromium have also produced myocardial damage, testicular damage and loss of spermatogenesis, and general vascular damage throughout the body [Tandon (1982)].

V. LEVEL OF TOLERANCE.

U.S. National Institute for Occupational Safety and Health (NIOSH) present standards (mg/l) are as follows: Chromium metal, 1.0; chromium (III) compounds, 0.5; water-soluble chromium (VI) compounds, 1.0. NIOSH recognized only insoluble chromium (VI) compounds as posing a carcinogenic hazard, and has recommended the reduction of limits on soluble and insoluble chromium (VI) compounds to 0.025 and 0.001, respectively, with a ceiling of 0.05 mg Cr / l averaged over a 15 min period [Mackison (1981)]. European countries have recommended a level of 0.1 and 0.02-0.05 mg/l for chromium (III) and (VI) compounds, respectively [WHO (1984)].

IV. STANDARD METHODS OF MEASUREMENT.

Flameless atomic absorption spectroscopy, inductively coupled plasma emission spectroscopy, and neutron activation analysis are widely used in the determination of chromium in environmental samples.

VII. SOURCE OF CHROMIUM POLLUTION OF SEAWATER IN KUWAIT.

Water effluent of the following industries and activities comprise the contributions to seawater pollution by chromium in Kuwait:

- Petrochemical industries as :
  Chromium compounds are added to sea cooling water to prevent equipment corrosion.
- Paint manufacture and painting activities.
- Electroplating activities.

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2.2 COPPER

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INTRODUCTION.

Copper, besides silver and gold is the metal longest used by man, and is completely miscible with gold. The most used alloys of copper are bronze (copper-tin) and brass (copper-zinc). Copper is widely distributed in nature in the elemental state, in sulfides, arsenites, chlorides, and carbonates. The element is oxidized in air sometimes giving a green coating of hydroxy carbonate and hydroxy sulfate. The concentration of copper in sandstones is 10-40 mg/l, shales is 30-150 mg/l, and marine black shales is 20-300 mg/l, in the continental crust estimated at 50 mg/l. Coal is relatively low in copper. More than 99.9% of copper carried to the ocean is precipitated mostly with clays and partially with manganese oxides.

I. CHEMICAL PROPERTIES.

Copper is a tough, soft and ductile reddish metal, with a high thermal and electrical conductivity second only to silver. Copper (II) is the most important form of copper. There is a large number of salts of various anions, many of which are water-soluble, in addition to a variety of complexes. With the d^9 electronic configuration, cupric compounds are normally paramagnetic with a single unpaired electron. Virtually all complexes and compounds of copper (II) are blue or green. Verdigris, the basic acetate of copper (II), is toxic. The copper (I) ion has the electronic structure $3d^{10}$ so that its compounds are diamagnetic and colourless except where colour results from the anion or charge-transfer bands. Tetrahedral coordination dominates though two and three coordination also occur. The coordination number rarely exceeds four although five coordination is known [Grane (1976)].

Copper (III) can occur in crystalline compounds and in complexes. Copper (III) with a d^8 shell is isoelectronic with

nickel (II). Many trivalent copper (III) peptide complexes have relatively long life-times in aqueous solution [Rybka (1980)].

II. TECHNOLOGY.

II.1. Uses.

The metal has a widespread use for kitchen utensils, as thermal and electric conductors, and in sanitation.

Copper solutions are used in various processes such as electroplating, printed circuit production, textile production, and as a catalyst in various chemical processes. Sprays containing copper sulfate are sometimes used in agriculture (vineyards).

II.2. Nutrient supplement.

Copper is an essential trace element, and almost every diet supplies a relatively large amount (10 mg or more) of the metal for body needs [Scheinberg (1960)]. The recommended daily allowance for adults is 2 mg. Indeed, it is difficult to prepare an acceptable diet that contains less than 2 mg copper daily.

II.3. Indication of Potential Danger.

Oral administration of copper above 15 mg causes nausea, vomiting, diarrhea, and intestinal cramp (this is caused by damage to the gastrointestinal system). Copper in dust, fumes, or sprays causes congestion of the nasal membrane. Various damage to lung tissue has been reported in cases of severe intoxication after exposure to copper sulfate sprays. Exposure to copper dust causes intoxication, haemolytic anaemia and death may follow. Liver and kidney functions may be disrupted giving rise to jaundice and cirrhosis.

III. PHYSIOLOGY.

III.1. Intake and Absorption.

A single day's diet may contain 10 mg or more copper. Studies indicate that about half of dietary copper is not

absorbed but rather excreted in the faeces. The mechanisms by which copper is absorbed and transported by the intestine are unclear [Sarkar (1987)]. Radioactive copper given by mouth to human subjects appears very rapidly in the blood. Copper is absorbed and transported in plasma bound to albumin [Bearn (1955)] and to amino acid [Sarkar (1966), Neumann (1957)].

III.2. Target Organs.

Copper is primarily accumulated in the liver, then accumulates in the kidney, brain, cornea and spleen.

III.3 Copper Related Diseases.

III.3.1. *Wilson's Disease.*

This disease is a genetic defect of metabolism characterized by severe progressive liver disease, a peculiar neurological syndrome and the presence of **Kayser-Fleisher** rings of the cornea [Wilson (1974)]. The disease is inherited in an autosomal recessive fashion. Patients with symptomatic Wilson's disease usually excrete more than 100 μg copper in 24 hr urine compared to less than 50 μg per 24 hr urine in normal individuals [Sarkar (1987)].

Faecal and serum copper levels are found to be below normal levels in most patients with Wilson's Disease.

Wilson's Disease is apparently synonymous with copper toxicity.

III.3.2. *Menkes' Disease.*

Menkes and coworkers [Menkes *et al.* (1962)] reported a new X-linked genetic disorder characterized by rapidly progressive cerebral degeneration and the presence of spirally twisted hair. Menkes' disease shows that copper is probably available but is not utilized in a normal manner. Copper ions react with the crystalline lens of the eye causing blindness.

III.4. Toxic Interaction with Other Metals.

Evidence exists that copper and molybdenum form an *invivo* complex. These two metals interact, especially in ruminants,

with inorganic sulfate in the diet affecting biliary and urinary excretion of copper and molybdenum [Todd (1969)].

Zinc and iron affect copper metabolism in nonruminant animals. Both metals protect swine from the adverse effect of high levels of dietary copper, and deficiencies of zinc and iron tend to intensify copper toxicosis in swine.

III.5. Delayed Risks of Chronic Copper Toxicity.

Copper accumulates in the liver when the excretory capacity of the liver cell is exceeded. There is an increase in the hepatic copper concentration if there is bile duct obstruction [Worwood (1969)]. In patients with Wilson's disease and in sheep with chronic copper toxicosis massive or submissive necrosis of the liver can free large enough amounts of copper in a sufficiently short time to cause considerable hemolysis [Days *et al*. (1970)]. In long-term copper toxicity, both brain and kidney are also affected.

IV. LEVELS OF TOLERANCE.

The U.S. Occupational Safety and Health Administration has adopted standards for exposure to airborne copper at work. The time weighted average for 8hr daily exposure to copper dust is limited to 1.0 mg/l air.

V. STANDARD METHODS OF MEASUREMENT.

Atomic absorption spectroscopy methodology is used frequently to estimate copper in water samples. For the analysis by this technique the optimal concentration range is 0.1-10 mg/l, the wavelength is 324.7 nm and the sensitivity is 0.04 mg/l for 1% absorption. The other techniques available for determining copper in aqueous solution or suspension include spectrophotometry, polarography, and anodic stripping voltammetry.

VI. SOURCES OF COPPER POLLUTION OF SEAWATER IN KUWAIT.

- The power generation and water production stations are the most important source of seawater pollution with copper.
- The water effluent of the petroleum refinery.
- The waste water when it is discharged to the sea.

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2.3 IRON

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INTRODUCTION.

Iron is an objectionable constituent in water supplies for domestic or industrial use. It is an important component of many soils where its concentration ranges from 7 to 550 mg/g [Bowen (1966)]. Especially in clay soils it is a major constituent, and the use of iron-containing fertilizers and fungicides contributes to iron concentrations in soil and run-off waters. Iron in water may be present in varying quantities depending upon the geology of the area and other chemical components of the water-way.

The principal inorganic iron compounds are ferrous (+2) or ferric (+3) oxides, carbonates, disulphides, sulphates, and chlorides, also iron forms iron pentacarbonyl ($Fe(CO)_5$). Other forms may be present in waste water streams as organometallic or humic compounds.

I. CHEMICAL PROPERTIES.

Iron is one of the most magnetic elements. The structural changes undergone by iron when heated or mixed with substances such as coal, phosphate, silica, sulphur, nickel, chromium, tungsten, molybdenum, or vanadium are fundamentally important for ferrous metallurgy.

II. TECHNOLOGY.

II.1. Uses.

Abundant iron-containing minerals are hematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($Fe_2O_3.H_2O$) and siderite ($FeCO_3$) which are obtained from iron mining. Iron pyrites (FeS_2) is mined as a sulphur rather than an iron mineral.

Iron and steel products are used in construction of bridges, ships, highways, and buildings, and in production of transportation vehicles and armaments. Important applications of iron compounds which constitute less than 1% of total iron consumption, include the following: as dyes in blue print photography (ferric ammonium acetate); as dyeing mordants (ferric nitrate, ferrous chloride); as intermediates in

organic synthesis (iron carbonyl); in sewage and water treatment (ferric chloride); as red pigments for rubber, paints, linoleum, (ferric oxide); as smoke inhibitors and in the manufacture of integrated circuits (ferrocene; di-2,4-cyclopentadien-1-yl iron, $Fe(C_5H_5)_2$); and in medicinal preparations.

Iron oxides are used as food-colouring agents. Ferric phosphate and pyrophosphate, ferrous gluconate, lactate, and sulphate, and reduced iron are classified as Generally Recognized as Safe (GRAS) substances for use as food ingredients in the United State [O.F.R.(1985) a].

III. PHYSIOLOGY.

III.1. Toxicity.

Iron is potentially toxic in all forms and all routes of exposure [Elinder (1979)]. In general, ferrous compounds are more toxic than ferric compounds. Iron pentacarbonyl is highly toxic, probably due to the potential for release of carbon monoxide [NIOSH (1977)]. Pulmonary exposure to iron, primarily as the oxides may occur during mining of iron ores, steel making, arc, welding, and metal polishing. Direct exposure to iron oxides is a serious risk, whenever these compounds are produced or used [Elinder (1979)].

Ferbam, the iron salt of dimethyldithiocarbamic acid, is widely used as an organic fungicide. The dithiocarbamate moiety may be the toxic component of the compound [Lee *et al.* (1978)].

III.2. Effect of Intoxication.

Prolonged iron loading by any route can give rise to pathological deposition of iron in tissues, which may be associated with fibrosis of the pancreas, diabetes mellitus, and liver cirrhosis [Roe (1966), Jacobs (1977)].

Intoxication in children has been reported after ingestion of 0.5 g or more of iron (about 2.5 g as ferrous sulphate). Vomitus frequently is bloody and stool turns black

due to blood loss from ulcerated gastrointestinal mucosa and the formation of iron sulphide. Patients may show signs of shock and metabolic acidosis. Late effects may induce renal failure, hepatic necrosis, and gastric and pyloric scarring.

Intramuscular injections of iron dextran have led to severe, sometimes fatal anaphylactic reaction [Marrow (1973)]. An association between intramuscular injection of iron dextran and *Eshreichia Coli* species has been reported in neonates (newly born children).

In humans, exposures to excessive amount of ferrous compounds are associated with kidney and liver damage.

III.3. Intake and Deficiency.

The daily intake of iron varies widely with the total amount of food consumed and the proportions of iron-rich and iron poor foods. Percentages of the U.S. Recommended Daily Allowances (18 mg Fe/day for adults) [O.F.R. (1985) b] supplied by single servings of various foods such as beef liver 42% beef kidney 22% cooked soybeans 14%. A typical European or North American diet provides about 6 mg Fe/1000 kcal; reported daily intake range from 9-36 mg Fe [Underwood (1977)].

Insufficient dietary intake and iron losses that exceed iron intake are the commonest causes of iron deficiency. Marked reduction in body stores of iron, anaemia, deficits in physical and mental performance and a number of immunological abnormalities are among the adverse effects. Increases in the artificial fortification of food with iron have been recommended to prevent iron deficiency in susceptible populations.

III.4. Target Organs.

The normal adult body contains about 3-5 g of iron, two-thirds of which is found in haemoglobin in the blood. Less than 10% of the body iron is found in myoglobin and iron-containing enzymes. About 20-30% of the body iron pool is bound in the storage proteins ferritin (water-soluble) and

hemosiderin (water-insoluble). These proteins are found primarily in the liver, bone marrow, and spleen, followed by kidney, heart, and skeletal muscle [Gubler (1956), Underwood (1977), Drabkin (1951), McDonald (1971)]. Excess iron accumulates in the lung, spleen, pancreas, and heart muscle, primarily as hemosiderin.

IV. STANDARD METHODS OF MEASUREMENT.

Care must be taken during collection to avoid contamination of samples with iron. All laboratory vessels, glassware and plasticware containers used in iron determinations should be soaked in 20% nitric acid for 48 hr or chelating detergent solutions and rinsed in double distilled water before use.

Direct analysis methods offer significant improvements in determination limits relative to colorimetric methods but may be subject to non-specific interferences generated by the matrix. Flame or flameless atomic absorption, inductively coupled plasma emission, inductively coupled plasma mass spectroscopy, differential pulse voltammetry with carbon paste electrodes have been used for the determination of iron [Gao *et al.* (1991)].

Liquid-liquid extraction and chelating resin may serve as dual purpose:

- Preconcentrating low levels of iron.
- Overcoming matrix interferences.

V. SOURCE OF IRON POLLUTION OF SEAWATER IN KUWAIT.

The following are the principal sources:

A. Seawater

- Occasional sewage disposal: treated sewage contains 0.17 mg iron/L [MEW (1980)].
- Ballast water of oil tankers contain rust due to corrosion of the ship's reservoir.

B. Potable Water

- Corrosion of galvanized pipelines of the potable water distribution system.

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2.4 LEAD

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INTRODUCTION.

Lead is the most abundant of the natural heavy elements. The primary form of lead in nature is galena (lead sulphide PbS), relatively insoluble ore. Lead also occurs as plattnerite (lead oxide PbO_2), cerussite (lead carbonate $PbCO_3$), and anglesite (lead sulphate $PbSO_4$) [Zimdahl and Hassett (1977)]. Lead is one of the oldest metals known to man and one of the most useful metals, because of its physical properties, malleability, and resistance to corrosion as well as its abundance.

The major source of lead in the environment is mining, smelting and refining, manufacturing processes. Lead is transported and distributed via air, and deposited on soil surfaces [Goyer (1988)].

The concentration of lead in deep ocean water is about 0.01-0.02 μg/l, in surface ocean water 0.3 μg/l and the concentration of soluble lead in uncontaminated fresh waters is generally less than 3 μg/l [Forster and Wittman (1979)].

I. CHEMICAL PROPERTIES.

Lead is a bluish or silver-grey soft metal. The oxidation states 0, +2 and +4 are possible. However, Pb (IV) exists only in extremely oxidizing conditions not usually found with the ranges of environmental pH conditions [Cotton and Wilkinson (1972)].

Lead is complexed by both inorganic (e.g. OH^-, CO_3^{2-}, Cl^-) and organic (e.g. humic and fulvic acid) ligands present in aquatic systems. Lead II forms strong complexes with OH^- and CO_3^{2-} and relatively weak complexes with Cl^- and other common inorganic ligands. However, in systems with very high Cl^- concentrations such as estuaries and sea water, $PbCl^+$ is the dominant species.

The inorganic salts of lead, lead sulphide and oxides of lead are generally poorly soluble in water. Lead perchlorate (450 g/100 ml H_2O) and lead acetate (44 g/100 ml H_2O) are the most soluble common forms of lead, the nitrate, chlorate, and

to a lesser degree the chloride are less soluble in descending order [Goyer (1988)].

Lead also forms stable organic compounds tetraethyllead and tetramethyllead, both are volatile and poorly soluble in water [Goyer (1988)]. Trialkyllead compounds are formed in the environment by the breakdown of tetraalkylleads. These trialkyl compounds are less volatile and more readily soluble in water [W.H.O. (1989)].

Humic matter and fulvic acid in natural environments also form complexes with Pb II, these complexes are stable at pH values between 4 and 6 [Saar and Weber (1980)].

II. TECHNOLOGY.

II.1. Uses.

The main uses of lead are in lead acid storage batteries and antiknock gasoline additives. In batteries, the main form of lead used is lead metal and lead oxides. Tetraethyl and tetramethyl lead are also used in antiknock gasoline, solder, weights and ballast, pigments, cable covering, sheet lead, bearing metals, caulking metals, pipes and type metal [Perwak *et al.* (1980)].

These uses have been influenced in recent years by substitution with alternative materials and new technologies as well as the awareness of environmental and health effects of lead.

III. PHYSIOLOGY

III.1. Intake, Absorption, and Excretion.

Atmospheric lead and lead in food are the two major routes of exposure for people in the general population. Atmospheric lead is largely in the form of dust or particles of lead oxide.

Absorption by the lungs is dependent on size distribution of lead-containing particles and volume of air respired per day [Nozaki (1966)].

Gastrointestinal absorption of lead is influenced by a large number of factors, particularly age and nutrition.

Adults absorb about 5-15% of ingested lead and retain less than 5% [Rabinowitz *et al.* (1974)]. Alexander *et al.* (1974) found that children between 3 months and 8 years absorb 50% more of ingested lead, and Ziegler *et al.* (1978) found that infants 14-746 days of age with daily lead intake of 5 μg/kg/day absorbed 41.5% and net retention averaged 31.8% of intake. Dietary lipids, certain milk components, particularly lactose increase absorption of lead. Low dietary calcium and phosphate and deficiencies of other essential minerals, including zinc and copper, may also enhance gastrointestinal absorption of lead [Mahaffey and Michaelson (1980)].

III.1.1. Lead in Blood. More than 95% of lead in blood is associated with red blood cells, associated with the membrane of the cell, and the other with red cell proteins, particularly haemoglobin. Plasma lead is mostly bound to albumin.

The relationship of dietary lead intake to blood lead indicate a range of 5.4-18.3 μg/dl for men and 4.4-13 μg/dl for women per 100 μg dietary lead intake per day [W.H.O. (1977)]. Whole-blood lead has a biological half-life of 25-28 years.

III.1.2. Lead in Tissue. The highest concentration of lead occurs in bone where the major fraction is bound in a non diffusible form. This fraction of bone lead may have a biological half-life of greater than 20 years. However, this pool equilibrates with bound blood lead in less than a day, so that bone lead may contribute to the persistence of blood lead levels in persons with excessive exposure for years after exposure ceases.

Only the diffusible lead fraction from plasma passes in and out of capillaries, permeates cell membranes, and enters parenchymal cells of the central nervous system, liver, kidney, and other organs. The relatively large content of lead in liver and kidney may be related to the excretory function of these two organs, whereas only trace amounts of

lead are present in muscle and brain. Lead in teeth increases with age and is proportional to blood lead.

III.1.3. Toxicity. The symptoms of lead poisoning were noted by Greek, Roman, and Arabian physicians long before they were ascribed to lead [Hunter (1978)].

The clinical signs and symptoms of lead toxicity were documented by occupational health physicians. Nonspecific symptoms and signs include loss of appetite, metallic taste in the mouth, constipation, pallor (from anaemia), malaise, weakness, insomnia, headache, irritability, muscle and joint pains, fine tremors, and colic. Lead lines (Burton's lines) or purple-blue discolouration of gingiva is a classical feature of severe lead toxicity in children with lead encephalopathy.

Lead toxicity effects involve the nervous system, heamalogic effects, and renal effects, effects on male reproductive organs and possibly the immune system.

Toxicity of inorganic lead salts is attributable to lead per se and the chemical form of the salt is of significance only in that it influences solubility and bioavailability.

Toxicity of organolead compounds may result from occupational exposure and abusive use of leaded gasoline such as "sniffing" for hallucinogenic effects.

III.1.4. Essentiality of Lead. The toxicity of a metal does not mitigate against its potential essentiality. The possibility of lead essentiality was studied by Schwarz (1977) who had found that rats fed diets containing 0.2 μg/ml lead did not grow well and that the addition of 1.0-2.5 μg/ml to the diet led to a positive growth response.

Kirchgessner and Reichmayr-Lais (1981) found that lead deprivation in rats depressed growth, hematocrit, and haemoglobin in rats and interpreted these findings as evidence that lead is an essential metal. However, further studies by Uthus and coworkers (1985) have shown that relatively low dietary lead can in fact alter iron metabolism in young rats,

which may explain the effects of lead deprivation.

Lead has been shown to interact with essential metals, particularly calcium, iron, and zinc. Studies show that there is a metabolic relationship between lead and calcium, animals maintained on low calcium diet (0.03%) exhibit decreased rather than increased lead absorption [Geerber and Deroo (1975)].

Calcium (0.1%) also increase the proportion of body lead found in soft tissues [Six and Goyer (1970)].

Iron deficiency appears to enhance the intestinal absorption of lead in rats [Six and Goyer (1972)]. In children there is a negative correlation between blood lead and serum iron levels [Delves *et al*. (1973)]. Iron-deficient adults may absorb about 24% of dietary lead instead of the normal level of 10% [Watson *et al*. (1980)]. Urinary excretion of zinc metal is influenced by a wide range of blood lead levels. Lead inhibits zinc-containing enzymes in haem synthesis [Willoughby *et al*. (1972)]. Copper deficiency enhances lead accumulation in liver and kidney [Petering (1974)].

IV. LEVELS OF TOLERANCE.

Gastrointestinal colic is usually not seen unless the exposure to lead is extreme, i.e. producing a blood lead level over 80 μg/dl. Severity of anaemia also depends on intensity and duration of exposure. In adults, lead-induced renal disease is commonly discovered after many years of exposure and often is diagnosed as chronic interstitial nephropathy. Oligospermia and possibly morphological aberrations in sperm have been noted at blood lead levels near 40 μg/dl. Subclinical effects on heme enzymes, particularly inhibition of δ-aminolevulinic acid dehydratase (ALA-D), occurs at blood levels as low as 20 μg/dl.

Children are less tolerant to lead than adults, particularly central nervous system effects and effects on heme synthesis. Inhibition of ALA-D and pyridine-5-nucleosidase occurs in children with blood lead levels as low

as 10 μg/dl.

The foetuses have higher risk of toxicity to lead than other people, particularly effects on the developing nervous system [Goyer (1988)].

V. LEAD IN THE ENVIRONMENT.

Atmospheric particles are composed of a wide variety of compounds depending on their source. These include crustal material (silicon dioxide and calcium salts), heavy metals (lead, chromium, arsenic, vanadium and selenium), carbonaceous compounds (elemental carbon and many organic compounds), water and inorganic electrolytes (acidic and hygroscopic) [Johnston and Wexler (1995)].

Lead as a pollutant has assumed particular importance due to its relatively high toxicity to humans, especially brain retardation in children.

Anthropogenic activities are responsible for most of the lead pollution [Scoullos (1986)]. Combustion of oil and gasoline alone accounts for 50% of all anthropogenic emissions and thus constitutes a major component of the global cycle of lead.

Air: For persons in the general population, exposure to lead occurs from inhaled air, dusts of various types, and food and water. Additional exposures may be related to particular environments (urban), occupational sources, and certain habits and activities such as pica in toddlers. Concentration of lead in air varies greatly in different parts of the world and is generally between 0.3 and 1.1 μg/l for urban areas and about 0.15-0.3 μg/l in rural areas [Goyer (1988)].

Soil: Lead in surface soil is influenced by atmospheric lead, proximity to road-sides and other emission sources, air lead deposited on soil surfaces mostly complexes with humic substances and dissolves in soil moisture. Lead in soil may be present as primary inorganic compounds, associated with humic substances, complexed with iron-manganese oxide films, and in soil moisture. Lead in primary minerals is natural and is tightly bound within the crystalline structure of the

minerals and is only slowly leached to surface soil. Concentrations in natural soil typically range from 10 to 30 μg/g but the upper layer of soil along roadsides may contain 30-2000 μg/g of lead within 25 m of the road due to automobile emissions [Goyer (1988)].

Water: Lead occurs in water in either dissolved or particulate form. The most important factors determining lead concentrations in water are the pH and hardness of the water and stream flow. At low pH, lead is dissolved from sediments and particles. Chemical treatment to soften water increases the solubility of lead, increasing lead uptake from distribution systems. Lead in ground water, the geochemical composition of the water bearing bedrock is the most important factor, so that well water is little influenced by acid rain, surface runoff, or deposition of rainborne lead.

Food: Lead in food is derived from root absorption from soil, and atmospheric deposition on above-ground parts. About 90% of lead in food is derived directly or indirectly from atmospheric deposition, so that the lowest possible consumption of dietary lead is probably in the order of 10-15 μg/day. Several studies report average dietary lead intake from 100 to 500 μg/day for adults [Elias (1985)]. Lead may enter food in all steps of transport and processing including packaging and preparation.

VI. STANDARD METHODS OF MEASUREMENT.

For collection of water samples particular attention must be given to avoid contamination and obtaining a sample that is representative of the source to be analyzed.

The sample should be acidified and stored at room temperature; long term samples should be stored at 4°C.

Atomic absorption spectroscopy (AAS) is the most popular method for routine determination. There are a variety of specific methods depending on the instrument to be used and method of sample preparation. Graphite furnace (GFAAS) provides high sensitivity as well as the ability to measure small samples. Anodic stripping voltammetry (ASV) is the most

sensitive analytical method for the determination of lead in biological material. X-ray fluorescence is attractive for certain uses because it is nondestructive and allows simultaneous identification of several elements using a high-energy irradiation source. Inductively coupled plasma-mass spectroscopy is a sensitive analytical method. It should be pointed out that all of the methods mentioned only measure total lead and not identify specific compounds of lead.

VII. SOURCE OF LEAD POLLUTION OF SEAWATER IN KUWAIT.

In Kuwait leaded petrol is used as fuel for motor cars, and many activities such as manufacturing of dry batteries, petrochemical industries, ship building and mending and sewage effluents.

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2.5 MANGANESE

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INTRODUCTION.

Manganese as an essential nutritional element, is found in every kind of plant and animal. Manganese is widely distributed in the earth's crust [NAS (1973)], where it is the twelfth most abundant element. It constitutes approximately 0.10% of the earth crust. The chemical forms of manganese in natural deposits include oxides, sulphides, carbonates, and silicates. Manganese is a minor element in seawater, its concentration in the open ocean is 2 μg/l, the limit for manganese in drinking water is 0.05 mg/l [EPA (1976)]. The most important commercial source is pyrolusite (β-MnO_2). Other important minerals are manganite (γ-MnOOH), hausmannite (Mn_3O_4), and rhodochrosite ($MnCO_3$).

I. CHEMICAL PROPERTIES.

Manganese can exist in 11 oxidation states from -3 to +7 [Reides (1981)]. The most common valences are +2, +4, and +7. The +2 valence is found in most biological systems, Mn (II) is a very poor reducing agent and is resistant to oxidation in neutral or acidic solutions. In natural waters, the oxidation of Mn (II) to MnOOH or to Mn (IV) is catalyzed by certain microorganisms [Stumm (1981)]. The +4 valence is the predominant natural form. MnO_2, the most stable Mn (IV) compound, is readily attacked by reducing reagents in acid solution [Baes (1976)]. The +7 valence permanganate (MnO_4^-) is a powerful oxidant. Mn VII is thermodynamically unstable in natural waters [Stumm (1976)].

I.1. Solubility and Precipitation.

$MnCO_3$ (rhodochrosite) has been suggested as the solubility-controlling solid for Mn^{+2} under reducing conditions and relatively high pH and CO_2 levels, at higher redox potentials (e.g. pH 7), where oxidation of Mn(II) occurs, the controlling solids are manganite (γ-MnOOH), pyrolusite (β-MnO_2), and mixed-valence Mn oxides [Lindsay (1979), Morgan (1976), Rai *et al.* (1984), Salmons (1984)].

The Mn III and Mn IV oxides and hydroxides are essentially insoluble under natural aquatic conditions [Morgan (1976)]. Natural organics can reduce manganese oxides to the soluble Mn (II) form, which increase the mobility of manganese and its availability to organisms, these reactions are photocatalyzed in seawater and river water [Sunda (1983)] and proceed more rapidly at pH >7 [Stone (1984)].

II. TECHNOLOGY.

II.1. Uses.

Manganese organometal compounds include methylcyclopentadienyl manganese tricarbonyl, which is added to gasoline as an antiknocking agent, and manganese ethylene bisdithiocarbamate used as a fungicide. Manganese is also used to form alloys with iron, aluminum, bronze, nickel-silver, and nickel-chromium. Other uses for manganese include dry cell batteries, glass, inks, ceramics, paints, welding rods, chemical oxidizing agents, and rubber and wood preservatives [G.P.O. (1985), Browning (1969)].

II.2. Source of Exposure.

The primary source of emission is the manufacturing of ferroalloys. Exposure occurs from breathing air which contains dust particles rich in manganese. The highest risks are those working directly with the production or manufacturing processes involving materials high in manganese content.

III. PHYSIOLOGY.

III.1. Essentiality of Manganese.

Manganese is an essential nutrient for plants, animals, and man. Under normal conditions diet would represent the major source of manganese intake for man and animals with only minor contributions from water and air [EPA (1984)].

A dietary deficiency of the element can result in a wide variety of structural and physiological abnormalities.

Despite the widespread pathological consequences of

manganese deficiency the underlying biochemical lesions have not been well defined. This is due in part to the large number of enzymes which have been reported to require manganese. However, the need for manganese by the glycol transferase involved in proteoglycan synthesis accounts for the skeletal deformities and postural defects associated with deficiencies of this element [Leach (1978)].

III.2. Manganese Intake and Absorption.

The daily intake of manganese from the diet is typically reported to range from 2-8 mg, with an average of about 3 mg [EPA (1984), Hurtey (1986), Rai (1984)]. Consistent with these data, manganese deficiency is thought to be extremely rare in man.

For the adult human it has been reported that 3% of dietary manganese is absorbed regardless of the amount of the element in the diet [Mena (1981)]. In contrast to adults, the absorption of manganese by very young animals has been found to be as high as 70%, suggesting that the risk of manganese toxicity may be particularly high during infancy [Mena (1981), Rehnberg *et al.* (1980), Rehnberg *et al.* (1981), Keen *et al.* (1986)].

III.3. Toxicity.

Manganese toxicity has been observed primarily among workers associated with the mining, refinery, and manufacturing of manganese [EPA (1984)], by inhalation of massive amount of airborne manganese (>5 mg/l) with particle size less than 5 μm. Manganese toxicity is characterized by a severe psychiatric disorder (manganism) which can include memory impairment, disorientation, hallucinations, speech disturbances, compulsive behavior, and acute anxiety. With progression of the toxicity individuals tend to show masklike faces, tremors, difficulty in walking, and exaggerated reflexes. Although manganese toxicity as a result of chronic inhalation of excess levels of the element is well recognized, there is still little information on the biochemical

mechanisms underlying its symptoms. Manganese in the environment is increasing due to the use of the manganese-containing compound methylcyclopentadienyl manganese tricarbonyl in gasoline as an antiknocking agent. The severity of the effects of manganese toxicity in humans gives evidence that this increase must be resolved.

In addition to the extensive neural tissue damage, an iron-responsive anaemia is a common finding with orally induced manganese toxicity [NASc (1980)]. This anaemia is presumably due to competitive gastrointestinal uptake of iron and manganese [Keen *et al.* (1984)].

An increase in respiratory diseases such as lung pneumonitis and pneumonia are frequently observed with milder cases of manganism [EPA (1984). The principal lesion observed in these individuals is epithelial necrosis followed by mononuclear proliferation [Cooper (1984)]. Reproduction and immune system dysfunction, nephritis, testicular damage, pancreatitis, and hepatic damage have been reported to occur with manganese toxicity.

IV. LEVEL OF TOLERANCE.

In the absence of an industrial point source of manganese contamination, typical ambient air concentrations of manganese range from 0.02 to 1 μg/l [EPA (1984)]. In areas surrounding manganese-emitting industries, the air contamination of the element ranges from 1 to 10 μg/l [Cooper (1984)]. The maximum permissible air concentration set by the Occupational Safety and Health Administration [O.S.H.A. (1981)] for manganese in the work place is 5 mg/l. The World Health Organization Study Group [WHO (1980)] suggested an occupational limit for Mn in air of 0.3 mg/l. The average level in seawater 0.1-5.0 μg/l and the surface water up to 500 μg/l [WHO (1980)]. Manganese concentration in drinking water has been reported to range from 1 to 100 μg/l with average values being less than 10 μg/l [EPA (1984), WHO (1981)]. Mn concentrations in common human food products range from 0.02 to 25 μg/g [Hurley (1986)].

V. STANDARD METHODS OF MEASUREMENT.

An effort must be made to minimize contamination of samples during collection and handling. As a precaution all glassware and plasticware used in the storage or processing of samples should be soaked in 20% nitric acid for at least 48 hr and then rinsed exhaustively with distilled water and rinsed with water samples. Washed glassware and plasticware should be stored in dust-free conditions prior to use.

The most common analytical methods which have the required sensitivity to measure manganese (1 ng/ml) include neutron activation analysis, x-ray fluorescence, proton induced x-ray emission, inductively coupled plasma emission spectroscopy, electron paramagnetic resonance, and electrothermal atomic absorption spectrophotometry [Keen *et al*. (1986), Mena (1981), Verick (1985)]. Among all these methods electrothermal AAS is a relatively inexpensive and sensitive technique.

For complicated matrices liquid-liquid extraction, and chelation resin techniques serve a dual purpose:

- Preconcentration of low levels of manganese.
- Overcoming of the matrix interference

VI. SOURCE OF MANGANESE POLLUTION OF SEAWATER IN KUWAIT.

Principal sources are

- Manganese dioxide, used in process of dry battery production.
- dust fall.
- Occasional sewage disposal to the sea, treated sewage containing 0.095 mg Mn/l [MEW (1980)].

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2.6 NICKEL

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INTRODUCTION.

Nickel is the twenty-fourth element in order of natural abundance in the earth's crust. Natural sources of aqueous nickel derive from solubilization of nickel compounds from soils and from biological cycles. Most nickel compounds are relatively soluble at pH values <6.5, whereas nickel exists predominantly as insoluble nickel hydroxides at pH >6.7.

Therefore, acid rain has a pronounced tendency to mobilize nickel from soil and to increase nickel concentrations in ground waters, leading eventually to increased uptake and potential toxicity for microorganisms, plants, and animals. Ore deposits of commercial importance are principally sulphides [pentlandites $(Fe,Ni)_9S_8$] and oxides (laterite). Nickel ores occur primarily in the form of the oxides, silicates and sulphides and are usually associated with other sulphides, silicate, or arsenide minerals. As the silicate, nickel is found in the lattice of hydrated magnesium-iron minerals such as garnierite [$3(Mg,Ni)O_2SiO_2.2H_2O$]. Pentlandite, the main sulphide ore also contains copper and iron (II). About 84% of all nickel produced is used in alloys.

I. CHEMICAL PROPERTIES

Nickel is a silver-white, hard, malleable, ductile, ferromagnetic, metallic element, having face-centered cubic crystals, capable of a high lustre and resistant to corrosion in many acids, salts and alkalies, in fresh and salt waters, and in wet and dry gases. Nickel ions act as acids in water. Nickel tends to complex with both inorganic and organic ligands in aquatic systems.

The oxidation states of nickel include -1, 0, +1, +2, +3 and +4 but the most prevalent oxidation state is +2.

The relatively insoluble nickel compounds that are environmentally important are the sulphide, hydroxide and carbonate. Their approximate solubility products (mol^2dm^{-6}) are $10^{-19.4}$ (α-NiS), $10^{-24.9}$ (β-NiS), $10^{-26.6}$ (γ-NiS), and $10^{-6.87}$ ($NiCO_3$)

[Martell (1976)]. Rai *et. al.* (1984) suggested that $NiFeO_2$ and NiS may be the solubility-controlling precipitates under oxidizing and reducing conditions, respectively. Since the solubility product of nickel hydroxide is about 10 orders of magnitude lower than that of nickel carbonate, the latter is highly unlikely to precipitate under typical environmental conditions.

Nickel, with chromium and mercury, is considered to be the most generally mobile of the heavy metals [Fuller (1977)]. The sorptive behavior of nickel in soil has not been extensively investigated, but iron and manganese oxides, clay minerals and organic matter are believed to be important sorbents of nickel [Rai *et al.* (1984)].

II. TECHNOLOGY.

II.1. Uses.

Nickel metal, nickel II sulphate, nickel II chloride and nickel II cyanide are used in electroplating [McNamara *et.al* (1981)], in the manufacture of magnetic tapes, in jewelry and coinage, in rods for arc welding, in surgical and dental protheses, in electric storage batteries, in paint pigments (especially yellow nickel titanate), and in the manufacture of moulds for ceramics and glass containers.

Stainless steel constitutes the most important nickel ferro-alloy, with the automotive industry the single largest consumer. Chief among nickel-copper alloys is Monel metal, containing about 66% Ni and 32% Cu. Owing to its corrosion resistance, Monel metal is widely used in dairy and food-manufacting industries. Nickel carbonyl (an intermediate in the mond process for refining Nickel) is employed for vapor plating in the metallurgical and electronics industries, and is a catalyst for synthesis of acrylic monomers in the plastics industry. Nickel is used as a catalyst in various industrial processes such as coal gasification, petroleum refining, and hydrogenation of fats and oils [Sunderman (1986), Sunderman (1983)].

II.2. Sources of Exposures.

Environmental concentrations of nickel are related to consumption of fossil fuels, since, the nickel content of coal ranges from 4-24 mg/kg [Bennett (1984)]. Atmospheric emissions of nickel derive from fly-ash that is released from coal-fired power plants. Nickel derived from petroleum is released into the environment in automotive exhaust fumes. Inhalation of nickel averages 0.4 μg/day (range = 0.2-1.0 μg/day) for urban dwellers and 0.2 μg/day (0.1-0.4 μg/day) for rural dwellers; approximately 35% of inhaled nickel is absorbed. Cigarette smoking can increase inhaled nickel by as much as 4 μg/pack of cigarettes [Bennett (1984), Grandjean (1984)].

Seawater contains 0.1-0.5 μg Ni/l. Surface waters average 15-20 μg Ni/l, and drinking water usually contains less than 20 μg Ni/l [Sundeman (1986)]. Drinking water samples occasionally contain high nickel concentrations owing to pollution of the water supply or leaching from nickel containing pipes or nickel-plated faucets. The average dietary intake of nickel by adult persons is approximately 165 μg/day but may reach 900 μg/day in diets rich in oatmeal, cocoa, chocolate, nuts, and soya products. Cutaneous exposure to nickel is ubiquitous from stainless steel utensils and nickel plated materials such as coins, jewelry, and clothing fasteners.

Occupational exposure to nickel and its compounds occur in:

1) Mining.
2) Nickel refining and smelting.
3) Nickel electroplating.
4) Producing and using nickel catalysts.
5) Fabricating parts and structures by welding.
6) Manufacturing Ni-Cd batteries.
7) Constructing nickel moulds in glass-bottle factories.
8) Spraying nickel-containing paints.
9) Recycling or disposal of nickel-containing products.

III. PHYSIOLOGY.

III.1. Intake and Absorption.

Following oral administration of a solution of soluble nickel, the element remains unabsorbed and is excreted in faeces. A minor fraction of ingested nickel (1-5%) is absorbed from the intestine, enters the plasma, and is excreted primarily in urine and to a minor degree in bile. Nickel is rapidly accumulated in the kidney, pituitary, lungs, skin, adrenal glands, and ovary or testis. This is discovered by the administration of radio-labeled nickel (^{63}Ni) to animals, during 3-5 days post-injection the ^{63}Ni is largely eliminated via the urine [Sunderman (1984)].

III.2. Metabolism.

The estimated body burden of nickel in healthy adults averages 0.5 mg/70 kg (7.3 μg/kg body weight) [Bennett (1984)]. In postmortem tissues from adults without known environmental, occupational, or iatrogenic exposure to nickel compounds, the highest concentration of nickel is found in bone, followed by lung, kidney, liver, and heart [Sunderman (1984)]. Although a major fraction of serum nickel is bound to nickeloplasmin, a macroglobulin, the nickel content of nickeloplasmin is not readily exchangeable with exogenous Ni^{2+}, and nickeloplasmin does not play an important role in the transport of Ni^{2+} [Decsy (1974)]. Divalent nickel ion is transported in blood primarily by binding to serum albumin and, to a lesser degree, by binding to serum ultrafilterable constituents, such as histidine [Barkar (1984)]. Divalent nickel ion is easily extracted from serum by the kidney and excreted in urine.

The main concentrations of nickel in sweat from healthy adults and in milk from lactating mothers are 10-20 times greater than the main concentrations of nickel in urine [Cohn (1978), Feeley *et. al.* (1983)]. Serum nickel concentrations are often increased in patients with acute myocardial infarction, sever myocardial ischemia, acute stroke, or

extensive thermal burns [McNeely *et. al.* (1983), Leach *et. al.* (1985)]. Increased nickel concentrations were reported in serum specimens from women after obstretrical delivery [Rubanyi *et. al.* (1982)], but postpartum hypernickelemia was not confirmed in a subsequent study [Nomoto *et. al.* (1983)].

III.3. Toxicity.

Human health hazards from exposure to nickel compounds [Sunderman (1981), Sunderman (1983), Brown (1985), Sunderman (1986)] fall into:

III.3.1. Allergy. Hypersensitivity to nickel is a common cause of allergic contact. The cutanous lesions of nickel dermatitis begin as a papular erythema of the hands or other areas of skin that contact nickel. The lesion gradually becomes eczematous and undergo lichenification in the chronic stage.

III.3.2. Cancer. Cancer of the lungs and nasal cavities gives rise to the highest mortality rates among nickel refinery workers. Risks of malignant tumors including cancers of the larynx, kidney, prostate, or stomach have been noted in certain groups of nickel refinery workers.

III.3.3. Nonmalignant Respiratory Disorders. Acute inhalation of nickel carbonyl causes coughing dyspnea (difficult breathing), tachycardia (rapid pulse), cyanosis (bluish skin), headache, dizziness, and profound weakness. The acute nickel carbonyl poisoning causes death, patients who recover from acute nickel carbonyl poisoning are prone to develop chronic respiratory insufficiency. Refinery workers who are exposed to nickel dusts and aerosols may suffer from respiratory disorders, including bronchitis and asthma, and may develop rhinitis and sinusitis, sometimes associated with anosmia (lack of smell), nasal polyps, or perforation of the nasal septum.

IV. LEVEL OF TOLERANCE.

As general guidelines [Sunderman (1986)] nickel concentration of 30 μg/l in urine or 8 μg/l in serum are suggested as biological tolerance limits for human exposures to nickel from environmental, occupational, or iatrogenic sources.

The National Institute for Occupational Safety and Health (NIOSH) recommended 15 μg Ni/l determined as a time-weighted average concentration for up to 10-hr work shift, 40-hr work week [NIOSH (1977)] as the U.S. standard for work place exposure to nickel metal and soluble nickel salts. The standard in United States, Japan, Sweden, Finland, and Poland for 40-hr time-weighted maximum average exposure to nickel carbonyl is 7 μg/l [Bencko (1983), NIOSH (1977)]. The comparable value for former USSR is 0.5 μg Ni/l [Izmerov (1984)].

V. STANDARD METHODS OF MEASUREMENT.

Water samples should be collected directly into acid-washed plastic containers, and stored in a noncontaminated area. The sample should be acidified with ultrapure hydrochloric acid or nitric acid to prevent nickel adsorption on the wall of the container. Electrothermal atomic absorption spectrophotometry and differential pulse absorption voltammetry (DPAV) are the most sensitive techniques for nickel determination.

The most widely used sample preparation procedure is based on the formation of water-insoluble metal complexes followed by extraction into an immiscible organic solvent.

VI. SOURCE OF NICKEL POLLUTION OF SEAWATER IN KUWAIT.

The major sources of entry of nickel in Kuwait's seawater are:

- Crude oil spills. Crude oil contains 5 μg/g nickel.
- Ballast water of oil tankers.
- Atmospheric emission of nickel related to consumption of crude oil from power and distillation plants.

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2.7 VANADIUM

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INTRODUCTION.

Vanadium is the ninth most abundant element in the earth's crust (0.014%), concentrated mainly in famic rocks and shales [Paschal and Bailey (1990)]. It is silver white, insoluble in hydrochloric acid, slowly dissolves in hydrofluoric acid, nitric acid, sulphuric acid (hot and concentrated) or aqua regia [Heyligar *et. al.* (1985)].

Vanadium occurs as patronite (VS_4), descloizite mottramites [(Zn, Cu) $Pb(OH)VO_4$], uranium-bearing carnotites [$K_2(UO_2)_2V_2O_8.3H_2O$] and titanomagnetites. These account for more than 80% of the world production of vanadium.

Crude oils contain appreciable trace amounts of V (from <1 to 1600 mg V/kg) [Bengtsson and Tyler (1976)], Kuwait's crude oil contains 20 μg/g [KISR (1982)].

The open ocean concentration of vanadium is stated to be about 1 μg/l, while coastal waters may contain 3-4 μg/l of vanadium [U.N.O. (1976)].

A U.N. study [U.N.O. (1976)] estimates the intake of vanadium through normal diet as 2 mg of vanadium each day. However, if present in higher concentrations, vanadium becomes toxic to living organisms and to human beings. Some reports [Cremer and Warner (1975)] indicate that concentrations of vanadium equal to or exceeding 1.0 mg/l constitute a hazard in the marine environment and levels less than 0.5 mg/l present minimal risk of deleterious effects.

I. CHEMICAL PROPERTIES.

Vanadium has a maximium oxidation state of +5. Compounds of vanadium may contain vanadium in oxidation states of -1, 0, +2, +3, +4 and +5. Vanadium is usually found bonded to oxygen as a negatively charged polymeric oxyanion that tends to complex to polarizable ligands, such as phosphorus and sulphur [Buckingham (1973), Cotton and Wilkinson (1980)].

Vanadium has the ability to be either an electronegative or an electropositive metal which leads to a great variety of chemical compounds. Vanadium usually occurs in the

pentavalent state. Pentavalent vanadium is stable in aqueous solutions over a wide range of pH.

Among pentavalent vanadium compounds the orange V_2O_5 is certainly the most prominent. Its dissolution in acids gives oxidizing solutions whereby VO_2^+ is reduced to the vanadyl cation. With strong bases V_2O_5 forms tetrahedral vanadates VO_4^{3-} which yield polynuclear species on lowering the pH, and ending up by precipitation of V_2O_5.

Vanadium in 4^+ state forms a large number of five and six coordinate complexes such as vanadyl acetylacetate and vanadyl porphyrins found in crude petroleum.

Vanadium III is a strong reducing agent that slowly attacks water with liberation of hydrogen and the production of vanadium 4^+ [WHO (1988)].

II. TECHNOLOGY.

II.1. Production.

Metallic vanadium does not occur in nature. Over 70 vanadium minerals are known, carnotite and vanadinite being the most important from the point of view of mining. Production of vanadium is linked with that of other metals such as iron, uranium, titanium and aluminium, and the production is started by reduction of titanomagnetites (contaning 1.6% V_2O_5) with carbon [Fichte *et al.* (1983).

Vanadium is blown out from the crude iron (with O_2) into the slags containing finally V III corresponding to 25% V_2O_5. These slags are the most important starting materials for the production of vanadium. Crushing and roasting of the vanadium slags results in water-soluble sodium vanadate. After leaching with addition of H_2SO_4 or HCl and NH_4^+ salts, sparingly soluble NH_4^+-vanadates (poly- or meta vanadate) are obtained by precipitation. Thermal decomposition of these produces pure V_2O_5. Vanadium metal is obtained by reduction of V_2O_5 with calcium or aluminium.

II.2. Uses.

Vanadium is mainly (75-80%) [WHO (1988)] used in ferrous metallurgy as an alloy additive in various types of steel. Ferrovanadium, an alloy with generally at least 50% vanadium, is obtained by reduction of V_2O_5 with aluminium in the presence of iron. Compared to reduction by Si, this procedure has the advantage of producing a high-quality Fe-V alloy in a short time with good yield [Wennig and Kirsch (1988)]. Vanadium use in nonferrous metals is important for the atomic energy industry, aircraft construction, and space technology. Vanadium is also used as a catalyst for oxidation reactions (e.g., for SO_2, naphthalene, benzene, and cyclohexane), and in the chemical industry, where pentoxide and metavanadates are especially important for the production of suphuric acid and plastics.

III. PHYSIOLOGY.

III.1. Biochemistry.

The element vanadium is essential for chicken, rats, and some plants, but its physiological role remains poorly understood in man in spite of recent advances [Nechay (1984)]. The complex biochemistry of vanadium compounds depends on the oxidation states of the metal from -1 to +5. The vanadium compounds can easily change their oxidation states under physiological conditions, so that vanadium is mostly in the +5 oxidation state (except in the presence of reducing agents). In plasma ^{48}V was observed bonded up to 77% to the serum Fe transport protein transferrin [Sabbioni *et al.* (1978), Harris *et al.* (1984)].

Since 1977 it has been known that vanadium as vanadate is a potent inhibitor for the Na^+ and K^+ ATPase, an enzyme universally present in eukaryotic organisms. The inhibition of this enzyme by VO_3^- is observed at the micromolar range in isolated cell membrane, i.e., human cardiac cell membrane. This enzyme is more resistant to VO^{2+} than VO_3^-. Inhibition of cholesterol synthesis by vanadium, accompanied by lower plasma

phospholipid and cholesterol levels, has been observed in man and animals [Underwood (1977), Dinoeva (1982), Wennig and Kisch (1988)].

III.2. Effect on man.

Among the local effects caused by vanadium exposure, the green tongue occurring in a proportion of the exposed is considered a sign of exposure rather than a toxic effect. Vanadium induced eczema has been reported in workers exposed to V_2O_5 with dust levels as low as 6.5 μg/l [WHO (1988)].

A dose-response relationship was observed when 11 volunteers were exposed to 0.4 mg V_2O_5/l condensation aerosol. Tickling and itching with dryness of the mucous membranes of the mouth were reported by 5 subjects at 0.16 mg/l, whereas at 0.08 mg/l none of the subjects noted any effects [WHO (1988)].

The kinetics of vanadium elimination in man is dose-dependent. At low dose, the mean half-life is 15 hr and the urinary excretion 9.3 μg V/g creatinine at the end of exposure. At high level, the half-life is 20 hr, the mean urinary excretion 60-70 μg V/g creatinine, and the 2 μg V/g creatinine level is reached about 600 hr after the exposure [Sabbioni and Maroni (1984)].

Vanadium compounds especially V_2O_5, are strong irritants of the eyes and the air ways. Acute and chronic exposure gives rise to conjunctivitis, rhinitis, reversible irritation of the respiratory tract, and to bronchitis, bronchospasms, and asthma-like diseases in more severe cases [Vouk (1979)].

IV. LEVEL OF TOLERANCE.

Several TLVs have been set in different countries e.g. in the USA and former USSR the level is 0.1 mg V_2O_5 fume/l [Wennig and Kirsch (1988)]. For dust the levels are normally higher, i.e., in western part of Germany and former USSR the level is 0.5 mg V_2O_5 dust/l [UNEP (1984)]. Air quality standards have been set in some Eastern countries at 0.002-0.003 mg V_2O_5 /l in 24 hr. In the eastern part of Germany recommendations were

made for agricultural soils, 50 mg V /kg (air dried soils) [Wennig and Kirsch (1988)].

V. STANDARD METHODS OF MEASUREMENT.

Vanadium is the least studied among the transition elements in the natural environment. It plays an important role as an environmental pollutant, being important in industrial wastes. High-salinity waters are known as environments in which the classical analysis method for trace metal concentrations are difficult to apply, because of the chemical interference of high concentration alkali metals, alkaline earths and halogens.

The concentration range of dissolved vanadium is typically between 0.5-3.0 μg/kg in seawater [Dupont *et al.* (1991)].

In marine conditions, vanadium occurs mostly in the dissolved state. Particulate vanadium is negligible compared to dissolved vanadium [0.01% according to Collier (1984)].

The only direct determination of dissolved vanadium in seawater is performed by cathodic stripping voltammetry. All other methods currently used require a preconcentration step. After chemical separation (preconcentration) vanadium can be analysed by different techniques: neutron activation, X-ray fluorescence, atomic absorption, and inductively coupled plasma spectroscopy.

VI. SOURCES OF VANADIUM POLLUTION OF SEAWATER IN KUWAIT.

Crude oil spills, especially related to oil loading facilities, are the major source for entry of vanadium into Kuwait coastal seawater. Most of this, however, ends up into sediments. The sulphuric acid plant at Shuaiba uses vanadium compounds as a catalyst. However, this may contribute only minor quantities since the catalyst is not discharged to the seawater.

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2.8 ZINC

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INTRODUCTION.

Zinc is the 27th most abundant element in the earth's crust, and its concentration averages about 70 μg/ml in most rock-forming minerals. Zinc occurs naturally as five stable isotopes Zn-64, 48.89%, Zn-66, 27.81%, Zn-67, 4.11%, Zn-68, 18.57%, and Zn-70, 0.62%, and six radioisotopes have been identified, including Zn-62, -63, -65, -69, -72, -73. Of these six radioisotopes, only Zn-65, and Zn-69 have sufficiently long half-lives to be useful as tracers (244 days and 58 min, respectively) [Bertholf (1988)]. The principal ores of zinc are the sulphides sphalerite (cubic ZnS) and wurtzite (hexagonal ZnS), smithsonite ($ZnCO_3$), and hemimorphite ($Zn_4Si_2O_7(OH)_2H_2O$), and usually in association with sulphides of other metals especially lead, copper, cadmium, and iron. The content of zinc in soil is highly variable, averaging about 54 μg/g. Zinc is also found chelated by naturally occurring organic acids such as humic and fulvic acids. The concentration of zinc in seawater averages 8 μg/l.

I. CHEMICAL PROPERTIES.

Zinc is a member of the group IIB triad (Zn, Cd, Hg) in the periodic table. Zinc has atomic number 30, atomic weight 65.37 (isotopic mean), and in pure form is a relatively soft bluish metal. Zinc is divalent in all its compounds and forms a variety of inorganic salts and organozinc compounds, and this is the only oxidation state of importance for zinc under environmental conditions. Zinc combines readily with many metals to form alloys. It is also widely used as galvanized steel, where the outer coating of almost pure zinc undergoes sacrificial corrosion due to the high electrochemical activity of zinc. The most industrially important inorganic zinc compound is zinc oxide. Zinc oxide is crucial to the vulcanizing process, where its high heat capacity greatly improves the thermal properties of rubber. Zinc oxide is a white hexagonal crystal whose high refractive index makes it valuable for use in paint. Zinc oxide is also used

pharmaceutically, in ceramics, and in photocopying papers. The solubility of zinc in natural waters is strongly affected by pH, temperature, and the presence of complexing ligands, competing ions and precipitating reagents. As its species formed with the common ligands in surface waters are soluble in neutral and acidic solutions, in the absence of strong sorbing material, zinc is readily transported in most natural waters and is one of the most mobile of the heavy metals [U.S. EPA (1980)].

The sorption of zinc in soil and sediments strongly impacts its mobility in the environment. For this reason, severe zinc contamination tends to be confined to the region of the source. Hydrous iron, and manganese oxides, clay minerals, carbonate minerals, and to a lesser extent, organic matter have been noted as sorbents that control the behavior of zinc in soil and sediment [Bodek *et al.* (1988), Hickey and Kittrick (1984), EPA (1974)]. The sorption of zinc increases greatly as the pH increases through a critical range of 5 to 7 [Callahan *et al.* (1979)].

II. TECHNOLOGY.

II.1. Production.

The basic process for smelting zinc involves roasting to drive off SO_2 and convert ZnS to ZnO, and then reduction of ZnO to zinc vapor, which is subsequently condensed to liquid and drained into moulds. The recovery of zinc in pure form from mined ores depends on the composition of the ore. Electrolytic zinc reduction is also quite common in the production of zinc. World wide yearly zinc production averages several million metric tons.

II.2. Uses.

Zinc sulfate is used in the production of plastics, zinc chloride is used in batteries, zinc sulphide and zinc silicate are used as phosphors in cathode ray tubes, zinc chromate is a wood preservative, zinc carbonate is used as a dietary

supplement for farm animals, zinc peroxide is an antiseptic, zinc acetate has some medical value, used as an emetic, and astringent, and zinc phosphide is highly poisonous (due to liberation of phosphine gas) and is used in rat and mouse poisons [N.R.C. (1979)]. The organozinc compounds are useful as fungicides, topical antibiotics and in lubricants.

Zinc is used extensively in the machine, building and automotive industries as a component of galvanized steel.

III. PHYSIOLOGY.

III.1. General.

Zinc is an essential element for good health. The trace element zinc helps to form the enzymes that enable proteins to become the "building blocks" of new cells. Deficiency can lead to various syndromes with disturbances of liver and spleen function, disturbances in sexual development, disturbances also of wound healing and causation of skin diseases. Zinc has been shown to have beneficial effects on muscle strength and endurance and in raising the threshold of fatigue.

The WHO has recommended a daily intake of 15 mg of zinc for the average person [Frank Porter (1991)].

III.2. Absorption.

Zinc absorption has been investigated on rat intestine, and it is found that, zinc absorption is an active transport process that is regulated by dietary zinc status. Absorption occurs primarily in the ileum and can be affected by a large variety of dietary components including aspirin, phytate and histidine [Smith *et al.* (1978), Antonson *et al.* (1979)]. In man absorption of zinc has similar properties although the effects of histidine on zinc absorption have been challenged [Schechter and Prakash (1979)].

III.3. Toxicity.

Zinc can cause harm to living matter through two main processes:

1- ingestion of toxic amounts of zinc with food or drink.

2- inhalation of fairly high concentrations of fresh formed zinc oxide fumes.

Bertholf (1988) reported that zinc toxicity including gastrointestinal distress and diarrhoea, appeared in military personnel who drank limeade in galvanized garbage cans. Food poisoning occurred following ingestion of acidic foods such as fruits and juices prepared or cooked in galvanized containers, and a toxicosis after drinking water containing 40 μg/ml zinc from new galvanized pipes in a new water supply net. Cases of chronic haemodialysis are at risk from exposure to a variety of metals contaminating the water supply, and in one case nausea and vomiting developed after use of a dialysate prepared with water that had been stored in a galvanized tank.

Inhalation of zinc fumes is responsible for a form of "metal fume fever", "brass-founders ague ", "brass chills", "zinc shakes", or "spelter shakes".

The inhalation produces a syndrome characterized by rapid breathing, shivering, fever, sweating, chest and leg pain and weakness i.e., the apparent effects are similar to those of a severe cold or flu. Symptoms usually abate within 1 or 2 days, and interestingly are not exacerbated by subsequent exposure within 2 days of onset. This phenomenon is not well understood, but has been termed "tachyphylaxis" or "quick immunity" [McCord (1969), Bertholf (1988)].

III.4. Target Organs.

Zinc has been found in every tissue examined and is the second most abundant trace metal in the human body.

The average adult human (body weight of 70 kg) contains between 1.4 and 2.3 g of zinc, as compared with 4.2-6.1 g of iron and 81-230 mg of copper.

About 64% of body zinc is found in muscle, and about 28% is in bone, corresponding only qualitatively to the relative

masses of these tissues [Tiplon and Cook (1963)].

IV. LEVELS OF TOLERANCE.

Zinc in water will impart a stringent taste at concentrations well below that required for gastrointestinal distress to be induced, and a survey of water supplies in the United States revealed none with a zinc concentration above 4 mg/l [EPA (1975)].

The guideline values and maximium allowable concentrations for zinc and zinc compounds have been set by many agencies, e.g. WHO (1984) 5.0 mg/l, European Community (1980) 0.1 mg/l [see appendix I].

V. STANDARD METHODS OF MEASUREMENT.

Flameless atomic absorption methods are applicable to zinc and have the advantage of requiring only a small sample amount and minimal pretreatment.

A direct determination of zinc in seawater and fresh water is by stripping voltammetry and inductively coupled plasma spectroscopy.

VI. SOURCES OF ZINC POLLUTION OF SEAWATER IN KUWAIT.

The main sources of zinc pollution of seawater in Kuwait are:

1. Effluent discharges from the following activities either directly or indirectly to seawater:

i. Electroplating industry.
ii. Galvanization.
iii. Dye casting.
iv. Cement industry.
v. Ship building industry.
vi. Soft drink and bottling industry.
vii. Burning of fossil fuels.

2. Occasional discharge of sewage and municipal waste water.

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CHAPTER 3

ANALYTICAL TECHNIQUE

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3. METHOD OF ANALYSIS.

Concentrations of trace metals can be determined through several means; volumetric, gravimetric, colorimetric and spectrophotometric analyses (polarograph, atomic absorption; flame and electrothermal, X-ray fluorescence and neutron activation analysis). Selection of a method of analysis depends on its detection limit and minimum accuracy required for the purpose.

Reliability and accuracy of analytical data depend not only on the analytical laboratory work. They are influenced by all procedures the sample derived from it are under-going from their collection to the statistical evaluation of the measurements.

For the analysis of several metal concentrations with high accuracy and reproducibility, spectrophotometric method of analysis are, by far, superior to other analytical procedures. Such merthods include atomic absorption spectrophotometry (electrothermal) and inductively coupled plasma connected with mass spectrometry.

3.I. ATOMIC ABSORPTION SPECTROPHOTOMETRY.

In the analysis of several metals, atomic absorption spectrometry (AAS) exhibits superior sensitivity to many other analytical procedures. It involves the aspiration of the sample (liquid/solid) into a flame or heated graphite tube in order to atomize it. A specific light beam is directed through the flame or graphite tube into a monochromator and onto a detector that measures the amount of light absorbed by the atomized element. Each metal has its own characteristic absorption wavelength. Hence a source lamp containing that element is used making the method relatively free from spectral or radiation interferences.

The concentration of the element in the sample is directly proportional to the absorbance at the characteristic wavelength in the flame or graphite tube (Lambert-Beer's Low).

The basic atomic absorption spectrophotometer consists of:

3.I.1. Source of Light. The source of light is used to provide a narrow spectral line of the element of interest. These sources are bright, stable and have a long life. Traditionally hollow cathode lamps (HCL), and electrodeless discharge lamps (EDL) are used.

3.I.2. Atomizer. The atomizer is used for the atomization of trace metals or elements. Three types of atomizers are available.

3.I.2.1. Flame. In flame atomization the gases are burned to atomize the elements. The gas combinations normally used with atomic absorption are.

Air/Acetylene. Air/Acetylene flame is the preferred flame for the determination of about 35 elements by atomic absorption. The temperature of the air/acetylene flame is approximately 2300·C.

Air/Hydrogen. Air/hydrogen flame is useful for the determination of the alkali metals (Cs, Rb, K, Na) because of its low temperature (approximately 2000·C).

Nitrous Oxide/Acetylene. Nitrous oxide/acetylene flame has a maximum temperature of about 2900·C and requires a special burner. It is used for the determination of elements which form refractory oxides.

Argon/Hydrogen. The Argon/Hydrogen flame uses diffused air as an oxidant. The flame has considerably less absorption in the far ultra-violet (190-220nm) zone than other flames. Hence it is useful in the determination of As (194nm) and Se (196nm). Its temperature is low at about 300-800·C.

Air/Propane. The air/propane flame temperature is about 1900°C. A special (3 slot) burner is required for its use.

The burners used for these flames are designed to give a long narrow flame in order to place a large number of the absorbing atoms in the light-path. The heat of the flame serves to evaporate the solvent and reduce the metal to the atomic state.

Aspiration of the sample into the flame is usually achieved by using air to aspirate the sample into a chamber where large droplets are separated and acetylene is mixed with the air (air/acetylene flame). The mixture is then passed immediately to the burner. The flame temperature should be sufficiently high to dissociate any molecular compound of the analyte element into free atoms.

3.I.2.2. Electrothermal, Flameless, Graphite Furnace. The graphite furnace is a special flameless sampling device, which can be used with all atomic absorption spectrophotometers. It provides extremely low detection limits in the range of 10^{-10} to 10^{-12}g for most metals.

The furnace power supply is programmed to pass increasing amounts of current through the graphite tube. This successively dries the sample, chars off any organic material and finally atomizes the sample at an atomization temperature of about 2700°C. During the drying and charring steps of analysis water vapours and organic materials are swept out of the graphite tube by a high flow of inert gas such as argon (300 ml/min). But in the atomization step the gas flow is reduced to allow the atom vapour to stay in the light-path for several seconds. The graphite tube is then water cooled for the next sample.

3.I.2.3. Hydride Generation System. This is used especially in the determination of low concentrations or levels of arsenic, selenium, bismuth and antimony as they form volatile compounds called covalent hydrides if they are treated with sodium borohydride under suitable chemical conditions. These hydrides are then released and passed into a heated cell where the gaseous compounds are broken down, hydrogen is released and the elements of the analyte are atomized.

3.I.2.4. Flameless Mercury System. Mercury is a unique element. It has an appreciable vapour pressure at room temperature. Therefore it is possible to determine mercury without the use of a conventional burner system.

Mercury can be determined by using the Hatch and Ott (1972) procedure. The mercury in the sample is reduced to its elemental form by using sodium borohydride or stannous chloride. The vapour is then swept into the absorption cell by nitrogen gas where mercury absorbs at the resonance wavelength of mercury.

3.I.3. Monochromator.

The monochromator has two functions:

A. To separate the resonance line from any other lines coming from the light source.

B. To prevent the detector being overloaded with light from the flame or with luminescence from the inert gas discharge of the hollow cathode lamp.

3.I.4. Detector.

The detector consists of a photomultiplier and associated circuitry. It is used to measure the intensity of the resonance line.

3.I.A. MATRIX MODIFICATION.

Atomic absorption spectrometry has been found a useful and easy technique for the determination of trace metals, owing to its extremely low detection limit and high

selectivity , but some problems arise in the analysis of heavy matrices which are mentioned below.

The large concentration of sodium chloride and other salts present in the saline water cause severe interference because of their large background absorption and their depression effect on the analyte signal. Ediger *et al.* (1974), Halliday *et al.* (1980) reported on the sodium and magnesium chloride interferences and their suppression effect on the trace elements. There are several ways to overcome these interferences.

- **By Adding Chemical Reagents To The Sample.**

Adding chemical reagents to the sample in the graphite furnace to alter the matrix or change the chemical state of the element prior to atomization. The following are examples of such processes:

- **Addition of Ammonium Nitrate NH_4NO_3.**

Ammonium nitrate can be added to relieve the effect of sodium chloride (NaCl) completely also to remove the suppression and enhance the signal of certain trace metals. Ediger *et al.* (1974) studied the effect of ammonium nitrate on the removal of sodium chloride interference, when a large excess of ammonium nitrate solution is dried with a sodium chloride solution to form a sodium nitrate and ammonium chloride residue. $NaCl + NH_4NO_3 \dashrightarrow NaNO_3 + NH_4Cl$. The ammonium nitrate, sodium nitrate and ammonium chloride are volatalized out of the graphite furnace at charring temperature near 500°C. The level of residual salts is then low enough to permit the background corrector to compensate for the remaining matrix absorption.

- **Addition of Organic Acid (as ascorbic or oxalic acid).**

Hydes (1980) reported that the organic acid acts as a flux. Sea water in the absence of organic acid dries in the graphite furnace as crystals. When the organic acid is added

the surface tension of the injected drop is reduced and no residue is visible at the end of drying stage. Guevremont (1981) used a mixture of citric acid 50% (10 mg/ml solution) as matrix modifier and 50% sea water.

- **Addition of Orthophosphate.**

Hodges (1977) used orthophosphoric acid and Subramanian *et al.* (1983) used phosphoric acid, to eliminate the interferences and background effects of sodium chloride and other alkali and alkali earth metals on the analytes.

3.I.B. Graphite Tube Treatment.

Many trace metals are determined directly without preconcentration by using the more sensitive graphite furnace technique. The graphite tube needs treatment to enhance the signal and to eliminate the matrix interference and this is done by the addition of lanthanum chloride and/or nitrate or ammonium molybdate as a pretreatment to the furnace tube. Thompson *et al.* (1977) used lanthanum salt to coat the graphite tube and this was achieved either by:

A. Injecting 15μl of a 20% w/v lanthanum nitrate hexahydrate solution into the tube and carefully evaporating to dryness by the slow manual increase of the voltage of the evaporation stage over a period of 90 sec. They reported that the coating step is very critical and care must be taken because slight obstructions are known to form in the tube and partially block the beam.
B. Impregnation of the tube with lanthanum. This was achieved by immersing the tube in the minimum volume of a concentrated solution of lanthanum nitrate which was left in a vacuum dessicator until all the solution had been absorbed.

An alternative method to remove matrix suppression is by a technique involving co-precipitation in the tube (i.e. in situ). Addition of ferric hydroxide or aluminium hydroxide was used by Weisel *et al.* (1984) to separate arsenic, cobalt,

chromium, molybdenum, nickel, and vanadium from seawater. Granston and Murray (1978) used ferric hydroxide to separate total chromium, chromium III and particulate chromium from seawater samples at natural pH and they recommended not to introduce excessive air into samples during separation.

3.II. INDUCTIVELY COUPLED PLASMA SPECTROPHOTOMETRY.

The plasma is a flame-like system, defined as a gas ionized sufficiently for its properties to depend significantly on the ionization. It is stable, chemically inert and a good conductor of electricity. In many repects, it provides a nearly ideal emission source.

When a gas is seeded with a few electrons and is caused to flow through a tube held within coils through which a high frequency current passes, the rapid changes in the magnetic field induce eddy currents in the gas. Resistance to the eddy current flow produces Joule heating. Once ionizing temperatures have been reached, the process is self-sustaining and an inductively coupled plasma (ICP) is formed almost instantly.

3.II.1. The Radio Frequancy (RF) Generator.

A radio frequency oscillator is used to supply power to the ICP. Basically, this generates an alternating current at a desired frequency. There are two general types of oscillator mostly used in plasma spectrometry:

Free Running: The basic frequency of oscillation is fixed by values of the components in the tank circuit, these, in turn are modified by any changes in the plasma impedance and in the coupling of the plasma to the load coil.

Crystal Controlled: A piezo-electric crystal is used to control the feedback and to maintain a constant frequency of operation.

Oscillators of both categories are used extensively and produce excellent results. The frequencies used in these generators are 27.12 MHz and 40.0 MHz.

3.II.2. Torches.

The plasma torch consists of a quartz tube placed inside the load coil. It is sufficient to generate an ICP when the laminar flow of argon within the tube is seeded with a few electrons from a Tesla coil. The resulting plasma takes on the toroid or doughnut shape and is self-sustaining, running as long as the high frequency current is supplied to the load coil and gas is supplied to the tube. The unique toroidal geometry of the torch is critical. Fine aerosol particles are introduced into the centre axial channel of the plasma, thus providing a relatively long residence time in the plasma's high temperature environment. This is one of the important factors leading to the high sensitivity of ICP.

The Greenfield Torch. The design of the Greenfield torch is based on the early work of Reed [Reed (1961)]. The Greenfield torch consists of three concentric tubes. The two outer tubes are made from silica and are used to contain the plasma. The inner tube is of borosilicate glass and is used to inject an aerosol through the plasma.

The torch is placed concentrically within the load coil of the RF generator. Argon gas is fed tangentially into the intermediate tube, and once the plasma has formed, argon, nitrogen, air, or other gas is introduced into the outer tube. A hole is then punched through the flattened base of the plasma by the introduction, through the injector of an aerosol in argon gas.

The Fassel Torch. It has two tangential gas entries to the outer and intermediate tubes. The aerosol is introduced through the small diameter tube along the torch axis. The good detection limits obtained with these torches are attributable to the use of an ultrasonic nebulizer that transports more analyte to the plasma than pneumatic nebulizers.

3.II.3. Sample Introduction System.

Most sample introduction systems used in ICP originate from flame atomic emission spectroscopy, or arc emission spectroscopy.

Pneumatic Nebulizers. Several types of nebulizers are used in ICP namely:

The concentric nebulizer.

Cross-flow nebulizer.

Babington nebulizer.

The fritted disc nebulizer.

The sample solution is fed to the nebulizer nozzle by the forced feed or aspiration resulting from the Venturi effect, the effect causing a reduced pressure at the nozzle. The solution is broken down into droplets under the influence of a high speed gas flow. This gas serves, at the same time, as aerosol transport gas. Since the flow rate of the latter should be about 1 l/min, a high pressure is generally required at the gas nozzle to generate an aerosol. Only a small portion of the introduced liqiud is nebulized, the larger fraction flows off to the waste. The aerosol, which consists of droplets of various sizes, is blown into a spray chamber where the larger droplets are separated out.

Ultrasonic Nebulization. Ultrasonic nebulization of liquid samples has been used in both AAS, and in early work using microwave plasma ICP. In an ultrasonic nebulizer (USN), a longitudinal acoustic wave is produced by an oscillator coupled to a transducer. The latter is orientated so that the direction of wave propagation is perpendicular to the interface between the gas and the sample liquid to be nebulized. By the transfer of the ultrasonic energy a particle motion is produced. Aerosol formation occurs by the action of "geysers" when the amplitude of the waves becomes sufficiently large.

In the case of aqueous solutions an operation frequency of 1 MHz was found to produce an aerosol with mean particle sizes of some micrometers (this type was used in early ICP

work by Wendt and Fassel (1965). Thus more analyte can be transported to the ICP at a slower nebuliser gas flow rate than that used with pneumatic nebulisers. This potentially gives a considrable increase in sensitivity, and improvment of detection limits, since the analytes have a longer residence time in the plasma. However, the increased efficiency does allow a greater quantity of water to enter the plasma, producing a cooling effect, and leading to high levels of interfering ions for ICP-MS.

3.II.4. HYDRIDE TECHNIQUES.

The power of detection of ICP for elements having volatile hydrides (arsenic, antimony, bismuth, germanium, lead, selenium, tin and tellurium) can be considerably increased by evolution of the in situ generated hydrides into the plasma. This technique is based on the generation of the volatile hydrides of these elements, which are transported to the higher temperature source which in turn can more efficiently produce and excite the free atoms and ions needed.

Thus, either stable alkali $NaBH_4$ solutions can be brought together with an acidified sample solution, or zinc pellets can be introduced into the reaction vessel containing the acidified sample solution.

$$1/2\ Zn + H^+ \rightarrow 1/2\ Zn^{2+} + H\ .$$

The hydrogen is formed in an active state (nascent hydrogen) and this then reduces the metal (arsenic, antimony,...etc.) to the hydride.

3.II.5. DETECTOR.

The detector is a quadropole mass spectrometer. This is a mass analyser based on electrostatic forces between charged metal rods and the ions as they pass along the axis of the spectrometer.

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CHAPTER 4

REVIEW OF PREVIOUS WORK AND METHODOLOGY

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4.I. REVIEW OF PREVIOUS WORK.

4.I.1. Sample Preparation.

In recent years, a number of publications have stressed the need for information concerning physical and chemical forms of trace metals in water in addition to total concentration data [Cranston and Marray (1978)] in order to obtain a full understanding of the distribution properties and behaviour of such metals.

Trace metals may be determined satisfactorily by several instrumental methods which are rapid and not requiring extensive separation. Prevention of serious errors during sampling and storage and preliminary treatment of sample are often necessary

4.I.1.1. Cleaning of Glass and Plastic Wares.

Patterson and Settle (1976) suggested cleaning techniques in which the plastic ware was initially rinsed in acetone, washed with micro-detergent, rinsed with glass-distilled deionized water (dd-water), soaked for at least one day in hot 3M hydrochloric acid (or one week in 6M hydrochloric acid at room temperature), rinsed with dd-water, soaked in 0.5-1M nitric acid for at least 3 days and rinsed with dd-water. But Batley and Gardner (1977) recommended that the new containers (glass or plastic) be soaked in 2M hydrochloric acid for 4 days and conditioned with prefiltered seawater for a week, all work done at room temperature. Later Gardner and Hunt (1981) recommended to soak the glass and plastic wares in 10% nitric acid overnight followed by 3 times washing with deionized water then once with 0.1M nitric acid and a further 3 times with deionized water.

4.I.1.2. Sample Collection.

The analytical methods for trace metals in water samples require the use of preconcentration methods in order to reduce the matrix interference besides concentrating the trace metals which are present at levels too low for direct determination by atomic absorption spectroscopy. The preconcentration step

needs a very pure uncontaminated sample hence it was essential to choose the correct type of sampling apparatus because of the ease of trace metal contamination at μg/l concentration [Riley (1975)].

For surface sampling a plastic or polypropylene bucket attached by a nylon rope is commonly used [Preston *et al.* (1972)]. This technique however, collects some of the surface water film which is enriched in heavy metal species. This problem could be obviated to some extent by the use of high-density polyethylene bottles or jerry cans which could be immersed by hand to well below the surface [Duce *et al.* (1972)].

For shallow waters (<100cm) Abdullah and Royle (1974) suggested that a simple vacuum pump drawing water through polythene tubing into a large Buchner flask was sufficient.

For depth sampling, the sampler was best constructed of polythene, polypropylene, polycarbonate, Teflon or perspex. In all cases, [Robertson (1968), IAEA (1970), and Spencer and Berwer (1970)] it was recommended that the sampler should be free of metals, neoprene rubber or other contaminating materials. If there are metal components in the sampler it should be coated with Teflon, and the rubber component in bottle caps replaced with Teflon or PVC caps.

Heavy metal impurities in polymer materials contaminate the sample. These generally result from catalysts, promoters or metal dyes used in the manufacturing process [Cresser (1957)]. These impurities were readily leached out with 10% nitric or hydrochloric acid. Karin *et al.* (1975) recommended a 3 days leach with 8M nitric acid for optimum removal of trace element contamination from polyethylene surfaces. By the acid leaching treatment the adsorption sites of the container material become activated and capable of removing trace metals from the sample [Batly and Gardner (1977)]. Hence it is essential that after acid treatment the containers should be well rinsed with distilled water followed by sample aliquots before sample collection.

4.I.1.3. Filtration.

Trace metal analyses are generally reported as both suspended particulate matter and on the "soluble" metal fraction of the water sample [Riley (1975)]. Filteration and centrifugation [IAEA (1970)] are the principal methods available for the separation of dissolved (filterable) and undissolved (unfilterable) trace metal fraction in water. Since it is essential that the separation should be carried out immediately after sample collection (to avoid trace metal redistribution on storage container) centrifugation was generally inconvenient and filtration was usually the only practicable procedure [Hunt (1979)] for attempting such separation but even this apparently simple operation may be associated with serious difficulties.

Filtration can also result in losses of trace metals. Depending on the speed of filtration, losses of between 10-30% of dissolved mercury from seawater have been observed when using untreated membrane filters [Gardner (1971)]. However, silicon treatment of glass fibres was successful in reducing losses to less than 7%. Several workers Duke and Woff (1968), Gardner and Riley (1974) showed that the equilibrium times for the adsorption and desorption of heavy metal in sediment-water mixtures were rapid and less than 72 hr., maximum adsorption occurred at pH values above 7.5.

The use of membrane filters with pore size of about 0.5 μm was generally considered to give separation of practical utility [Hunt (1979)]. The U.S. EPA (1974) has chosen 0.45 μm membrane filter (cellulose esters) as the basis of its standard separation technique. Several authoritative texts have also recommended this kind of filter paper [Strikland *et al*. (1968), APHA (1975), AOAC (1975)]. Spencer and Manhein (1969) investigated the trace metal content of Millipore HA filters (table 4). Batley and Gardner (1977) recommended acid prewashing of filter paper and filter apparatus to reduce trace metal contamination. Acid washing is obviously a sensible precaution to minimise contamination but it may also activate adsorption sites capable of removing metals from solution.

Table (4)

Concentration of contaminants in Millipore HA filter paper.

Elements	Concentrations (μg/g)
Iron Fe	5.90
Copper Cu	4.80
Zinc Zn	3.15
Chromium Cr	3.10
Aluminium Al	2.80
Manganese Mn	0.51
Lead Pb	0.35
Nickel Ni	0.34
Silver Ag	0.049
Cobalt Co	0.025

[Spencer and Manhein (1969)]

4.I.1.4. Sample Storage.

The choice of container is determined by both its adsorptive properties and the presence of surface impurities.

Glass is shown to function as a weak ion exchanger [Helfferich (1972)]. In acidic and slightly alkaline solution the negatively charged acid groups of the surface permit cation exchange [Adams (1972) and Doremus (1969)].

Teflon or high density polyethylene or polypropylene are the preferred material for the container. Bowdith *et al.* (1976) and Robertson (1968) recommended polyethylene bottles for storage because most polyethylene is very pure except for traces of iron.

Pyrex is also suitable but soft or soda glass should be avoided [Batley and Gardner (1977)].

There is often a delay between the time of collection and analysis or treatment of a sample, and hence a specific method for preservation and storage of the sample after collection must be followed to prevent contamination and storage losses during this interval [ASTM (1975)]. This is especially important in chemical speciation of trace metals as transformation of chemical species can occur during storage [Sheldon *et al.* (1967)]. Large ionic metal additions will drastically disturb the solution equilibria in the natural sample and the adsorptive behaviour of metal species may be quite different from that of natural water.

Bevan *et al.* (1975), Halliday and Liss (1976) recommended freezing of water sample after filtration, while Baker (1967) did not recommend freezing because this affected the distribution of heavy metals species unless a flash-freezing technique was used. Baier (1971) also reported no difference in lead concentration between frozen and unfrozen seawater samples. Batly and Gardner (1977) also reported no significant difference with respect to cadmium, lead and copper speciation between samples stored at room temperature and at 4°C over a 3 month period for seawater. The same was found for fresh water samples [Florence (1977)]. Harrison *et al.* (1975) confirmed the use of freeze drying methods for

storage and preconcentration of water samples.

4.I.1.5. Sample Pretreatment.

Perkin Elmer (1980) recommended that for the estimation of total metal, the unfiltered sample should be acidified with concentrated nitric acid (1ml HNO_3 /l sample) at the time of collection, and if suspended material is present, digestion with hot nitric acid or hydrochloric acid is recommended. The ASTM (1975) recommended the acidification of the sample after filtration with either hydrochloric acid or nitric acid because the acidification before filtration will release metals from particulate matter. Florence and Batley (1976) suggested the acidification with 2M nitric acid and boiling gently in a polyethylene bottle for 10-15 min to liberate all the trace metals in seawater samples. Batley and Farrar (1978) recommended the ultraviolet irradiation of acidified water to release the bonded heavy metals in natural water.

4.I.1.6. Sample Preconcentration.

The concentrations of dissolved and particulate trace metals in natural water are very low. Therefore the determination of these elements requires a prior concentration step which ideally enriches the transition and heavy metal ions enabling their determination by most of the available analytical methods free from interference and also aids in the speciation of metals in water. In order to satisfy these conditions several preconcentration or separation techniques have been employed.

4.I.1.6.1. Chelating Ion Exchange Resin.

Chelex-100 resin was chosen for evaluation as it has been used by several workers. Riley and Taylor (1964), Leyden (1975), Lee *et al.* (1976), Jan and Young (1978), Kingston *et al.* (1978), Orpwood (1980), Rasmusson (1981), Yetes (1982), and Danielsson *et al.* (1982) reported that chelex was capable of concentrating many metals simultaneously with good recovery

values. The resin was also commercially available in a pure form and a variety of mesh sizes. The resin was used in the ammonium form rather than the calcium form [Figura and McDhuffie (1979)] or hydrogen form [Lee *et al.* (1976), Florence and Batley (1976)] which would tend to give eluates rich in those elements and could cause interference problems in subsequent analysis. All the workers avoid the hydrogen form of the resin because the first few hundred ml of effluent from resin in this form would suffer a decrease in pH value through displacement of hydrogen ions by other cations in samples and this could lead to low recovery values. Abdullah *et al.* (1976) recommended the ammonium form of the resin because ammonium improves the recovery of trace metals from natural water.

Riley and Taylor (1964) and other workers preferred the resin to be in the column form rather than in batchwise extraction [Yates (1982)] because of the greater efficiency of the former technique.

The size of the resin column varies from 4 to 15 cm [Riley and Taylor (1978), Lee *et al.* (1976), Danielsson *et al.* (1982), Rasmusson (1981), Kingston *et al.* (1978)].

Columns were eluted with 25ml of 2M nitric acid. Pakals and Batley (1978) used 2M hydrochloric acid after elution with nitric acid and Riley and Taylor (1964) used 4M ammonia. But Danielsson and Magnusson (1982) found that ammonia interferes in the determination of trace metals.

4.I.1.6.2. Liquid-Liquid Extraction.

The most widely adopted preconcentration technique used with atomic absorption spectroscopy for both flame and flameless procedures is chelation solvent extraction [Morrison and Frieser (1958), Stary (1964), Joyner *et al.* (1967)]. The most commonly used chelation solvent extractant is probably ammonium pyrrolidine dithiocarbamate-methyl isobutyl ketone (APDC-MIBK) [Brooke *et al.* (1967)]. In addition, APDC and diethyl ammonium diethyl dithiocarbamate (DDDC) may be used as a combined extractant. The chelates may be extracted into

MIBK, chloroform or Freon TF (1,2,2,trifluoroethane). An advantage of the use of chloroform is that it can be recovered and reused, thus saving in costs over the other solvents [Aston (1985)]. The disadvantage of MIBK is that it will dissolve in water over a period of time. The basic method for the use of NaDDC and chloroform is reported by Bryan and Hummerstone (1973), and Danielsson *et al.* (1978) reported details for using APDC and DDC with Freon TF. Also Bruland *et al.* (1979) used APDC but with chloroform.

Extraction of trace metal ions by dithiocarbamate is known to depend on several factors such as:

1. Type of dithiocarbamate and its amount.
2. Organic solvent used.
3. Chemical form of metal ion.
4. pH of solution.
5. Shaking time.

This extraction method can be generally classified into two major categories. The first one involves the extraction of metal dithiocarbamate complexes into organic solvent and then analyzing the solvent directly. The second one is to extract the metal complexes into the organic solvent which is then followed by a nitric acid back extraction and analysis of the trace elements in the acid solution [Magnusson (1981)]. The acid back extraction i.e. extraction of metals from an organic solvent to an aqueous solution, can be replaced by using a dilute mercury (II) solution as used by Lo *et al.* (1982).

4.II. METHODOLOGY

INTRODUCTION.

Due to the difficulty of analysing trace metals, especially in seawater samples, a set of experiments was carried out to optimize the conditions to obtain the best results.

This section of work has concentrated on the following:

- Cleaning.
- Sampling.
- Storage.
- Treatment and Analysis of trace metals in seawater samples.

Two preconcentration techniques were utilized: A column ion exchange technique with chelex-100, and a solvent extraction technique.

The preconcentration techniques tested were selected either because they are widely used or because they seem quite promising. The procedures were either copied from the original author or slightly adapted.

4.II.1. INSTRUMENTATION.

The following instruments were used during the experimental work:

- pH meter (Consort) and glass pH electrode measuring in the range from 2 to 9.
- Stirring Plate.
- Millipore Filtration unit, Flask (2 litre), Funnel (250 ml), Filter support and Filter paper (0.45 μm pore size).
- Water Bath at 90°C temperature for sample digestion.
- Atomic absorption spectrophotometer (Perkin Elmer model 5000) coupled with graphite furnace (HGA model 500) and autosampler (As 40) were used in the analysis. The analytical conditions for trace metals (Cr, Cu, Fe, Mn and Ni) are shown in Appendix II and III.
- Atomic Absorption Spectrophotometer (Perkin Elmer model 503) was used in Zn determination by using flame air/acetylene (40/60 ml/min).
- Perkin Elmer model 56 recorder and PRS 10 printer were

used.

- Inductively Coupled Plasma Mass Spectrometery (Perkin Elmer elan 5000). The analytical conditions are shown in Appendix II.

4.II.2. Chemical Reagents.

4.II.2.1. Double Distilled Water. Pure double distilled water was obtained by redistilling distilled water in a pyrex distillation system.

4.II.2.2. Nitric Acid (2M). Nitric acid (Aristar) (126.5 ml) was added into a 1 litre volumetric flask then a double distilled water was added, completed to the mark and mixed well. The solution was prepared daily.

4.II.2.3. Ammonia Solution (2M). Ammonia solution (25% NH_4 Analar) (112.1 ml) was added to a 1 litre volumetric flask containing double distilled water, completed to the mark and mixed well. The solution was prepared daily.

4.II.2.4. Acetate Buffer Solution. Ammonium acetate (NH_4CH_2COOH) (145 g) was dissolved in 1 litre double distilled water (pH 7.0).

4.II.2.5. Celex-100 Resin. 100-200 mesh size in the sodium form (Bio-Rad) was used.

4.II.2.6. Freon TF. 1,1,2-trichloro-1,2,2-trifluoroethane. This was redistilled.

4.II.2.7. MIBK. Methyl Isobutyl Ketone solvent.

4.II.2.8. Purified 2% Ammonium Pyrrolidine Dithiocarbamate + Diethylammonium Diethyl Dithiocarbamate. 2.0 g of ammonium pyrrolidine dithiocarbamate (APDC), and 2.0 g of diethylammonium diethyl dithiocarbamate (DDDC) were weighed

out, dissolved in 100 ml of deionized distilled water, and purified by shaking with 100 ml of Freon TF in a separatory funnel.

4.II.2.9. 8-Hydroxyquinoline. 2.0 g of 8-hydroxyquinoline was weighed out and dissolved in about 20 ml of water, then 6 ml glacial acetic acid was added. The solution was diluted to 100 ml with water.

4.II.2.10. 4% Ammonium Pyrrolidine Dithiocarbamate (APDC). 4.0 g of ammonium pyrrolidine dithiocarbamate (APDC) was weighed out, dissolved in 100 ml of deionized distilled water, and purified by shaking with 100 ml of MIBK in a separatory funnel.

4.II.2.11. Standard Solutions (stock solutions of 1000 mg/L). Stock solutions of iron as ferric nitrate, of chromium as chromic chloride, of zinc as zinc acetate, of nickel as nickel chloride, of copper as cupric nitrate were obtained from BDH as Atomic Absorption grades. The stock solutions were diluted as required to give working solutions immediately before use.

4.II.2.12. Working Solutions. A series of mixed standards (Cr, Cu, Mn, and Ni) were prepared (0.02, 0.04 and 0.06 μg/ml) in 2M nitric acid (HNO_3). Concentrations of 0.05, 0.1 and 0.15 μg/ml were used in Fe analysis and 1.0, 3.0 and 5.0 μg/ml in Zn analysis.

4.II.3. TECHNIQUES.

4.II.3.1. Cleaning of Glass and Plastic Wares. The glass and plastic wares were soaked in 10% nitric acid (Analar) overnight followed by washing three times with deionised distilled water, then 2 times with double distilled water. One of the washings was done just before use [Gardner and Hunt (1981)].

4.II.3.2. Sample Collection. The seawater sample was collected under the surface (1m) in a polyethylene container 25 litres (precleaned) using a simple vacuum pump. The water passed through a polyethylene tube into the container [Abdullah and Royle (1974)]. Later in the lab the sample was shaken well and distributed into 1 litre polyethylene bottles (precleaned).

4.II.3.3. Sample Preparation. The samples were acidified with 1 ml (per l) of concentrated nitric acid (Aristar). The sample pH was 1.5 (± 0.25) (after addition of acid). The samples were spiked before acidification if needed.

The polyethylene bottles were kept in a water bath at temperature 90°C for 30 min [Florence and Batley (1976)] because the total concentration (dissolved and suspended metals) of trace metals have to be investigated.

4.II.3.4. Filtration. The pretreated samples were filtered through 0.45 μm millipore filter paper prewashed with 20 ml of 0.2M nitric acid (Aristar) followed by 100 ml of double distilled water [Batley and Gardner (1977)]. The filtration apparatus was washed with 10% nitric acid (Aristar).

4.II.3.5. Storage. The pretreated samples were stored in polyethylene bottles at room temperature (22°C) [Batley and Gardner (1977)].

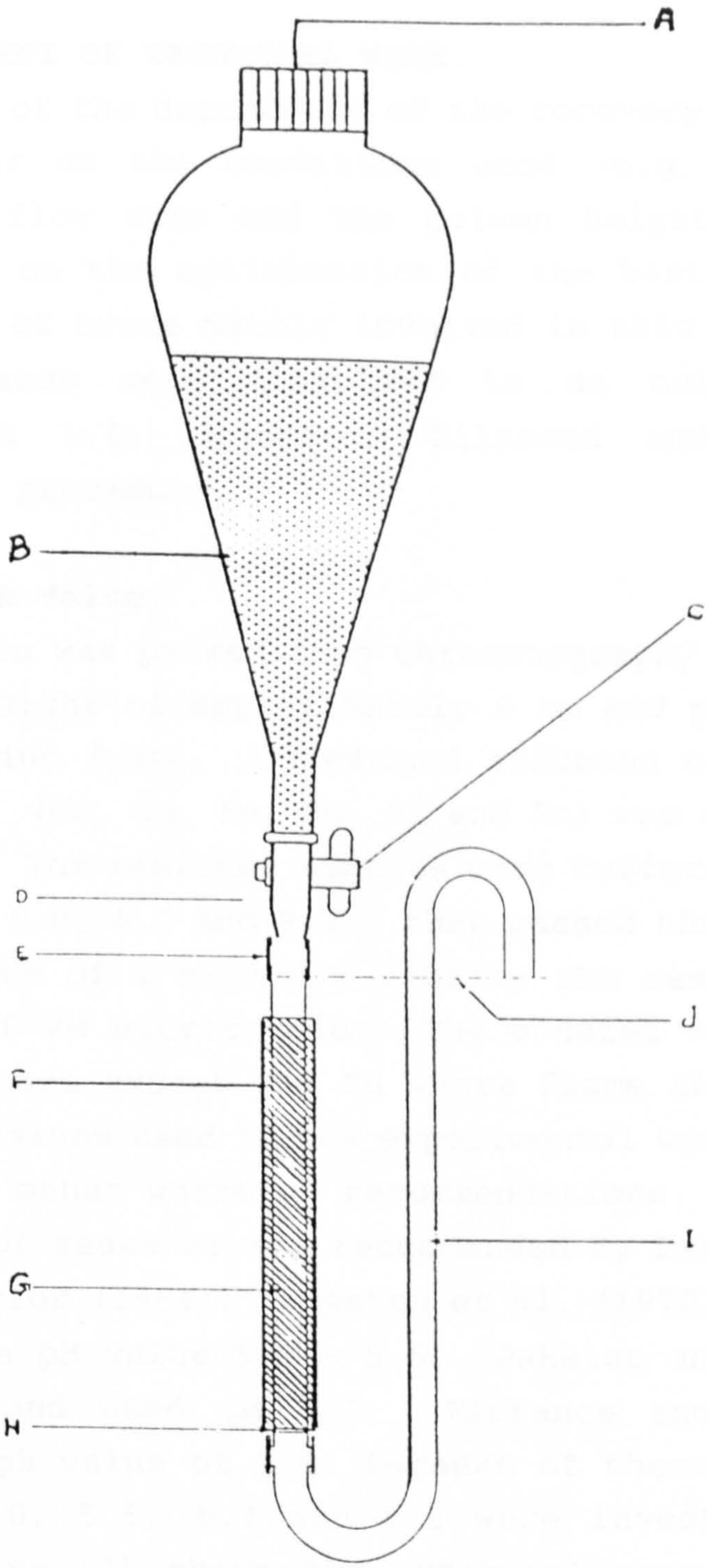
4.II.3.6. PRECONCENTRATION WITH CHELEX-100.

4.II.3.6.1. Column Preparation and Purification. Chelex-100 resin was cleaned in 1:4 hydrochloric acid (Aristar) and then in 1:4 nitric acid (Aristar) for one week in each bath. Between each acid wash the resin was rinsed with double distilled water, Chromatography columns (i.d. 1.5 cm) were then packed with a slurry of chelex-100 (100-200 mesh size) hydrogen form. Then the resin was washed with 25 ml of 2M nitric acid (Aristar) to elute any traces of contaminants present in the resin and then washed with double distilled

water. The resin was then converted to the ammonium form by the addition of 4M ammonia solution, and washed with double distilled water. 10ml of 2M ammonium acetate was added to buffer the resin and the column was washed with double distilled water and the pH value was measured to check the basicity of the column (pH 7.6-8.0). After this step the column was ready for sample passage. Figure (6) shows the ion-exchange apparatus.

4.II.3.6.2. Column Preconcentration and Preparation Procedure. The pH of the pretreated sample was adjusted to the required value. The sample was passed through the resin with flow rate 0.2 ml/min until the shrinkage of the resin was completed. The flow rate was then increased to 1.0 ml/min and left overnight. A 70 ml of 2M ammonium acetate was added and passed through the column at a flow rate 0.5 ml/min. Then the column was washed with 10 ml of double distilled water. Then trace metals were eluted with 25 ml of 2M nitric acid (Aristar) and collected, after which 5 ml of water was passed and collected. The column was then washed with 5 ml of double distilled water.

The eluate volume was reduced by evaporation to near dryness and then transferred into a 25 ml volumetric flask and made up to volume with 2M nitric acid (Aristar).



KEY:

A Hole for sample introduction
B Polyethylene separating funnel
C Stop cock
D Polyethylene cap
E PVC tubing used to connect tubes
F Chromatography column
G Chelex-100 resin
H Porous polyethylene frit, welded to the inside of the tube F
I Swan neck glass
J Water level will not fall below this level

Figure (6) Ion Exchange Apparatus.

4.II.4. DEVELOPMENT OF TECHNICAL WORK.

Because of the dependence of the recovery of trace metals from seawater on the conditions used (e.g. the pH of the sample, the flow rate and the column height) this work is concentrated on the optimization of the best conditions for the recovery of trace metals involved in this project. Trace metal standards were dissolved in an acidified natural seawater (pH 1.6) digested, filtered and used in the optimization procedure.

4.II.4.1. pH Value.

The resin was packed into chromatography columns (1.5 mm dia.) to a height of approximately 8 cm and prepared for use in the ammonium form. A combined solution of 0.03 μg/ml of each element (Cr, Cu, Fe, Mn, Ni and Zn) was added to 1 litre of seawater. The seawater samples were buffered to various pH values (2.0, 5.0, 6.7 and 8.2), then passed through the column at a flow rate of 1 ml/min. Finally the resins were washed with 25 ml of 2M nitric acid. The eluates were analysed by graphite furnace except for Zn where flame AAS was used.

The pH values used in the experimental work were selected according to other workers' recommendations. The natural pH value (8.2) of seawater was recommended by Lee *et al.* (1976). Riley and Taylor (1964), Kingston *et al.* (1978), and Rasmussen (1981) used a pH value 5.0 - 5.5. Pakalns and Batley (1978) recommended and used pH 6.7. Florence and Batley (1976) suggested a pH value of 2.0. Because of these variations, pH values of 2.0, 5.5, 6.7 and 8.2 were investigated in this study. Figure (7) shows the graphical presentation of the recovered concentrations of different trace metals at different pH values (For the purpose of these graphs, the vertical scale indicates concentrations converted to a notional volume of 1 litre. Thus, a recovery shown as 0.03 mg/l corresponds to 100% recovery).

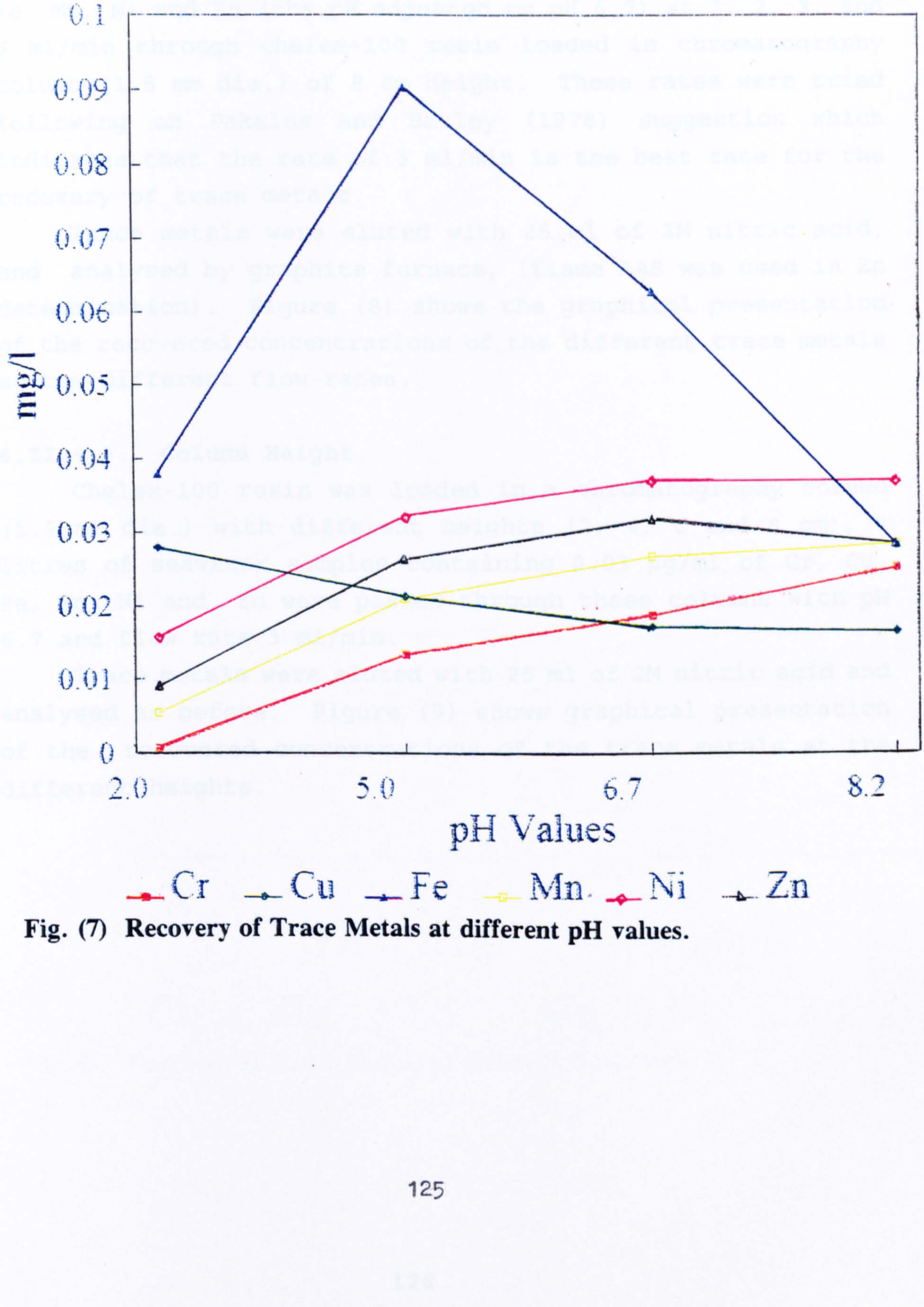


Fig. (7) Recovery of Trace Metals at different pH values.

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4.II.4.2. Flow Rate.

The flow rate of the samples was investigated by passing a 1 litre sample (seawater) containing 0.03 μg/ml of Cr, Cu, Fe, Mn, Ni and Zn (the pH adjusted to pH 6.7) at 1, 2, 3, and 5 ml/min through chelex-100 resin loaded in chromatography column (1.5 mm dia.) of 8 cm height. These rates were tried following on Pakalns and Batley (1978) suggestion which indicates that the rate of 3 ml/min is the best rate for the recovery of trace metals.

Trace metals were eluted with 25 ml of 2M nitric acid, and analysed by graphite furnace, (flame AAS was used in Zn determination). Figure (8) shows the graphical presentation of the recovered concentrations of the different trace metals at the different flow rates.

4.II.4.3. Column Height.

Chelex-100 resin was loaded in a chromatography column (1.5 mm dia.) with different heights (2, 4, 6 and 8 cm), 4 litres of seawater samples containing 0.03 μg/ml of Cr, Cu, Fe, Mn, Ni and Zn were passed through these columns with pH 6.7 and flow rate 3 ml/min.

Trace metals were eluted with 25 ml of 2M nitric acid and analysed as before. Figure (9) shows graphical presentation of the recovered concentrations of the trace metals at the different heights.

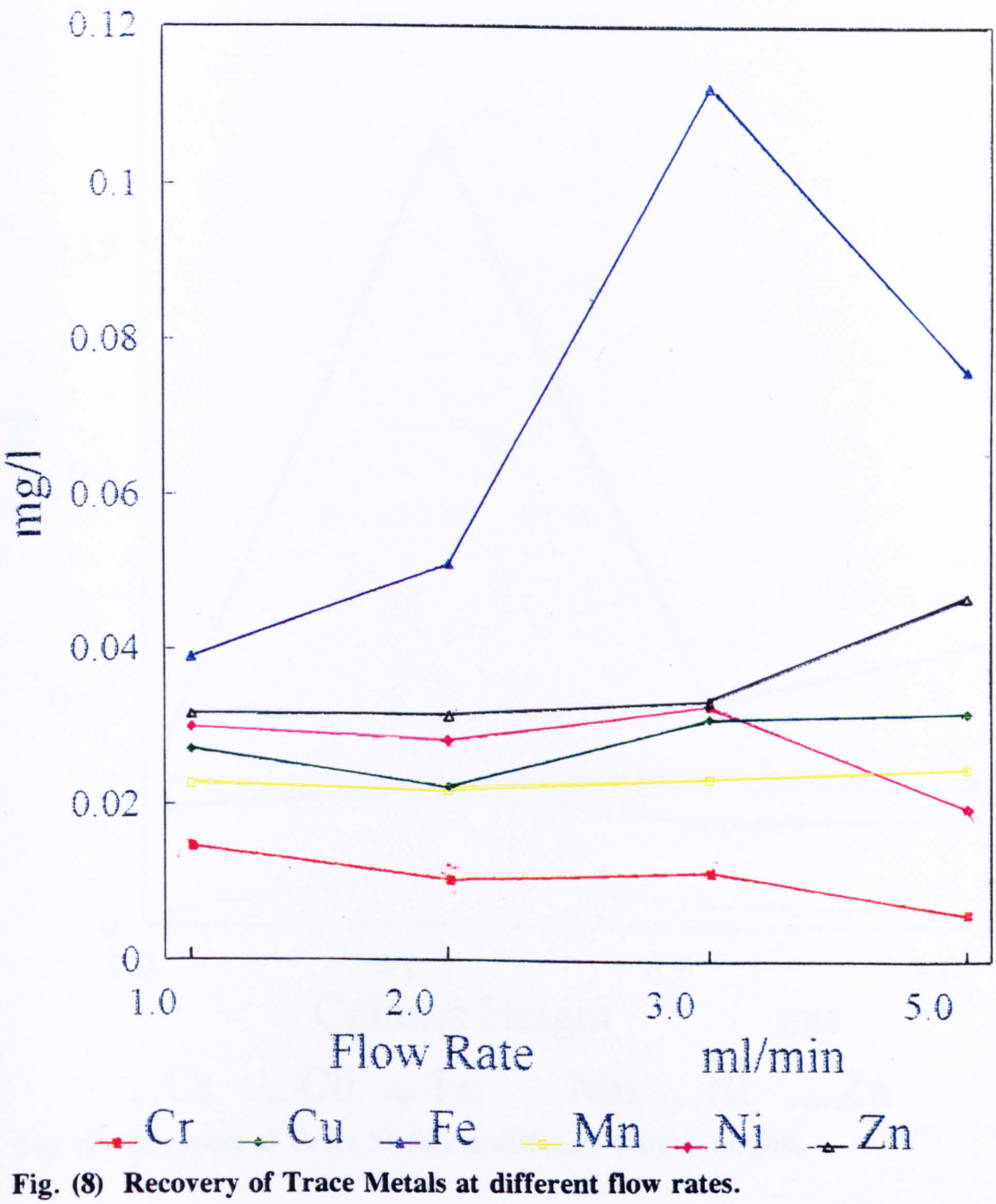

Fig. (8) Recovery of Trace Metals at different flow rates.

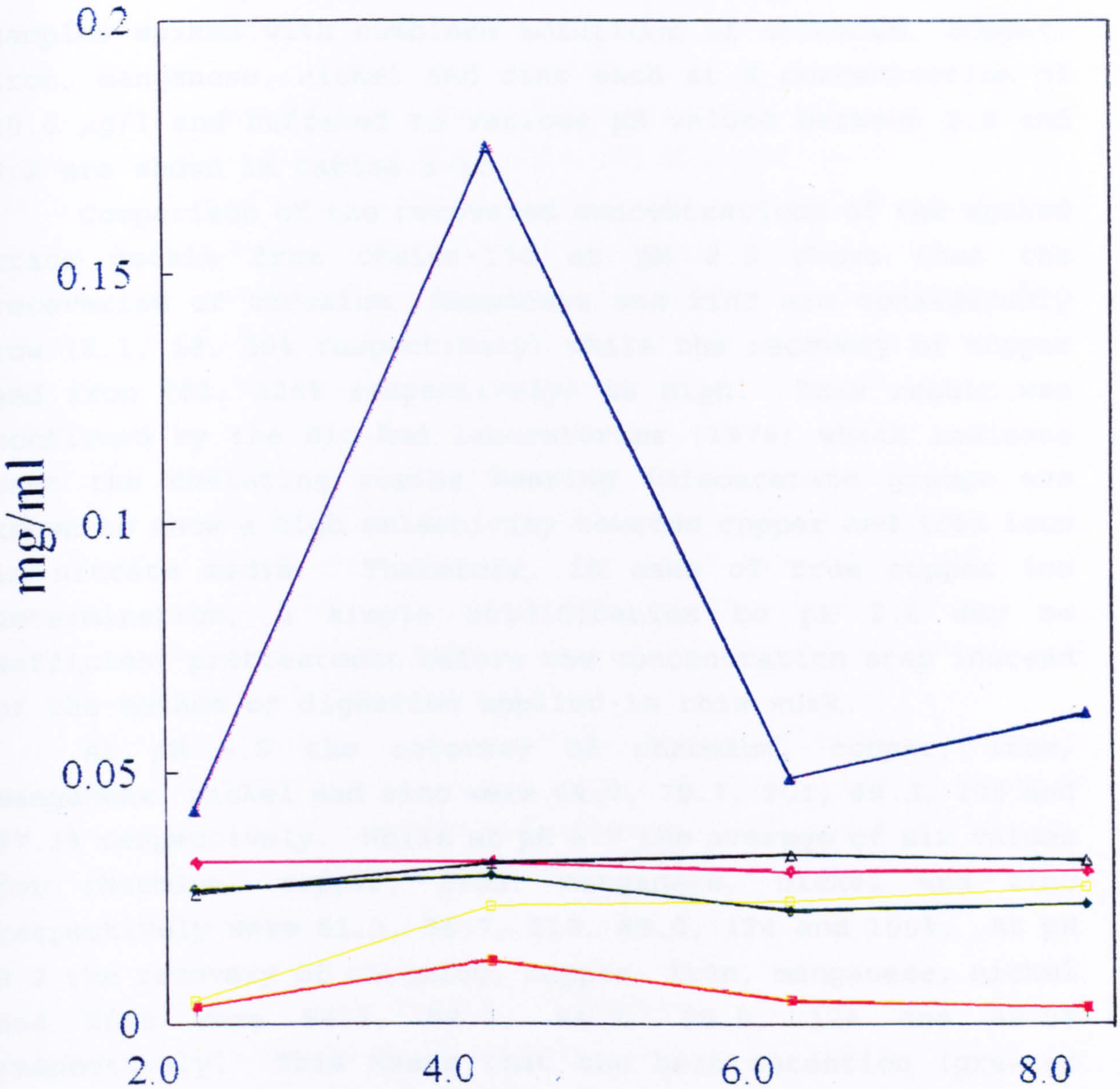

Fig. (9) Recovery of Trace Metals at different column heights.

4.II.4.4. RESULTS AND DISCUSSION.

- **Effect of pH.** The results of the analyses of seawater samples spiked with combined solutions of chromium, copper, iron, manganese, nickel and zinc each at a concentration of 30.0 μg/l and buffered to various pH values between 2.0 and 8.2 are shown in tables 5-10.

Comparison of the recovered concentrations of the spiked trace metals from chelex-100 at pH 2.0 shows that the recoveries of chromium, manganese and zinc are considerably low (2.1, 18, 30% respectively) while the recovery of copper and iron (93, 126% respectively) is high. This result was confirmed by the Bio-Rad laboratories (1978) which indicate that the chelating resins bearing iminoacetate groups are known to show a high selectivity towards copper and iron ions in nitrate media. Therefore, in case of free copper ion determination, a simple acidification to pH 2.0 may be sufficient pretreatment before the concentration step instead of the method of digestion applied in this work.

At pH 5.0 the recovery of chromium, copper, iron, manganese, nickel and zinc were 44.7, 70.7, 301, 69.3, 108 and 87.3% respectively. While at pH 6.7 the average of six values for chromium, copper, iron, manganese, nickel and zinc respectively were 81.3, 56.7, 210, 89.0, 124 and 106%. At pH 8.2 the recovery of chromium, copper, iron, manganese, nickel and zinc were 84.3, 58.3, 94.7, 95.0, 124 and 95.0% respectively. This means that the best retention (greater than 81%) of the trace metals under investigation is when the pH value of the sea water sample is higher than 5.0.

There are high recoveries of nickel and iron at the different pH values (tables 7 and 9): this may indicate interferences or contamination which will be investigated later.

- **Effect of Flow Rate.** The effect of increasing flow rate on recoveries was investigated by passing 1 litre of seawater samples containing 30.0 μg/l of chromium, copper, iron,

manganese, nickel and zinc through 8 cm column of chelex-100 at 1-5 ml/min flow rates and the pH were adjusted to pH 6.7, this pH value was chosen as the best recovered value of most of the parameters. The results of analyses are shown in tables 11-16.

The recoveries of chromium and nickel were essentially constant up to 3 ml/min flow rate and dropped above this rate. At flow rate of 5 ml/min the recoveries of chromium and nickel respectively were 20.7 and 65.3%. Manganese and zinc showed higher recoveries (82.0 and 155% respectively) at higher flow rate (5.0 ml/min) and this indicates that manganese and zinc are strongly bonded to the iminoacetate groups of the chelex resin.

The recovery of iron increased with increase of the flow rate 130, 166 and 373% at 1, 2 and 3 ml/min respectively but it dropped sharply when the flow rate was increased to 5 ml/min (254%). The increase in the amount of iron content is due to contamination from the double distilled water and chemicals used in the analysis.

The recovery of trace metals was essentially constant during the investigation (1, 2 and 3 ml/min) this is because of the swelling and contraction of the resin (as the counter-ion is changed) which creates difficulties in maintaining column flow rate.

- **Effect of Column Height.** Seawater samples were passed through 2, 4, 6 and 8 cm columns of 100-200 mesh chelex-100 resin at a flow rate of 3 ml/min. The seawater samples were buffered to pH 6.7. The trace metals were eluted from the resin with 25 ml of 2M nitric acid. Tables 17-22 show the results of the analyses.

The column with 2 cm height shows poor recovery of the investigated trace metals, this may result from the short contact time between the trace metals and the chelating resin, or because of the capacity of the resin is small. The 4, 6 and 8 cm heights show good recoveries, but the columns with 6 and 8 cm results show less recovery than the 4 cm column

height (Cr, Cu, Fe and Ni). This could mean that the volume of the 2M nitric acid (25 ml) passed through a long path of chelex-100 resin is not sufficient to elute the trace metals. This is confirmed by Pakalns *et al.* (1978) who studied the problems of recovering trace metals from the resin column and concluded that a minimum of 25 ml of dilute nitric acid is required to elute metals from a 50-100 mesh resin, and using finer particle size 100-200 mesh is more efficient for metal removal, but the elution with 25 ml is very inefficient, it requires more than 100 ml of acid for quantitative spike recovery.

The results presented in tables 5-22 and figures 7, 8 and 9 show that the metals (Cu, Fe, Mn, Ni and Zn) are recovered satisfactorily with the exception of Cr. Riley and Taylor (1964) reported that Cr is very strongly retained by the resin and that no reagent could be found which would elute it completely. This comment is in agreement with the result of this work.

The recovery of Fe (more than 100%) indicates a very high contamination factor which could arise from the chemicals used or leached from the resin during the analyses.

Note on tables 5-22: The column headings 1st, 2nd ...etc, refer to replicate measurements. Each cell in the table gives the average of three determinations.

4.II.4.5. CONCLUSION.

The trace elements determined here are present in a very complex matrix (comprising both inorganic and organic constituents) and low concentrations. Therefore, they required prior concentration.

Passing seawater samples at pH 6.7 through column of chelex-100 resin (100-200 mesh size) in the ammonium form with 4 cm height and at flow rate 3 ml/min was the most suitable condition for concentrating trace metals and minimising the interference of alkali and alkali earth metals.

Table (5).

Recovery of Cr std. in seawater at different pH values. Concentrations in μg/ml.

pH	1st	2nd	3rd	4th	5th	6th	mean	s.d.
2.0	0.0006	0.0007	0.0010	0.0002	0.0005	0.0010	0.00067	0.00028
5.0	0.0219	0.0234	0.0244	0.0004	0.0045	0.0058	0.01340	0.0109
6.7	0.0344	0.0314	0.0344	0.0003	0.0110	0.0110	0.01880	0.0204
8.2	0.0369	0.0329	0.0329	0.0120	0.0100	0.0270	0.02530	0.0115

Table (6).

Recovery of Cu std. in seawater at different pH values. Concentrations in μg/ml.

pH	1st	2nd	3rd	4th	5th	6th	mean	s.d.
2.0	0.0250	0.0250	0.0250	0.0295	0.0350	0.0280	0.0279	0.00395
5.0	0.0230	0.0210	0.0210	0.0190	0.0230	0.0200	0.0212	0.00160
6.7	0.0160	0.0160	0.0140	0.0198	0.0178	0.0198	0.0172	0.00230
8.2	0.0170	0.0120	0.0160	0.0177	0.0187	0.0175	0.0165	0.00240

Table (7)

Recovery of Fe std. in seawater at different pH. Concentrations in μg/ml.

pH	1st	2nd	3rd	4th	5th	6th	mean	s.d.
2.0	0.0375	0.0500	0.0530	0.0210	0.0280	0.233*	0.0379	0.0138
5.0	0.0590	0.0690	0.1440	0.0270	0.0170	0.226	0.0903	0.0800
6.7	0.0540	0.1140	0.0920	0.0300	0.0250	0.038*	0.0630	0.0389
8.2	0.0260	0.0380	0.0430	0.0240	0.0110	0.286*	0.0284	0.0126

*Excluded

Table (8)

Recovery of Mn std. in seawater at different pH values. Concentrations in μg/ml.

pH	1st	2nd	3rd	4th	5th	6th	mean	s.d.
2.0	0.00019	0.00026	0.00037	0.0196	0.0073	0.0049	0.0054	0.0075
5.0	0.0200	0.0270	0.0250	0.0156	0.0188	0.0184	0.0208	0.0043
6.7	0.0260	0.0280	0.0280	0.0253	0.0270	0.0259	0.0267	0.0011
8.2	0.0300	0.0310	0.0300	0.0270	0.0260	0.0270	0.0285	0.0021

Table (9)

Recovery of Ni std. in seawater at different pH values. Concentrations in μg/ml.

pH	1st	2nd	3rd	4th	5th	6th	mean	s.d.
2.0	0.0140	0.0060	0.0038	0.0290	0.0212	0.0207	0.0158	0.0097
5.0	0.0350	0.0260	0.0180	0.0360	0.0430	0.0360	0.0323	0.0089
6.7	0.0380	0.0350	0.0380	0.0370	0.0390	0.0370	0.0373	0.0014
8.2	0.0380	0.0390	0.0380	0.0370	0.0340	0.0370	0.0372	0.0017

Table (10)

Recovery of Zn std. in seawater at different pH values. Concentrations in μg/ml.

pH	1st	2nd	3rd	4th	5th	6th	mean	s.d.
2.0	0.00425	0.0094	0.0051	0.0220	0.0110	0.0029	0.0090	0.0070
5.0	0.0290	0.0250	0.0260	0.0260	0.0250	0.079*	0.0262	0.0016
6.7	0.0390	0.0220	0.0290	0.0300	0.0300	0.0410	0.0318	0.0070
8.2	0.0290	0.0320	0.0270	0.0270	0.0310	0.0250	0.0285	0.0027

*Excluded

Table (11)

Recovery of Cr std. in seawater at different flow rates. Concentrations in μg/ml.

ml/min	1st	2nd	3rd	4th	5th	6th	mean	s.d.
1	0.0059	0.0069	0.0104	0.0164	0.0241	0.0246	0.0147	0.0083
2	0.0063	0.0058	0.0068	0.01697	0.0168	0.0097	0.0104	0.0052
3	0.0118	0.0083	0.0073	0.0108	0.0108	0.0185	0.0113	0.0039
5	0.0041	0.0074	0.0024	0.0105	0.0054	0.0077	0.0062	0.0029

Table (12)

Recovery of Cu std. in seawater at different flow rates. Concentrations in μg/ml.

ml/min	1st	2nd	3rd	4th	5th	6th	mean	s.d.
1	0.0160	0.0180	0.0390	0.0282	0.0282	0.0332	0.0271	0.0088
2	0.0220	0.0170	0.0170	0.0232	0.0282	0.0257	0.0222	0.0045
3	0.0230	0.0210	0.0220	0.0410	0.0385	0.0410	0.0311	0.0100
5	0.0240	0.0260	0.0180	0.0537	0.0357	0.0332	0.0318	0.0125

Table (13)

Recovery of Fe std. in seawater at different flow rates. Concentrations in μg/ml.

ml/min	1st	2nd	3rd	4th	5th	6th	mean	s.d.
1	0.048	0.044	0.106*	0.044	0.0*	0.020	0.039	0.0128
2	0.075	0.067	0.071	0.0038*	0.020	0.020	0.051	0.280
3	0.121	0.085	0.103	0.139	0.073	0.150	0.112	0.0303
5	0.112	0.122	0.082	0.042	0.053	0.048	0.076	0.0345

*Excluded

Table (14)

Recovery of Mn std. in seawater at different flow rates. Concentrations in μg/ml.

ml/min	1st	2nd	3rd	4th	5th	6th	mean	s.d.
1	0.0186	0.0206	0.0216	0.0265	0.0240	0.0245	0.0226	0.0029
2	0.0191	0.0201	0.0211	0.0226	0.0241	0.0230	0.0217	0.0019
3	0.0212	0.022	0.0212	0.0250	0.0250	0.0255	0.0233	0.0020
5	0.0236	0.0242	0.0242	0.0249	0.0239	0.0269	0.0246	0.0012

Table (15)

Recovery of Ni std. in seawater at different flow rates. Concentrations in μg/ml.

ml/min	1st	2nd	3rd	4th	5th	6th	mean	s.d.
1	0.0210	0.0198	0.0210	0.0379	0.0407	0.0398	0.0300	0.0104
2	0.0220	0.0197	0.0210	0.0348	0.0415	0.0301	0.0282	0.0088
3	0.0220	0.0220	0.0200	0.0459	0.0402	0.0468	0.0328	0.0128
5	0.0210	0.0250	0.0210	0.0295	0.0124	0.0086	0.0196	0.0077

Table (16)

Recovery of Zn std. in seawater at different flow rates. Concentrations in μg/ml.

ml/min	1st	2nd	3rd	4th	5th	6th	mean	s.d.
1	0.0272	0.0308	0.0367	0.0334	0.0297	0.0324	0.0317	0.0033
2	0.0290	0.0297	0.0387	0.0290	0.0331	0.0297	0.0315	0.0038
3	0.0243	0.0256	0.0177	0.0442	0.0381	0.0496	0.0333	0.0126
5	0.0432	0.0502	0.0436	0.0653	0.0422	0.0354	0.0467	0.0103

Table (17)

Recovery of Cr std. in seawater at different column heights (cm). Concentrations in µg/ml.

height cm	1st	2nd	3rd	4th	mean	s.d.
2	0.00485	0.00435	0.00165	0.0127*	0.0036	0.0017
4	0.01495	0.01185	0.01265	0.01145	0.0127	0.0016
6	0.00440	0.00685	0.00602	0.00397	0.0053	0.0014
8	0.00146	0.00214	0.00854	0.00114	0.0033	0.0035

*Excluded

Table (18)

Recovery of Cu std. in seawater at different column heights (cm). Concentrations in µg/ml.

height cm	1st	2nd	3rd	4th	mean	s.d.
2	0.0276	0.0244	0.0265	0.0312	0.0274	0.0028
4	0.0300	0.0310	0.0280	0.0280	0.0293	0.0015
6	0.0210	0.0187	0.0246	0.0248	0.0223	0.0030
8	0.0236	0.0241	0.0236	0.0230	0.0236	0.0005

Table (19)

Recovery of Fe std. in seawater at different column heights (cm). Concentrations in µg/ml.

height cm	1st	2nd	3rd	4th	mean	s.d.
2	0.0413	0.0403	0.0390	0.0493	0.0425	0.0047
4	0.1210	0.0303*	0.1930	0.2100	0.1750	0.0470
6	0.0304	0.0540	0.0540	0.0573	0.0489	0.0489
8	0.0647	0.0807	0.0537	0.0487	0.0620	0.0140

*Excluded

Table (20)

Recovery of Mn std. in seawater at different column heights (cm). Concentrations in μg/ml.

height cm	1st	2nd	3rd	4th	mean	s.d.
2	0.0047	0.0052	0.0039	0.0252*	0.0046	0.0006
4	0.0136	0.0203	0.0281	0.0307	0.0232	0.0078
6	0.0260	0.0270	0.0230	0.0206	0.0242	0.0029
8	0.0267	0.0277	0.0265	0.0273	0.0271	0.0006

*Excluded

Table (21)

Recovery of Ni std. in seawater at different column heights (cm). Concentrations in μg/ml.

height cm	1st	2nd	3rd	4th	mean	s.d.
2	0.0313	0.0346	0.0313	0.0313	0.0321	0.0017
4	0.0344	0.0311	0.0311	0.0316	0.0321	0.0016
6	0.0320	0.0303	0.0305	0.0300	0.0307	0.00089
8	0.0303	0.0301	0.0302	0.0305	0.0303	0.00017

Table (22)

Recovery of Zn std. in seawater at different column heights (cm). Concentrations in μg/ml.

height cm	1st	2nd	3rd	4th	mean	s.d.
2	0.0225	0.03298	0.0258	0.0218	0.02577	0.005
4	0.0329	0.0329	0.0295	0.0315	0.0317	0.0016
6	0.0333	0.0316	0.0348	0.0348	0.0336	0.0015
8	0.0303	0.000	0.0362	0.0303	0.0323	0.0034

4.II.5. Preconcentration with Organic Solvents.

The preconcentration technique involves chelation with a complex of ammonium pyrrolidine dithiocarbamate (APDC) and 8-hydroxyquinoline , or a complex of ammonium pyrrolidine dithiocarbamate (APDC) and diethylammonium diethyl dithiocarbamate (DDDC). This is followed by double extraction into either methyl isobutyl ketone or Freon TF as solvent followed by back extraction to an aqueous phase with nitric acid.

4.II.5.1. Extraction into Methyl Isobutyl Ketone and Back-Exraction into Nitric Acid.

200 ml of the pretreated seawater sample was transferred into a teflon separatory funnel, and buffered to about pH 4 with 2 ml of ammonium acetate. Then 2 ml of a purified solution contaning 4% (w/v) of APDC and 1 ml of 2% (w/v) 8-hydroxyquinoline, then 15 ml of MIBK were added. The funnel was shaken vigorously for 3 min, and the phases then allowed to separate (15 min). The upper phase was withdrawn by means of a Finn Pipette directly into a 50 ml teflon separatory funnel, which was closed tightly. The pH of the aqueous phase was adjusted to 9.2 with ammonia, another 5 ml of MIBK was added, and the separatory funnel was shaken vigorously for 3 min in order to extract Mn, and allowed to stand for at least 5 min for phase separation. The upper phase was then withdrawn and added to the 50 ml separatory funnel. Then 0.5 ml of concentrated nitric acid (Aristar) was added to the combined extract, the funnel was shaken vigorously for 30 sec., and allowed to stand for at least 5 min. Finally, a 9.5 ml of deionized distilled water was added, shaken vigorously for 30 sec., and allowed to stand for 15 min. Then the aqueous phase was transferred to a 10 ml polyethylene bottle which was closed tightly [Sturgeon *et al*. (1980)]. Table (23) shows the results of the extraction analysis, performed by the GF-AAS.

Table (23)

Recovery of metals in Seawater by Extraction into MIBK and Back Extraction in HNO_3 Acid. Rows refer to different trials.

Metal					
Cr	Cu	Fe	Mn	Ni	Zn
Added µg/ml					
0.005	0.003	0.2	0.002	0.02	0.025
Found µg/ml					
0.0007	0.0019	0.105	0.0012	0.0125	0.016
0.001	0.0019	0.080	0.0015	0.0114	0.014
0.0011	0.0019	0.099	0.0013	0.0116	0.007
0.0015	0.0017	0.121	0.0014	0.0122	0.013
0.0007	0.0018	0.128	0.0011	0.0119	0.008
0.0008	0.0019	0.115	0.0012	0.0117	0.012
0.0009	0.0017	0.105	0.0015	0.0120	0.011
0.0010	0.0018	0.123	0.0014	0.0124	0.008
0.0015	0.0016	0.122	0.0011	0.0122	0.008
0.000	0.0016	0.012	0.0013	0.0125	0.012
% Recovery*					
	65.0	53.0	60.0	62.3	65.2
	65.0	40.0	75.0	65.8	57.2
	62.0	50.0	65.0	62.3	29.4
	55.0	61.0	70.0	57.8	53.4
	58.0	64.0	55.0	60.8	33.4
	62.0	58.0	60.0	59.3	49.4
	55.0	53.0	75.0	58.3	45.4
	58.0	62.0	70.0	59.8	33.4
	52.0	61.0	55.0	61.8	33.4
	52.0	62.0	65.0	60.8	49.4

* Chromium recoveries were near zero in all cases.

4.II.5.2. Extraction into Methyl Isobutyl Ketone.

200 ml of the pretreated seawater sample was transferred into a teflon separatory funnel, and buffered to about pH 4 with 2 ml of ammonium acetate. Then 2 ml of purified solution containing 4% (w/v) of APDC and 1 ml of 2% (w/v) 8-hydroxyquinoline, then 15 ml of MIBK were added. The funnel was shaken vigorously for 3 min, and the phases then allowed to separate (15 min). The upper phase was withdrawn by means of a Finn Pipette directly into a 50 ml teflon separatory funnel, which was closed tightly. The pH of the aqueous phase was adjusted to 9.2 with ammonia, another 5 ml of MIBK was added, and the separatory funnel was shaken vigorously for 3 min in order to extract Mn, and allowed to stand for at least 5 min for phase separation. The analysis was then performed by the graphite furnace method.

Table (24) shows the results of the extraction.

Table (24)

Recovery of metals in Seawater by Extraction into MIBK.

Rows refer to different trials.

Metal				
Cu	Fe	Mn	Ni	Zn
Added µg/ml				
0.003	0.200	0.002	0.020	0.025
Found µg/ml				
0.0029	0.198	0.0017	0.0193	0.023
0.0030	0.186	0.0019	0.0202	0.021
0.0029	0.192	0.0021	0.0198	0.024
0.0028	0.193	0.0019	0.0199	0.024
0.0027	0.190	0.0022	0.0183	0.022
0.0026	0.192	0.0019	0.0197	0.023
0.0029	0.197	0.0019	0.0192	0.020
0.0028	0.194	0.0020	0.0197	0.021
0.0029	0.188	0.0018	0.0199	0.024
0.0028	0.198	0.0019	0.0199	0.023
% Recovery				
97.0	99.0	85.0	96.5	93.2
100	93.0	95.0	(101)	85.2
98.0	96.0	(105)	99.0	97.2
93.0	96.5	95.0	99.5	97.2
90.0	95.0	(110)	91.5	89.2
87.0	96.0	93.5	98.5	93.2
97.0	98.5	99.0	96.0	81.2
93.0	97.0	(101)	98.5	85.2
96.0	94.0	89.5	99.5	97.2
92.0	99.0	97.5	99.5	93.2

4.II.5.2. Extraction into Freon and Back-Extraction into Nitric Acid.

200 ml of the pretreated seawater sample was transferred into a teflon separatory funnel, and buffered to about pH 4 with 2 ml of ammonium acetate. 5 ml of purified solution containing 2% (w/v) of APDC and DDDC, then 20 ml of Freon were added. The funnel was shaken vigorously for 3 min, and the phases then allowed to separate (15 min). Then the lower phase was withdrawn into a 50 ml teflon separatory funnel (except few drops), which was closed tightly. Another 10 ml of Freon was added, and the separatory funnel was shaken vigorously for 1 min, and allowed to stand for at least 5 min for phase separation. The lower phase was combined with the first extract. Then 0.5 ml of concentrated nitric acid (Aristar) was added to the combined extract, the funnel was shaken vigorously for 30 sec., and allowed to stand for at least 5 min. Finally 9.5 ml of deionized distilled water was added, shaken vigorously for 30 sec., and allowed to stand for 15 min. Then the aqueous phase was transferred to a 10 ml polyethylene bottle which was closed tightly. The analysis was then performed by the graphite furnace [Danielsson *et al.* (1978)].

The results of the extraction are given in table (25).

Table (25)

Recovery of metals in Seawater by Extraction into Freon and back Extraction into HNO_3 Acid. Rows refer to different trials.

Metal				
Cu	Fe	Mn	Ni	Zn
Added μg/ml				
0.003	0.200	0.002	0.020	0.025
Found μg/ml				
0.0017	0.115	0.0010	0.012	0.021
0.0014	0.122	0.0013	0.012	0.019
0.0012	0.112	0.0011	0.012	0.017
0.0016	0.109	0.0012	0.012	0.015
0.0015	0.121	0.0010	0.012	0.018
0.0013	0.115	0.0012	0.012	0.015
0.0012	0.111	0.0011	0.012	0.014
0.0013	0.113	0.0011	0.012	0.014
0.0015	0.115	0.0009	0.012	0.020
0.0015	0.118	0.0012	0.012	0.020
% Recovery				
57.0	58.0	50.0	60.5	84.0
47.0	61.0	65.0	61.0	76.0
40.0	56.0	55.0	58.5	68.0
53.0	55.0	60.0	59.5	60.0
50.0	61.0	50.0	59.5	72.0
43.0	58.0	60.0	60.5	60.0
40.0	56.0	55.0	57.5	56.0
43.0	57.0	55.0	58.0	56.0
49.0	58.0	45.0	60.0	80.0
50.0	59.0	60.0	60.0	80.0

4.II.5.4. Extraction into Freon.

200 ml of the pretreated seawater sample was transferred into a teflon separatory funnel, and buffered to about pH 4 with 2 ml of ammonium acetate. 5 ml of purified solution containing 2% (w/v) of APDC and DDDC, then 20 ml of Freon were added. The funnel was shaken vigorously for 3 min, and the phases then allowed to separate (15 min). Then the lower phase was withdrawn into a 50 ml teflon separatory funnel (except few drops), which was closed tightly. Another 10 ml of Freon was added, and the separatory funnel was shaken vigorously for 1 min, and allowed to stand for at least 5 min for phase separation. The lower phase was combined with the first extract. Then the analysis of the organic phase was performed by the graphite furnace.

Table (26) shows the result of the extractions.

Table (26)

Recovery of metals in Seawater by Extraction into Freon. Rows refer to different trials.

Metal				
Cu	Fe	Mn	Ni	Zn
Added µg/ml				
0.003	0.200	0.002	0.020	0.025
Found µg/ml				
0.0027	0.193	0.0018	0.0193	0.024
0.0029	0.196	0.0019	0.0194	0.023
0.0026	0.187	0.002	0.0196	0.023
0.0027	0.192	0.0019	0.0197	0.022
0.0028	0.197	0.0019	0.0194	0.024
0.0029	0.194	0.0019	0.0193	0.023
0.0029	0.190	0.0019	0.0196	0.023
0.0026	0.198	0.002	0.0198	0.024
0.0027	0.193	0.0019	0.0199	0.022
0.0027	0.193	0.002	0.0198	0.021
% Recovery				
90.0	96.5	90.5	96.5	97.2
97.0	98.0	95.0	97.0	93.2
87.0	93.5	(100)	98.0	93.2
90.0	96.0	95.5	98.5	89.2
93.0	98.5	97.0	97.0	97.2
97.0	97.0	89.0	96.5	93.2
97.0	95.0	96.5	98.0	93.2
87.0	94.5	98.0	99.0	97.2
90.0	96.5	96.0	99.5	89.2
89.0	96.5	98.5	99.0	85.2

Total chromium recovery test.

Cr^{III} was oxidized to Cr^{VI} with $KMnO_4$ in acidic media as follows:

A seawater sample of 200 ml was placed in 500 ml beaker, and 8 ml of HNO_3 was added. The solution was boiled for 10 min. After the solution was cooled at room temperature, filteration was carried out through 0.45 μm filter paper. 1 ml of $KMnO_4$ (5%) solution was added to the solution, which was covered with a watch glass, and heated without boiling on a hot plate for 30 min [Miyazaki and Barnes (1981)]. The solution was extracted with MIBK (Sect. 4.II.5.2.). The results are given in table (27).

Table (27)

Recovery of Cr in Seawater by Extraction into MIBK.

Rows refer to different trials.

Metal	Added μg/ml	Found μg/ml	% Recovery
Cr	0.0025	0.0018	72.0
		0.0016	64.0
		0.0015	60.0
		0.0017	68.0
		0.0016	64.0
		0.0016	64.0
		0.0015	60.0
		0.0015	60.0
		0.0014	56.0
		0.0018	72.0

4.II.5.5. DISCUSSION.

This section discusses the results reported in sections 4.II.5.1 to 4.II.5.4.

The most important criterion in the development of organic extraction technique was to achieve quantitative yields with a high degree of precision.

BUFFERING SOLUTION.

Ammonium acetate: was used because it has a good buffering capacity at the optimum pH for extraction (about pH 4).

CHELATING AGENT.

Ammonium pyrrolidine dithiocarbamate (APDC). Although it can form complexes with more than 30 metallic elements within a range of pH, it cannot be used as a chelating agent alone. It is not good enough because its complexes with manganese and iron were quite unstable.

8-Hydroxyquinoline. 8-hydroxyquinoline does not extract all the metals equally under a range of pH's. However it was used in this study because of the difficulty encountered in extracting manganese, except when a relatively large amount of APDC were present, as well as the extreme instability of the manganese APDC complex in MIBK. A double chelating system consisting of APDC and oxine was used allowing recovery of manganese as the oxinate complex.

APDC-DDDC. the combination of these two chelating agents worked well for the extraction of a variety of metals over a fairly wide pH range [Kinrade and Van Loon (1974)]. In addition, APDC and DDDC discriminate extremely well against the major cations in seawater. APDC and DDDC are quickly destroyed in acid solutions [Kinrade and Van Loon (1974)].

ORGANIC SOLVENTS.

The choice of organic solvent depends on a number of factors:

- it should be immiscible with aqueous solution.
- it should not tend to form emulsions.
- it should have good burning characteristics.
- it should enhance rather than suppress the atomic absorption sensitivity.

Methyl Isobutyl Ketone. has relatively the highest solubility in water (~2% in seawater) [Sturgeon *et al.* (1980)] among the organic solvents commonly used with AAS extractants. On the other hand, it is the most suitable with the flame AAS technique. Also it gave the greatest enhancements of metal absorbances as compared to the absorbance value measured for an aqueous solution.

Freon FT. is considered almost harmless, less toxic and almost insoluble in water (0.017% w/w at 21.1°C) [Danielsson *et al.* (1978)], and separates quickly from the aqueous phase after shaking. The only drawback is the low solubility of the complexes in it.

- **Extraction into methyl isobutyl ketone and back extraction into nitric acid.** The results of the analyses were shown in table 23.

By analyzing the extract, there was a high blank concentration of chromium in comparison with the spiked samples, the blank gives 0.0056 μg/ml, while the spiked samples give concentrations range between 0.005 and 0.0065 μg/ml. Thus, the recovery of chromium is very low. At the same time the recovery of copper, iron, manganese, nickel and zinc range between 45% and 65%. However, other authors have said that the recoveries of these trace metals were 90-98% [Guardia and Vidal (1983), Sturgeon *et al.* (1980), Florence and Batley (1975)]. Back extraction of these elements from MIBK is slow, and the efficiency can be increased by shaking the MIBK-acid mixture for a longer period of time [Sturgeon *et*

al. (1980)]. According to this recommendation, the shaking time is a critical and an important factor in these methods and this method involves manual and very vigorous shaking which become tedious and time consuming.

- **Extraction into methyl isobutyl ketone.** By the extraction into methyl isobutyl ketone the recoveries of the investigated trace metals were high, ranging between 81% and 110%, and these were shown in table 24. To achieve these results, the analysis of extracts must be done in the same day of extraction, iron extracts have to be analyzed within 2hr, because its absorbance is found to decrease after that time, because of slow precipitation [Guardia and Vidal (1983)], and to avoid the solubility of MIBK in water [Everson and Parker (1974)].

The recoveries of Cu, Fe, Mn, Ni and Zn spikes from seawater were evaluated from direct analysis of the MIBK phase, with an aqueous standard for calibration, without taking account of the amount of MIBK (~2%) which dissolves in seawater.

- **Extraction into Freon and back extraction into nitric acid.** From table 25, the recoveries of trace metals were not as high as reported by Danielsson *et al.* (1978). This may be because of the relative inexperience of the author using this technique.

- **Extraction into Freon.** Extraction into Freon caused a signal enhancement for copper but severe signal suppression for nickel, but by using the optimized furnace conditions (see Appendix III), adequate sensitives were obtained. The recoveries of the investigated trace metals were high (85-98%), the values fluctuate from run to run by about 12%. The results of the analyses were shown in table 26.

4.II.5.6. CONCLUSION.

The determination of trace metals in seawater is pursued with great difficulty. Quantitation of extremely low concentrations of analyte accompanied by a matrix consisting of 4.2% dissolved solids, imposes a great demands on instrumental techniques. Sample preparation schemes were designed both to preconcentrate the trace metals and separate them from major interfering components prior to analysis. All these methods increase sample manipulation and the demand of relatively large amounts of pure reagents and very clean surface containers brought into contact with the sample which may introduce contamination, or give rise to unacceptably high blanks.

The optimum recoveries of Cu, Fe, Mn, Ni and zn were acheived with extraction using MIBK or Freon, i.e., without back-extraction into nitric acid. The shaking time is a very critical factor in the extraction techniue.

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CHAPTER 5

REPRODUCIBILITY

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INTRODUCTION.

Inductively coupled plasma mass spectrometry (ICP-MS) is rapidly becoming an established method of trace multi-element determinations [Fassel and Kniseley (1974), Gary (1975), Houk *et. al.* (1980), Date and Gary (1981), Date and Gary (1983), Olivares and Houk (1985)]. This technique possesses superior powers of detection on a true simultaneous multielement basis, and offers detection limits in the range of 0.01-0.1 μg/l, the capability of performing on the order of 10 elemental determinations/min, and the unique ability to provide isotopic information about the sample. Based on these characteristics, a reproducibility and performance study was carried-out on electrothermal atomic absorption spectroscopy and inductively coupled plasma mass spectrometry [Ketterer *et al.* (1989)].

5.I.1. Reproducibility of Results.

To assess the reproducibility of results using the AAS and ICP-MS instruments, a water sample was collected from Kuwait's potable water network and analyzed 10 times. Tables (29-40) show the results of the trace metals (Cr, Cu, Fe, Pb, Mn, Ni, V and Zn), analyzed under the AAS conditions and the ICP-MS conditions mentioned in appendix II.

Discussion.

Under the specified conditions, the results showed that the calculated standard deviation for atomic absorption spectroscopy (Ni 0.0, Mn $3X10^{-05}$, Cu $4.7X10^{-04}$, Fe $4.8X10^{-04}$), and the inductively coupled plasma mass spectroscopy (Pb 0.017, V 0.02, Cr 0.05, Mn 0.09, Ni 0.10, Zn 0.27, Fe 0.94, and Cu 1.58). This proves the AAS (0.0%-1.18% c.v.) technique is more accurate than ICP-MS (1.08%-4.47% c.v.) in analysing trace metals. However, ICP-MS was adopted, since it offers lower detection limits than AAS (table 28) for many elements. It also gives an easier and faster method of analysis, avoiding the need (found with AAS) to prepare several solutions for each sample (see chapter 4).

Table (28)

Limits of Detection for GF-AAS Compared to ICP-MS.

Elements	AAS concentration in μg/l	ICP-MS concentration in μg/l
Chromium	2.5	1.0
Copper	2.5	0.5
Iron	2.0	2.0
Lead	1.0	0.05
Manganese	0.2	0.05
Nickel	1.0	0.5
Vanadium	5.0	0.05
Zinc*	--	1.0

* Zinc is analysed by Flame AAS and the detection limit is 0.2 μg/ml.

Table (29)

Reproducibility of Chromium analysis by ICP-MS.

Sample	Concentration µg/l
1	3.322
2	3.343
3	3.252
4	3.255
5	3.292
6	3.209
7	3.256
8	3.202
9	3.289
10	3.234
Average	3.265
Standard deviation	0.046
Coefficient of variation %	1.409

Table (30)

Reproducibility of Copper analysis by ICP-MS.

Sample	Concentration µg/l
1	57.806
2	60.250
3	60.022
4	56.271
5	56.654
6	56.180
7	56.753
8	56.169
9	56.797
10	56.013
Average	57.292
Standard deviation	1.584
Coefficient of variation %	2.765

Table (31)

Reproducibility of copper analysis by AA 5000.

Sample	Concentration mg/l
1	0.057
2	0.058
3	0.056
4	0.057
5	0.057
6	0.057
7	0.057
8	0.057
9	0.057
10	0.057
Average	0.057
Standard deviation	0.00047
Coefficient of variation %	0.825

Table (32)

Reproducibility of iron analysis by ICP-MS.

Sample	Concentration µg/l
1	38.771
2	41.917
3	42.119
4	40.407
5	40.973
6	40.174
7	40.270
8	40.718
9	40.885
10	40.339
Average	40.657
Standard deviation	0.942
Coefficient of variation %	2.317

Table (33)

Reproducibility of iron analysis by AA 5000.

Sample	Concentration mg/l
1	0.040
2	0.041
3	0.041
4	0.041
5	0.040
6	0.041
7	0.040
8	0.041
9	0.041
10	0.041
Average	0.0407
Standard deviation	0.00048
Coefficient of variation %	1.179

Table (34)

Reproducibility of lead analysis by ICP-MS.

Sample	Concentration µg/l
1	0.388
2	0.398
3	0.406
4	0.377
5	0.393
6	0.362
7	0.363
8	0.366
9	0.367
10	0.360
Average	0.378
Standard deviation	0.017
Coefficient of variation %	4.471

Table (35)

Reproducibility of manganese analysis by ICP-MS.

Sample	Concentration µg/l
1	4.135
2	4.302
3	4.372
4	4.260
5	4.157
6	4.107
7	4.149
8	4.108
9	4.195
10	4.126
Average	4.191
Standard deviation	0.091
Coefficient of variation %	2.164

Table (36)

Reproducibility of manganese analysis by AA 5000.

Sample	Concentration mg/l
1	0.0046
2	0.0046
3	0.0046
4	0.0046
5	0.0046
6	0.0046
7	0.0047
8	0.0046
9	0.0046
10	0.0046
Average	0.0046
Standard deviation	0.00003
Coefficient of variation %	0.652

Table (37)

Reproducibility of nickel analysis by ICP-MS.

Sample	Concentration µg/l
1	9.396
2	9.488
3	9.406
4	9.345
5	9.477
6	9.343
7	9.316
8	9.198
9	9.385
10	9.186
Average	9.354
Standard deviation	0.101
Coefficient of variation %	1.080

Table (38)

Reproducibility of nickel analysis by AA 5000.

Sample	Concentration mg/l
1	0.0095
2	0.0095
3	0.0095
4	0.0095
5	0.0095
6	0.0095
7	0.0095
8	0.0095
9	0.0095
10	0.0095
Average	0.0095
Standard deviation	0.0
Coefficient of variation %	0.0

Table (39)

Reproducibility of vanadium analysis by ICP-MS.

Sample	Concentration µg/l
1	1.019
2	1.070
3	1.063
4	1.053
5	1.035
6	1.033
7	1.019
8	1.066
9	1.070
10	1.042
Average	1.047
Standard deviation	0.02
Coeffient of variation %	1.91

Table (40)

Reproducibility of zinc analysis by ICP-MS.

Sample	Concentration µg/l
1	12.733
2	12.918
3	13.235
4	13.483
5	12.651
6	12.892
7	12.747
8	12.881
9	12.580
10	12.969
Average	12.909
Standard deviation	0.273
Coefficient of variation %	2.115

5.II.2. Analysis of the Riverine Water Reference Material SLR-2.

Direct determination. Table (41) shows that 14 elements could be determined directly in ICP-MS using the standard Riverine water sample. The obtained results showed excellent agreement with the certified values for Al, V, Cr, Mn, Co, Ni, As, Cd, Ba, and Sb. This agreement indicates that the ICP-MS technique, to analyze the mentioned elements, can be considered an acceptable technique with a very high confidence limits. In the case of Fe, Cu, Zn, and Pb the difference in concentration values are expected due to contamination of the deionised distilled water used in the preparation and blank solution.

The very slight variation in the results between the obtained results and the certified values could be attributed to: 1. the difference in the operational conditions used in the analysis, or 2. the difference in isotope composition ratio between the reference sample and the standard chemicals used for calibration. It is worth mentioning that Beauchemin and coworker (1987) reported that direct isotope dilution technique gave accurate and precise results in analysing river water. It is suggested to use the ICP-MS technique to study the isotope ratio in a separate study.

Table (41)

Results of analysis of Trace Elements in Reference Material Riverine Water SLR-2 using ICP-MS.

Elements	Obtained values µg/l	*Certified value µg/l
Aluminium	86.1 ±1.4	84.4 ±3.4
Vanadium	0.26 ±0.027	0.25 ±0.06
Chromium	0.52 ±0.081	0.45 ±0.07
Iron**	265 ±3.82	129 ±7.0
Manganese	10.61 ±0.16	10.1 ±0.3
Cobalt	0.04 ±0.016	0.063 ±0.012
Nickel	0.75 ±0.13	1.03 ±0.1
Copper**	5.81 ±0.21	2.76 ±0.17
Zinc	5.71 ±0.44	3.33 ±0.15
Arsenic	0.81 ±0.13	0.77 ±0.09
Cadmium	0.034 ±0.018	0.028 ±0.004
Barium	14.88 ±0.07	13.8 ±0.3
Antimony	0.297 ±0.055	0.26 ±0.05
Lead	0.44 ±0.04	0.129 ±0.011

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* National Research Council, Canada, 1990.

** The high concentration is contamination from DDW.

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CHAPTER 6

TRACE METAL ANALYSIS OF KUWAIT'S FRESH WATER SUPPLY

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6. INTRODUCTION.

Assessment of selected trace metals in Kuwait's fresh water supply was performed. The fresh water supply is mainly produced from about 95% distillate of seawater using Multi-Stage Flash process, the remaining quantities are of brackish quality produced from ground water.

The source of contamination by the selected elements could be attributed to:

1- Seawater.
2- Ground water.
3- Distribution network.

Kuwait is located on the north west side of the Arabian Gulf which has an area of about 241,000 km^2 (square kilometer) [Leeden *et al.* (1990)]. The Gulf is characterized by relative shallowness, connected to the Arabian sea through the Strait of Hormuz. The average depth is 40 meters and the maximum depth is 110 meters in the south, while the depth in the Gulf of Oman reaches 900 meters. The coasts in general are shallow on the Arabian side while the greatest depths occur along the Iranian shore. Moreover, it is characterized with arid weather and a very low rate of fresh water discharging into it. It is also characterized by very high temperature and a high rate of evaporation. These conditions along with limited anti-clockwise circulation of surface current [Al Asfour (1982)] produce the high rate of salinity in the study area i.e 47000 ± 2000 mg/l total dissolved solids [Al Awadi and Abdel-Jawad (1987)]. Seasonal variation of seawater temperature in Kuwait (Doha site) ranges between 14°C to 35°C during winter and summer seasons respectively, as shown in figure (10). Occasionally it goes down to about 10°C during winter. The coast of Kuwait which extends along the north-west shore of the Gulf is heavily utilized to desalinate this quality of seawater.

In a country like Kuwait, water is a very valuable resource and is of strategic importance. At present, desalination plants supply almost all the requirements of

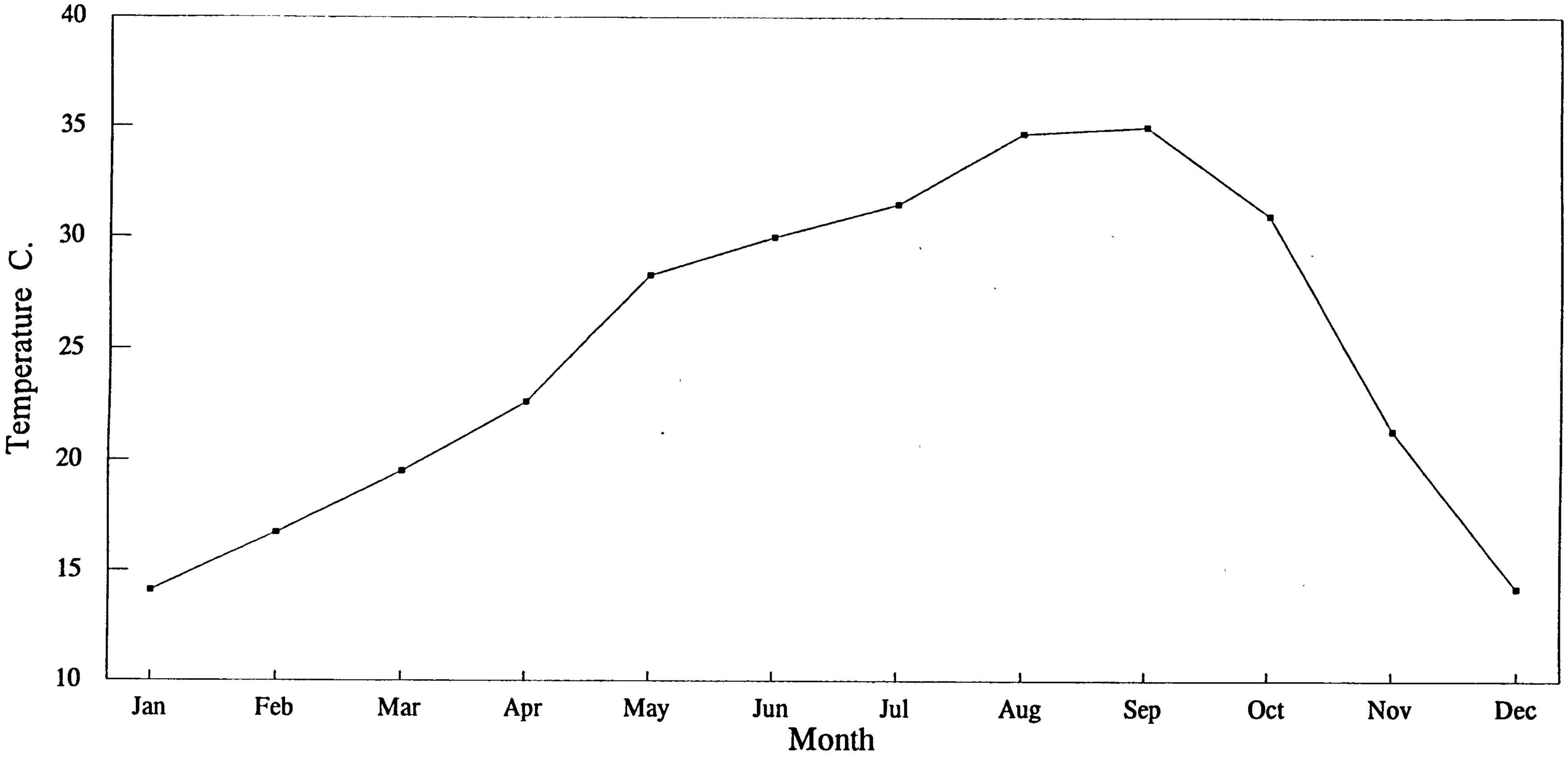

Fig. (10) Seasonal variation of seawater temperature in Kuwait (Doha site). Monthly average.

fresh water.

The seawater of Kuwait has the characteristics shown in table (1), chapter (1).

Ground water is available mainly in brackish quality ranges between 3,000-10,000 mg/l (table 2, chapter 1). Ground water is divided into annual renewable and non renewable fossil ground water. The renewable ground water is not very important since it is very limited in the state of Kuwait, because of the insufficient amount of rainfall, and the high evaporation rate. The fossil ground water is stored in the sedimentary deep aquifers.

The main aquifer system consists of the shallow alluvial Kuwait and Dammam formations [Anonymous (1986)]. Ground water is relatively constant in quality from season to season. However, ground water supplies may be highly variable in quality from one well location to another. Generally the quality range from poor to fair, except in some localities in the northern parts of the country (Rawdatain and Um Alaish).

Ground water production from Kuwait and Dammam aquifers is concentrated in 3 sites, namely Al-Shagaya, Um-Qudair and Sulaibiya.

As a result of the Iraqi occupation and the armed conflict in Kuwait, 6 to 8 million barrels of crude oil were spilled into the marine environment, and about 2 to 3 million barrels of crude oil, burnt or accumulated on the ground surface, were being spilled out daily during about 300 days into the environment. The deposited crude oil and airborne particulates in the terrestrial areas may have long term effects on the ground water aquifers [Literathy (1992)].

Kuwait's distribution system is comparatively new. The materials used consist mainly of ductile iron cement lined pipes, steel, galvanized steel, and copper alloys. By the end of 1993 the total length of the entire network was about 10326 km, mainly of ductile iron (MEW 1994). Although, most of its components are made of cement or cement lined materials. The water quality deteriorates on its way to the consumer where it comes out of the taps turbid and coloured.

Knowing the suspected source of contamination with the studied trace metals, a sampling strategy was prepared to collect water samples from all those sources in a systematic manner.

The sequence of production and transmission of potable water in Kuwait starts with the **seawater** which enters the power generation and distillation production stations to produce **distilled water**, which in turn, is pumped to blending plants, where it is blended with **ground water**. The produced water **(potable water)** from blending plants is stored in **ground level reservoirs** (1852 MIG), then pumped **(pumping stations)** into the network and stored in 34 **elevated towers** (660000 IG) located in several areas to maintain water pressure in the distribution networks and to offset water peak consumption.

In areas where piped water is not yet available (about 12%), consumers obtain their needs from **lorry filling stations** located in all different areas.

Based on these facts, water samples were collected from:

- Power generation and distillation stations (Doha, Shuaiba and AzZour stations).
- Blending plants (Doha, Shuaiba and AzZour plants).
- Ground water production wells utilized for blending with distillate (Sulaibiya, Al-Shagaya and Um-Qudair).
- Ground level reservoirs (Doha, Shuaiba and AzZour reservoirs).
- Pumping stations (Doha, Shuaiba and AzZour pumping stations).
- Elevated towers (Jahra, and Mina Abdulla towers).
- Lorry filling stations (Jahra, Shuaiba and Wafra).

The sampling points are shown on figure (11).

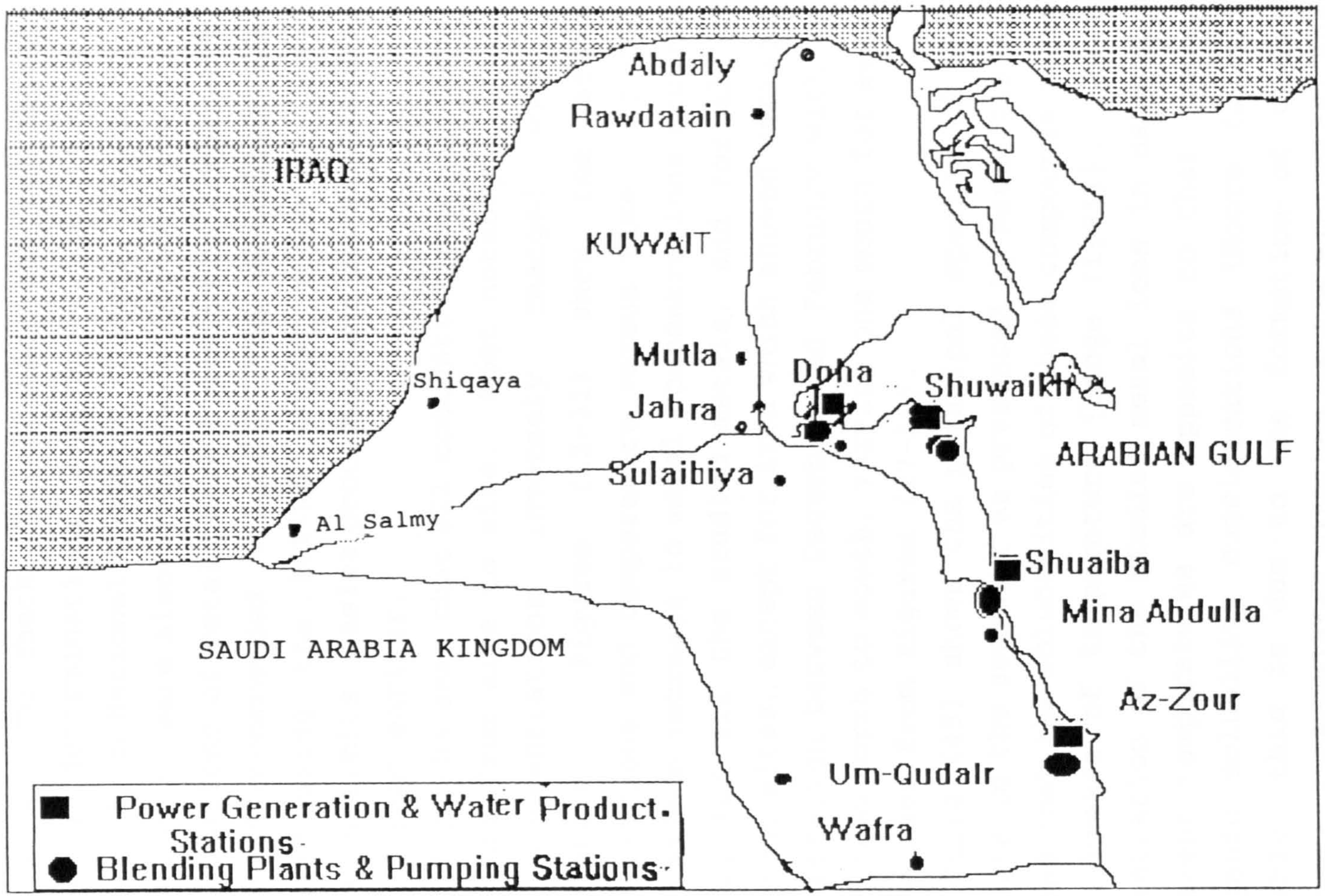

Fig. (11) Map of the State of Kuwait showing the locations of sampling points used in this study.

6.1. RESULTS AND DISCUSSION.

6.1.1. Seawater.

Seawater samples were collected and analysed throughout the year 1994-1995. The presented results for the eight metal ions under study are shown in tables (42-48). Each result represents the average of twenty samples collected through 13 months duration. Each sample has been analysed in five replicates. To check the accuracy and reliability of the analytical determinations, samples of the Standard Reference Material from National Research Council, Canada as mentioned in chapter 5, were also processed along with the test samples. Concentrations of metals were found to be comparable with the certified/recommended values. The presented results are produced using the ICP-MS method since it offers lower detection limits, easier procedure and produces faster results as discussed earlier.

It can be seen that all concentrations vary from month to month and from site to site. Most notably, it can be seen that concentrations inversely changed with seawater temperature. Figures (12-31) show the seasonal ion concentrations and temperature versus time. It can be seen that maximum increase in metal concentrations occurred during January for all the studied metals, and for all the three different sites, except for iron which showed variable maximum concentration between December and February with an obvious trend from north to south, varying one month for each site, as can be seen from figures (17-19).

Table (49) shows the principal species of the studied elements in the seawater as presented by Mason (1966). It can be seen that the solubilities of these compounds increase with the increase of temperature [Lange (1961)]. However, the concentration of the studied metal ions in natural water at different temperatures are opposite to that predicted from inorganic solubility considerations [Moore (1984)]. Most probably, this is due to the formation of organometallic complexes interrelated with the marine biological activities.

Table (42)

Annual chromium concentration in Kuwait seawater (μg/l).

Month	AzZour	Shuaiba	Doha
July	1.06	<1.0	1.73
August	1.11	<1.0	1.92
September	1.12	<1.0	1.86
October	1.06	<1.0	1.91
November	1.21	<1.0	1.97
December	1.37	<1.0	1.97
January	3.06	<1.0	3.30
February	2.98	<1.0	3.07
March	2.40	<1.0	2.52
April	2.07	<1.0	2.09
May	1.80	<1.0	1.97
June	1.26	<1.0	1.77
July	1.20	<1.0	1.55
August	1.09	<1.0	1.77

Table (43)

Annual copper concentration in Kuwait seawater (μg/l).

Month	AzZour	Shuaiba	Doha
July	4.15	1.10	5.68
August	4.00	1.50	5.64
September	5.10	2.25	7.17
October	4.90	3.55	8.20
November	5.00	5.15	9.00
December	8.30	6.35	9.55
January	13.30	7.05	11.55
February	7.00	4.62	10.7
March	6.40	3.65	9.15
April	5.50	3.15	7.90
May	4.20	2.75	7.40
June	3.20	2.43	6.53
July	3.10	2.09	5.67
August	2.92	1.90	5.27

Table (44)

Annual iron concentration in Kuwait seawater (μg/l).

Month	AzZour	Shuaiba	Doha
July	14.90	9.40	22.80
August	20.20	10.30	23.40
September	20.70	12.20	26.45
October	18.50	13.50	24.54
November	16.50	17.50	29.20
December	20.40	28.60	66.40
January	32.30	62.70	60.70
February	43.20	40.90	42.50
March	29.30	29.10	39.70
April	28.70	24.30	32.20
May	28.50	23.10	30.05
June	19.30	19.10	24.50
July	17.40	13.79	20.60
August	10.30	9.80	16.60

Table (45)

Annual manganese concentration in Kuwait seawater (μg/l).

Month	AzZour	Shuaiba	Doha
July	<0.05	<0.05	<0.05
August	<0.05	<0.05	<0.05
September	0.10	0.10	0.15
October	0.20	0.20	0.60
November	0.23	0.23	0.90
December	0.49	0.49	2.03
January	1.07	1.07	4.10
February	0.60	0.66	3.35
March	0.51	0.51	2.80
April	0.40	0.40	1.50
May	0.40	0.40	1.53
June	<0.05	0.20	0.20
July	<0.05	<0.05	0.20
August	<0.05	<0.05	<0.05

Table (46)

Annual nickel concentration in Kuwait seawater (μg/l).

Month	AzZour	Shuaiba	Doha
July	4.15	1.28	1.25
August	4.65	1.44	1.40
September	4.70	1.50	1.54
October	4.27	1.60	1.61
November	4.39	1.70	1.71
December	4.51	2.82	1.77
January	5.29	3.58	3.58
February	5.20	2.70	2.70
March	4.57	2.0	1.99
April	4.72	1.91	1.87
May	4.45	1.73	1.66
June	4.42	1.70	1.68
July	4.51	1.41	1.37
August	4.17	1.30	1.30

Table (47)

Annual vanadium concentration in Kuwait seawater (μg/l)

Month	AzZour	Shuaiba	Doha
July	2.09	1.85	1.05
August	2.14	2.14	1.30
September	2.70	2.94	1.73
October	3.22	3.45	2.08
November	4.13	4.13	2.70
December	5.28	5.25	3.50
January	8.10	6.29	4.69
February	6.29	4.13	3.94
March	2.70	2.70	2.86
April	2.20	2.20	2.29
May	1.54	1.95	2.00
June	1.85	1.65	1.84
July	1.94	1.55	1.32
August	1.92	1.20	1.05

Table (48)

Annual zinc concentration in Kuwait seawater (μg/l).

Month	AzZour	Shuaiba	Doha
July	1.90	1.05	1.73
August	1.10	1.15	2.05
September	1.63	1.24	2.28
October	1.92	1.68	2.37
November	2.29	1.98	2.61
December	2.10	2.24	2.94
January	3.90	4.16	7.16
February	3.50	3.67	5.10
March	2.55	3.31	4.27
April	1.77	3.31	3.96
May	1.52	1.78	2.26
June	1.40	1.54	2.02
July	1.30	1.09	1.77
August	1.49	1.05	1.17

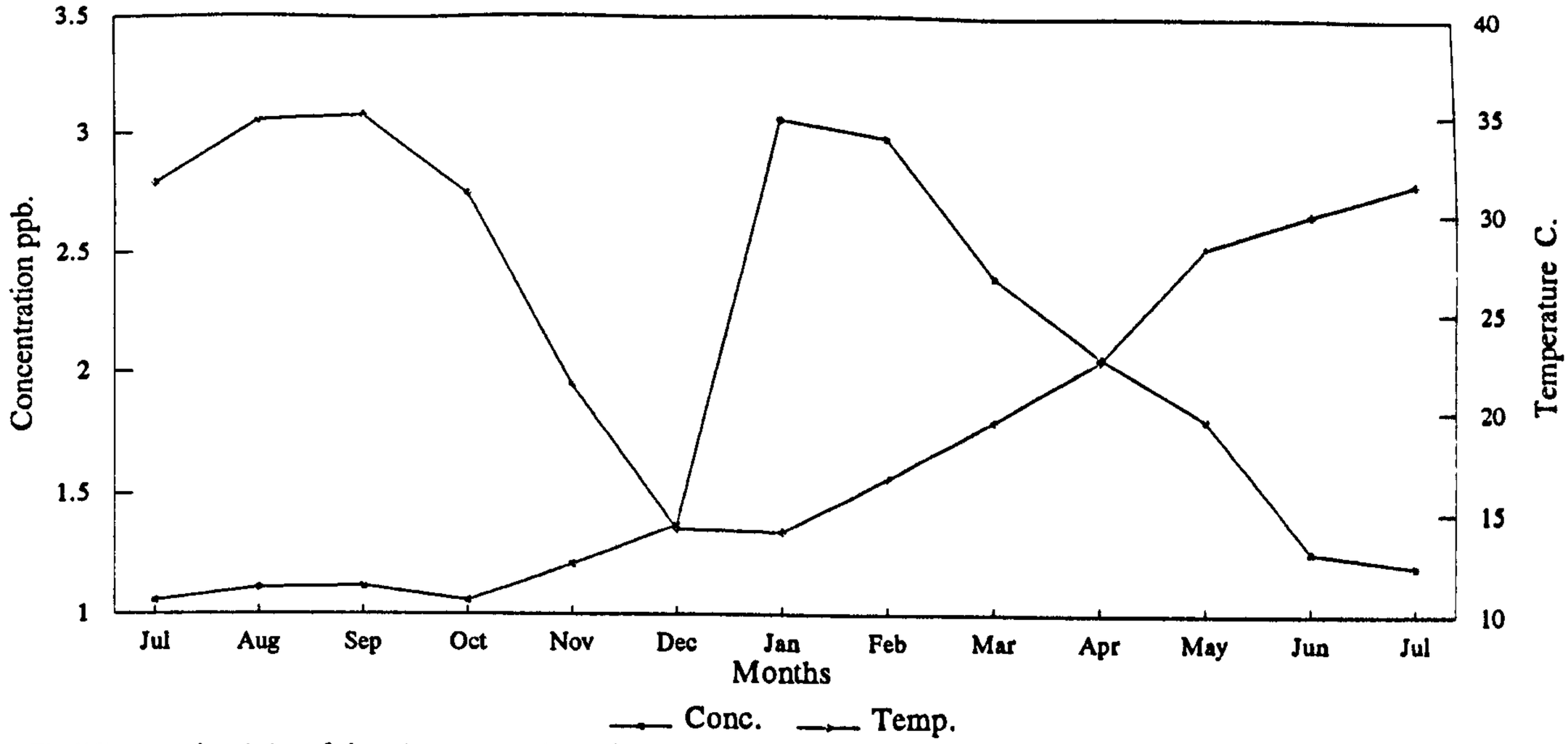

Fig (12) Annual variation of chromim concentration and temperature in AzZour seawater versus time.

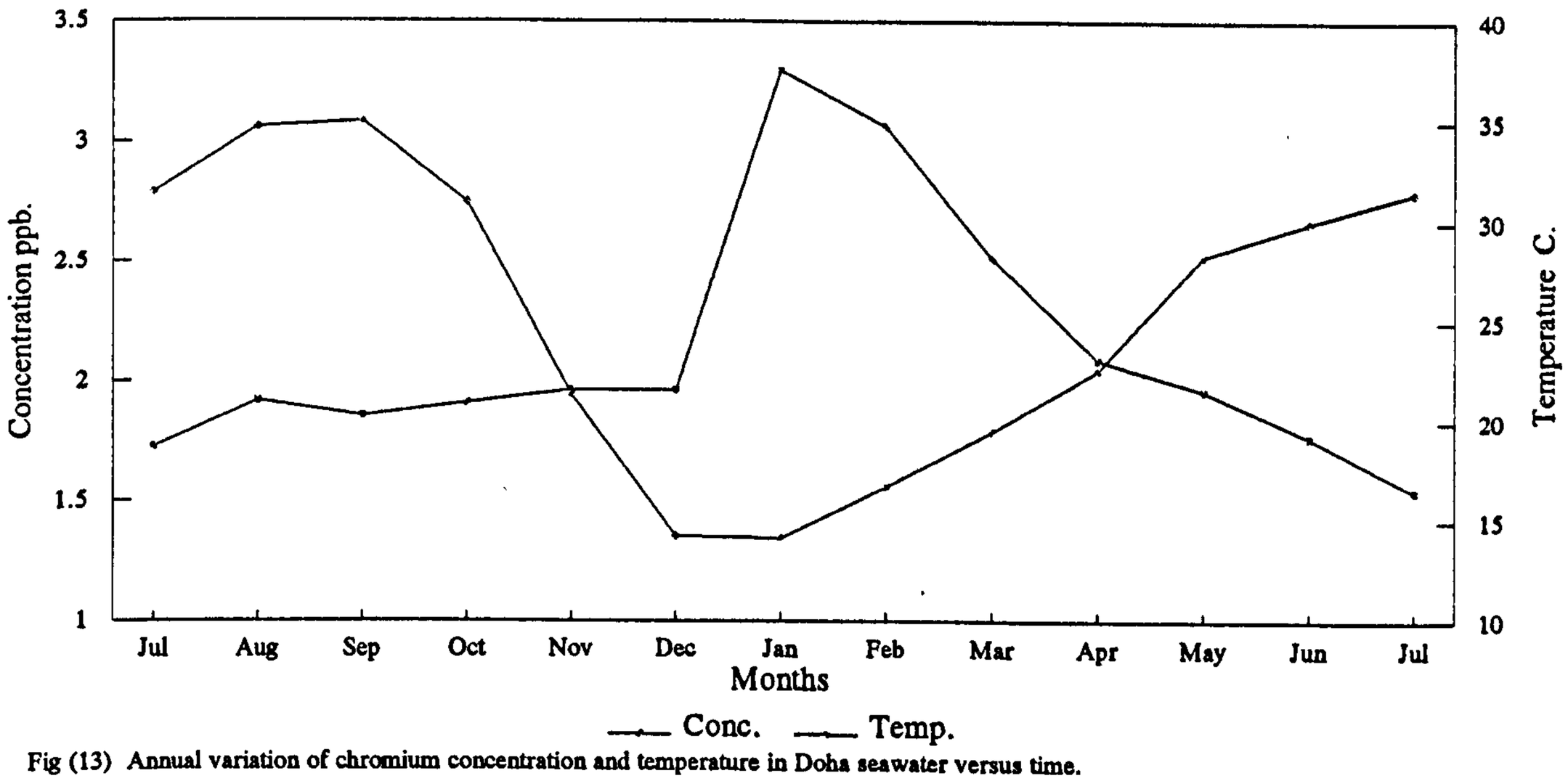

Fig (13) Annual variation of chromium concentration and temperature in Doha seawater versus time.

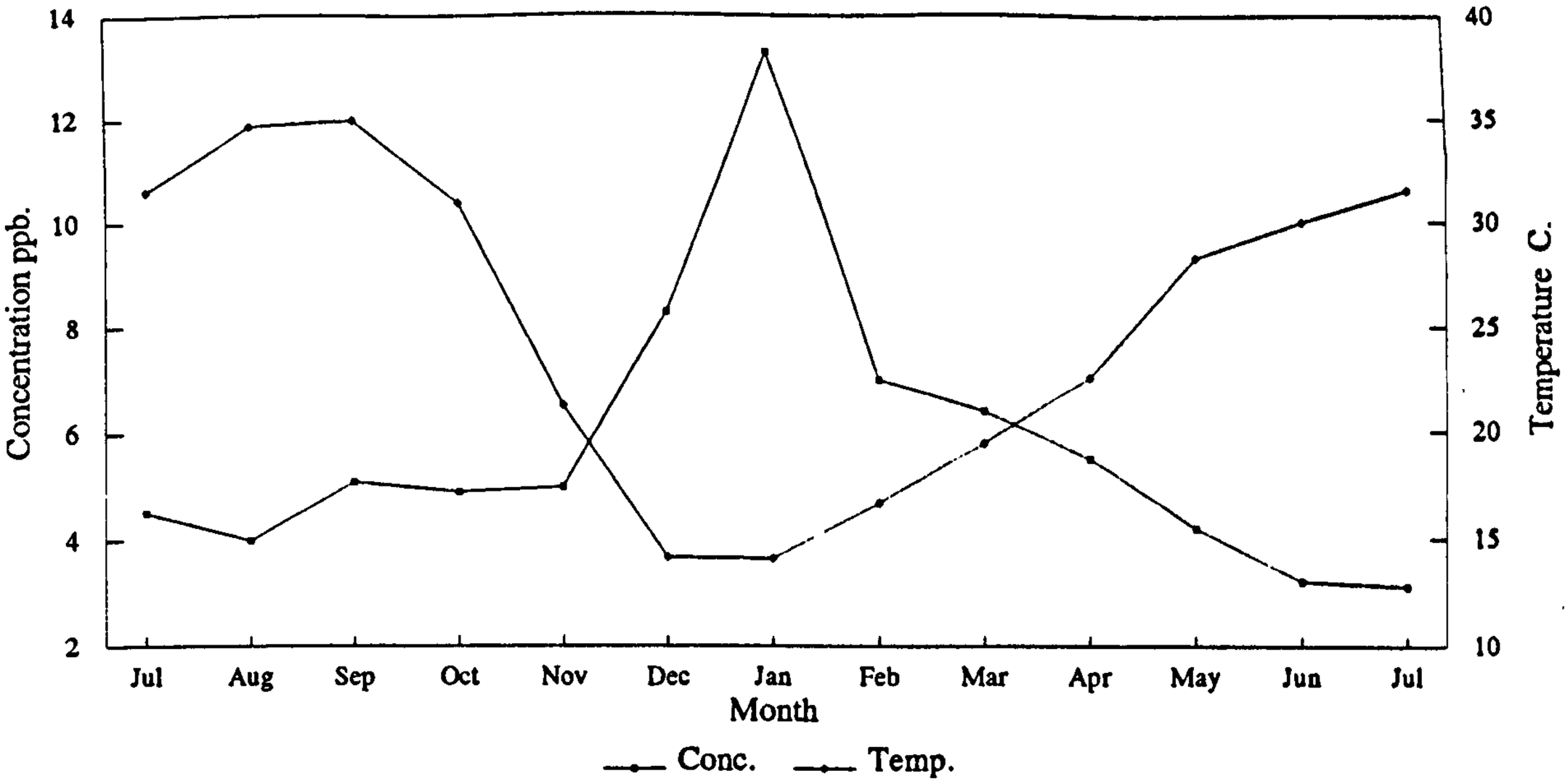

Fig. (14) Annual variation of copper concentration and temperature in AzZour seawater versus time.

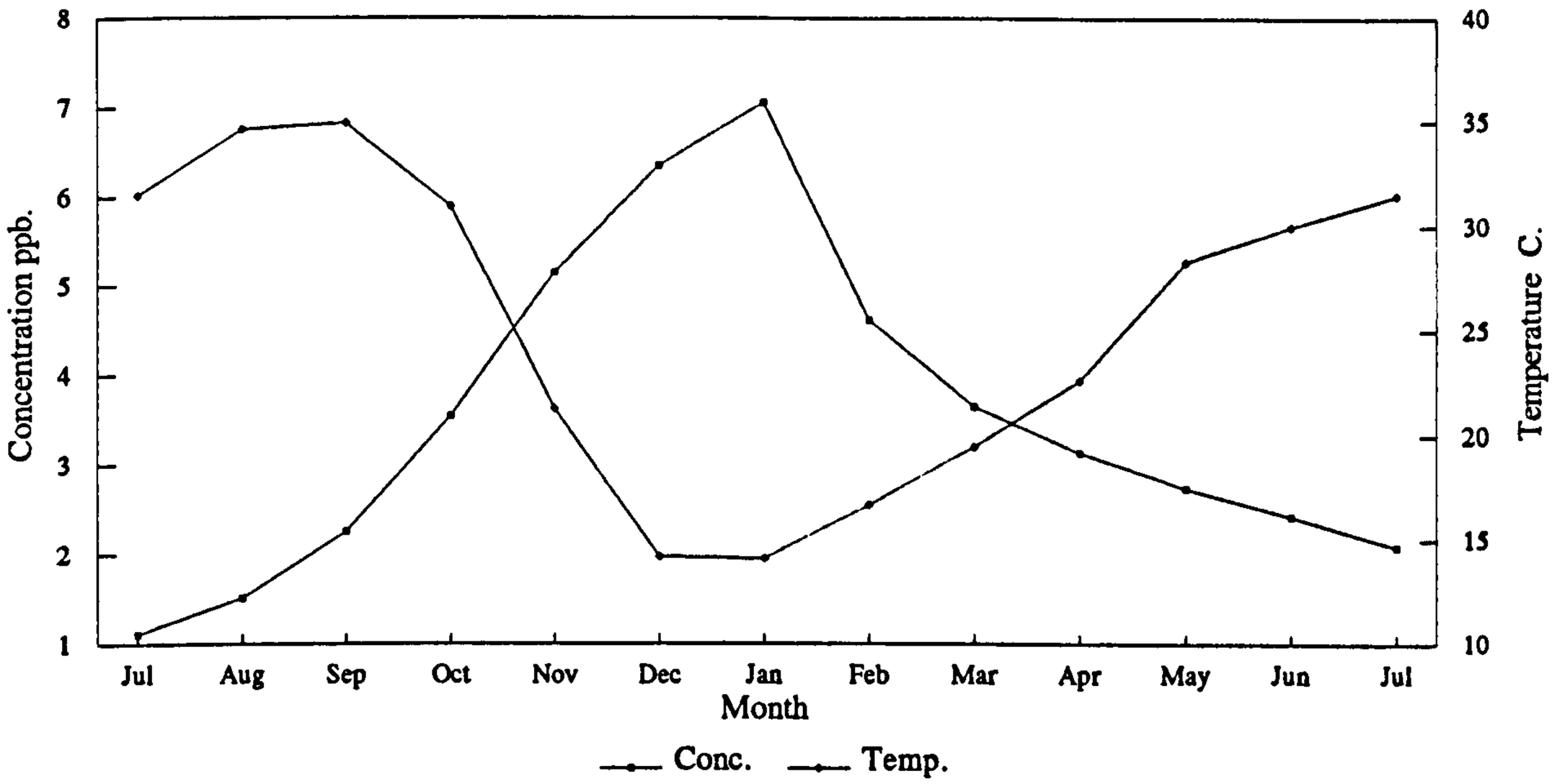

Fig. (15) Annual variation of copper concentration and temperature in Shuaiba seawater versus time.

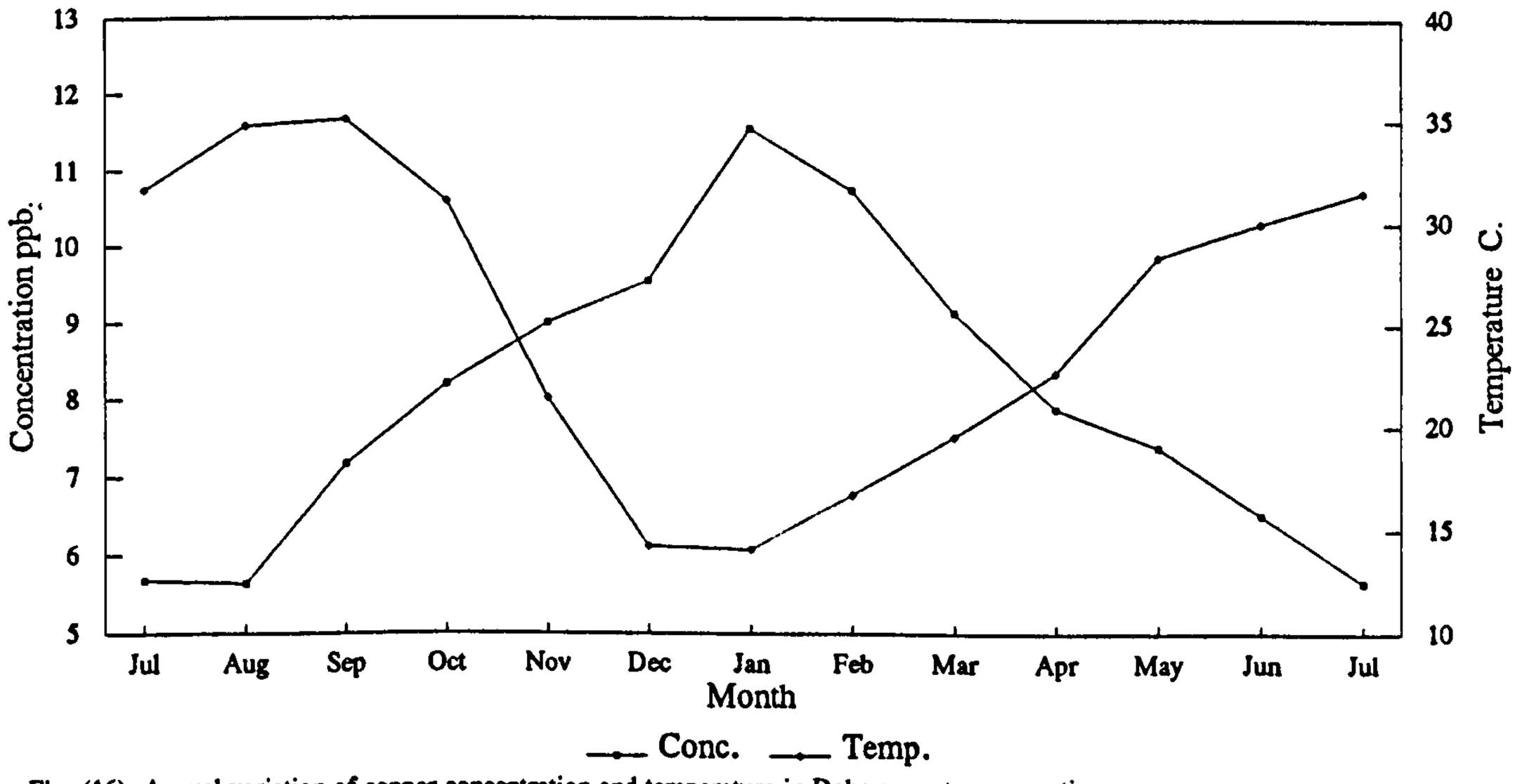

Fig. (16) Annual variation of copper concentration and temperature in Doha seawater versus time.

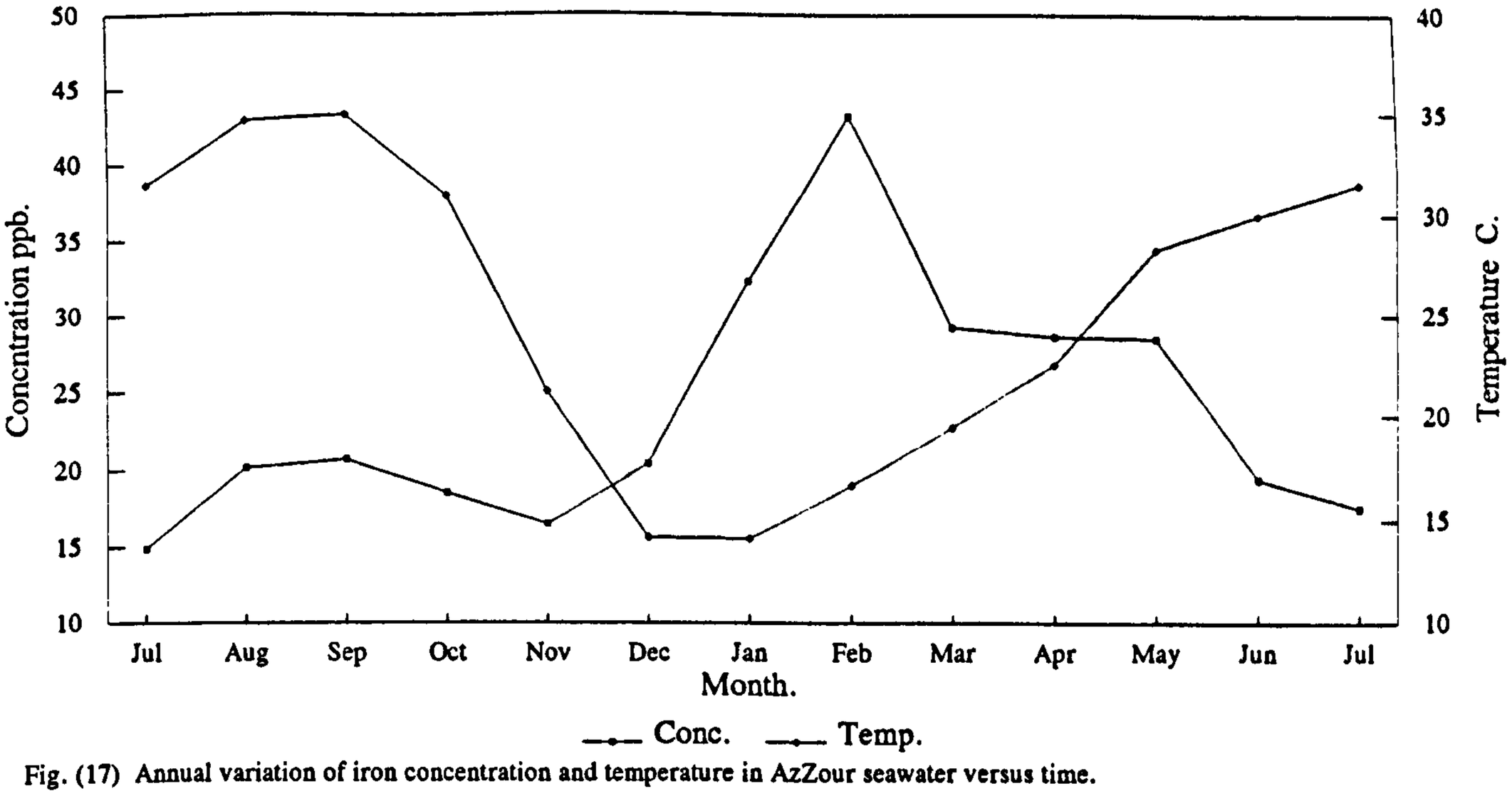

Fig. (17) Annual variation of iron concentration and temperature in AzZour seawater versus time.

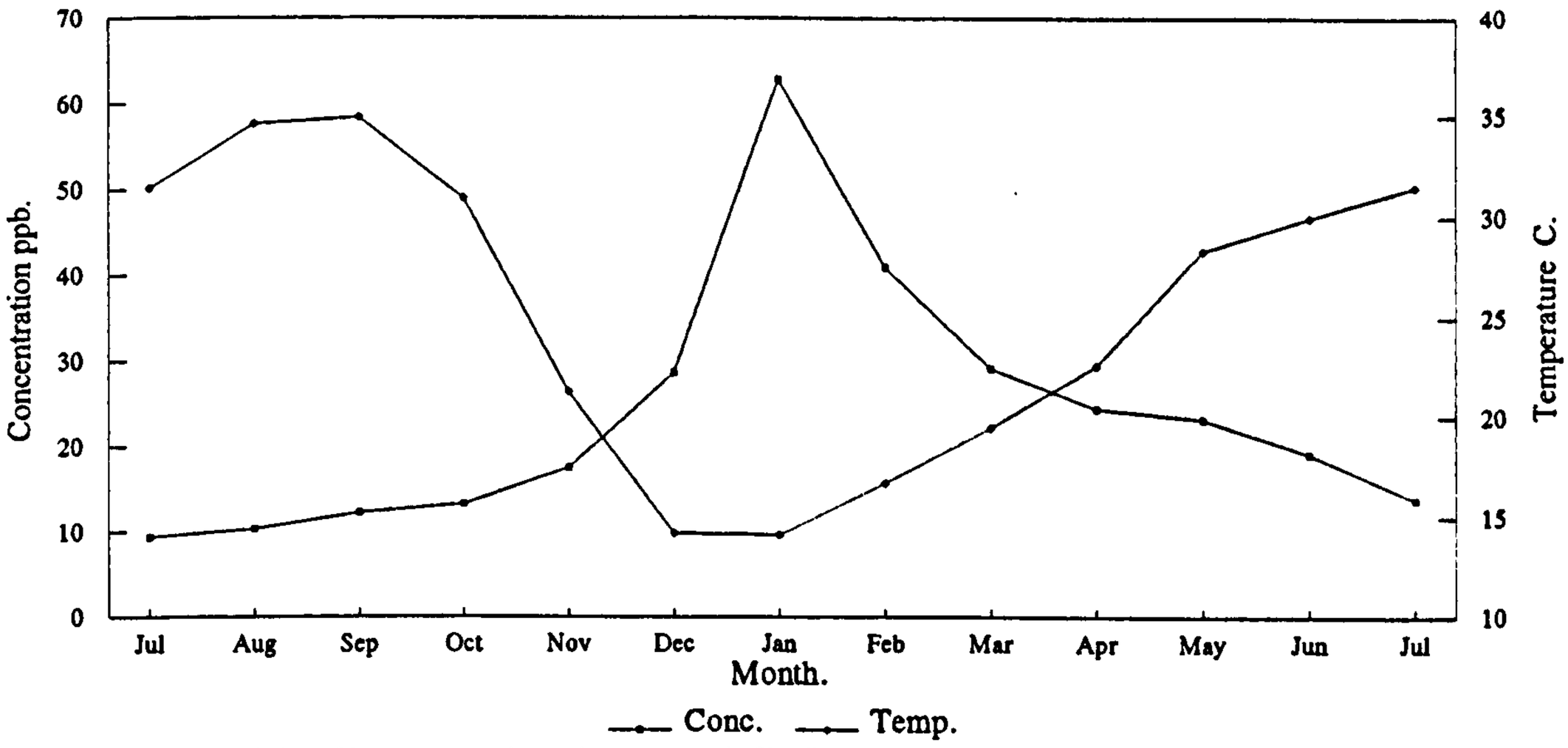

Fig. (18) Annual variation of iron concentration and temperature in Shuaiba seawater versus time.

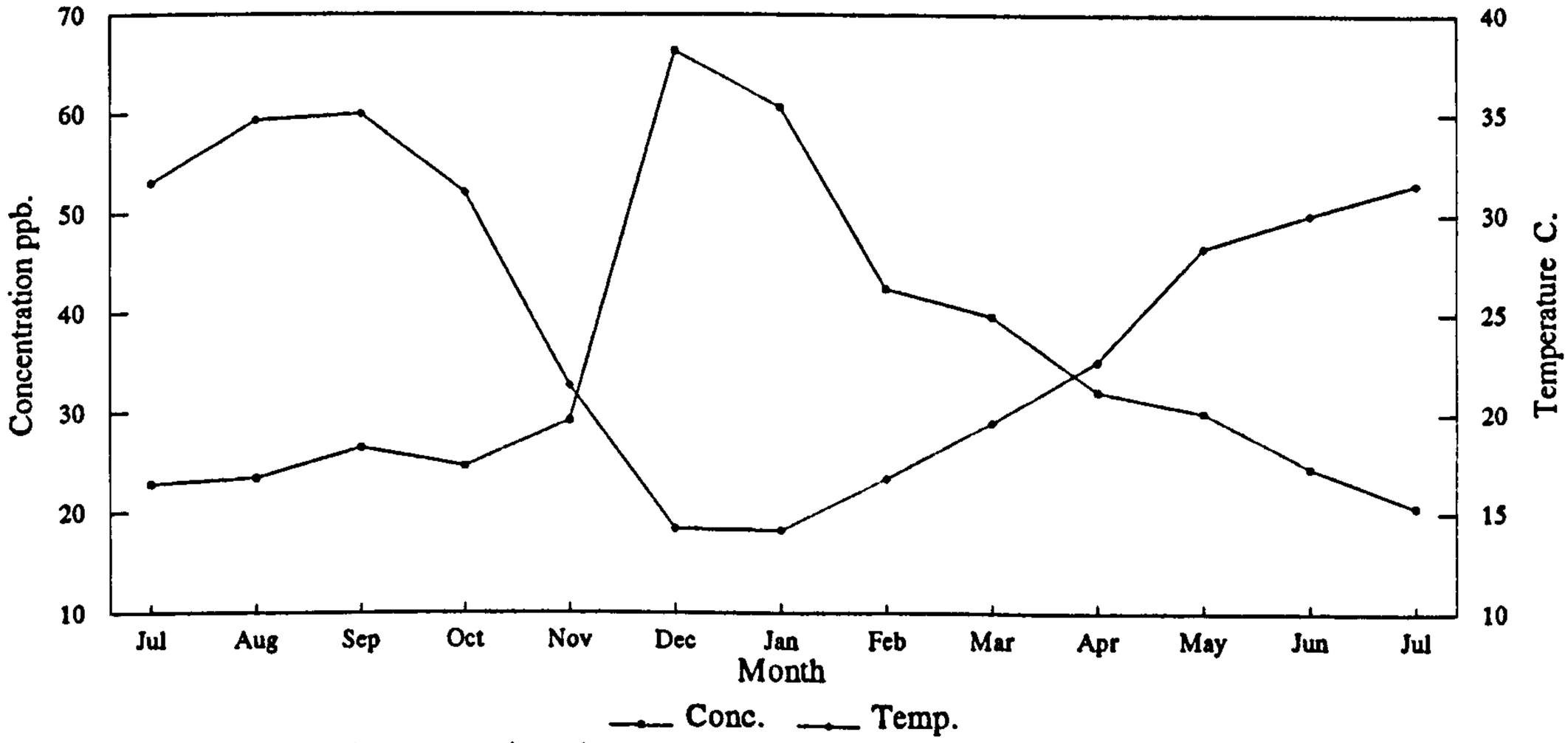

Fig. (19) Annual variation of iron concentration and temperature in Doha seawater versus time.

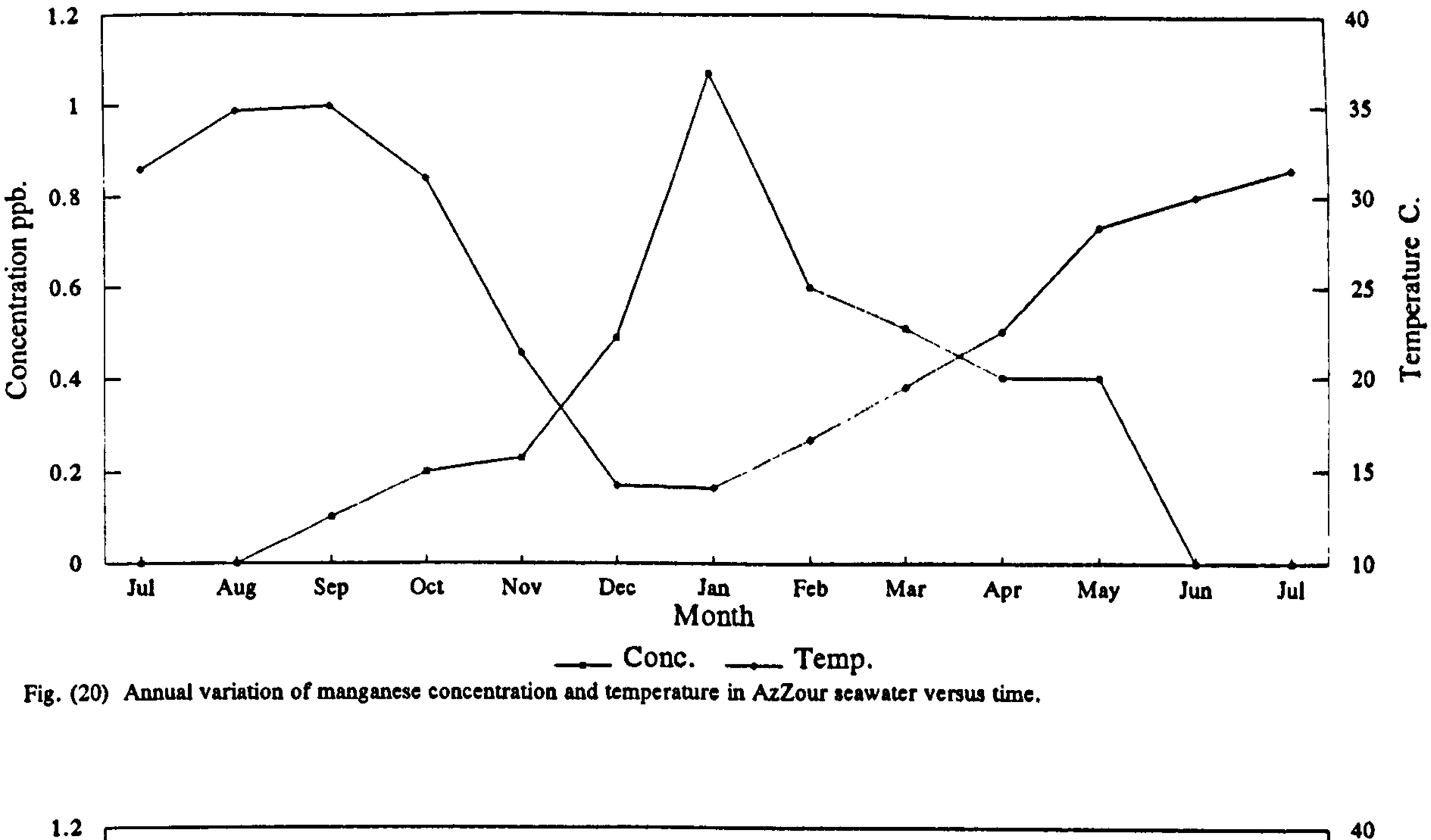

Fig. (20) Annual variation of manganese concentration and temperature in AzZour seawater versus time.

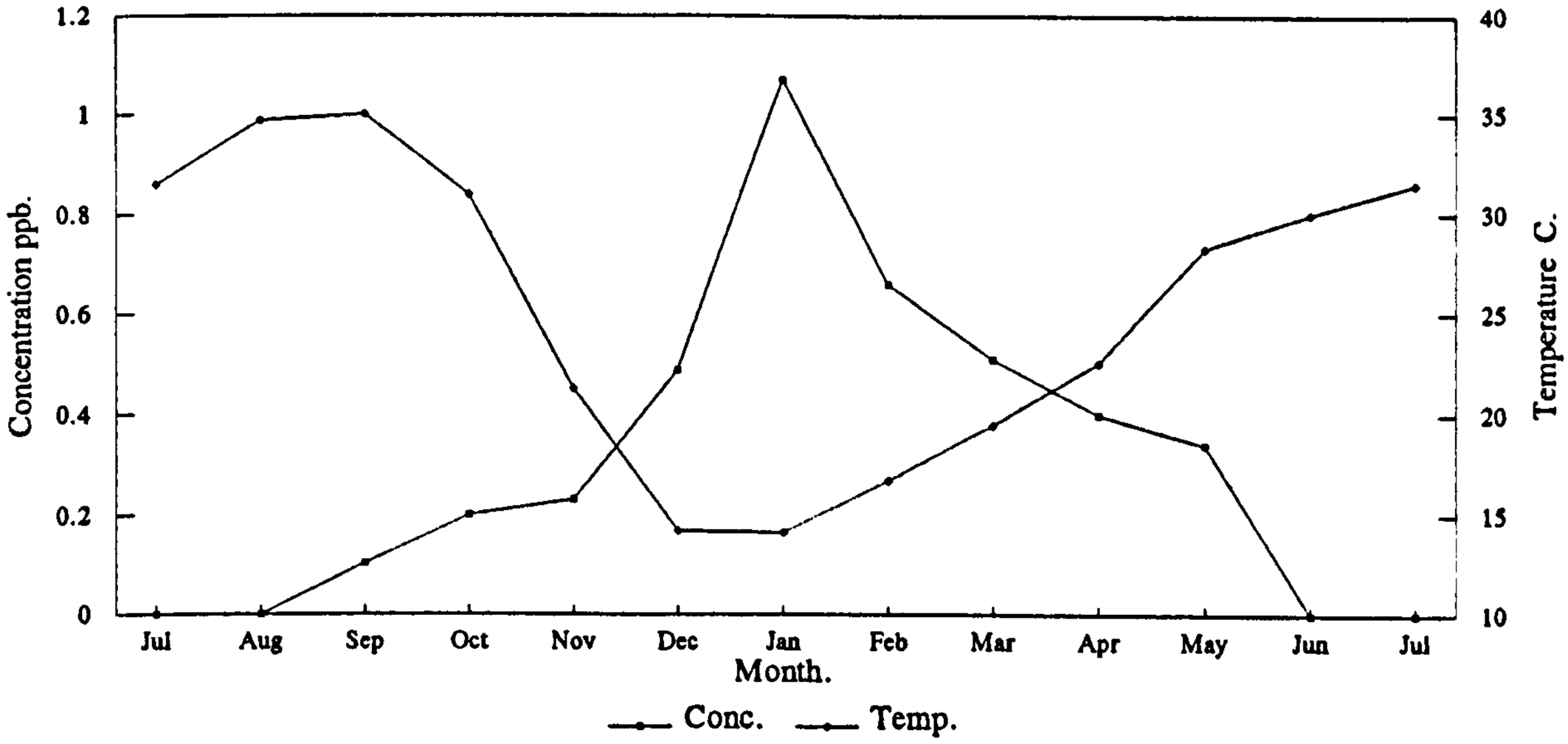

Fig. (21) Annual variation of manganese concentration and temperature in Shuaiba seawater versus time.

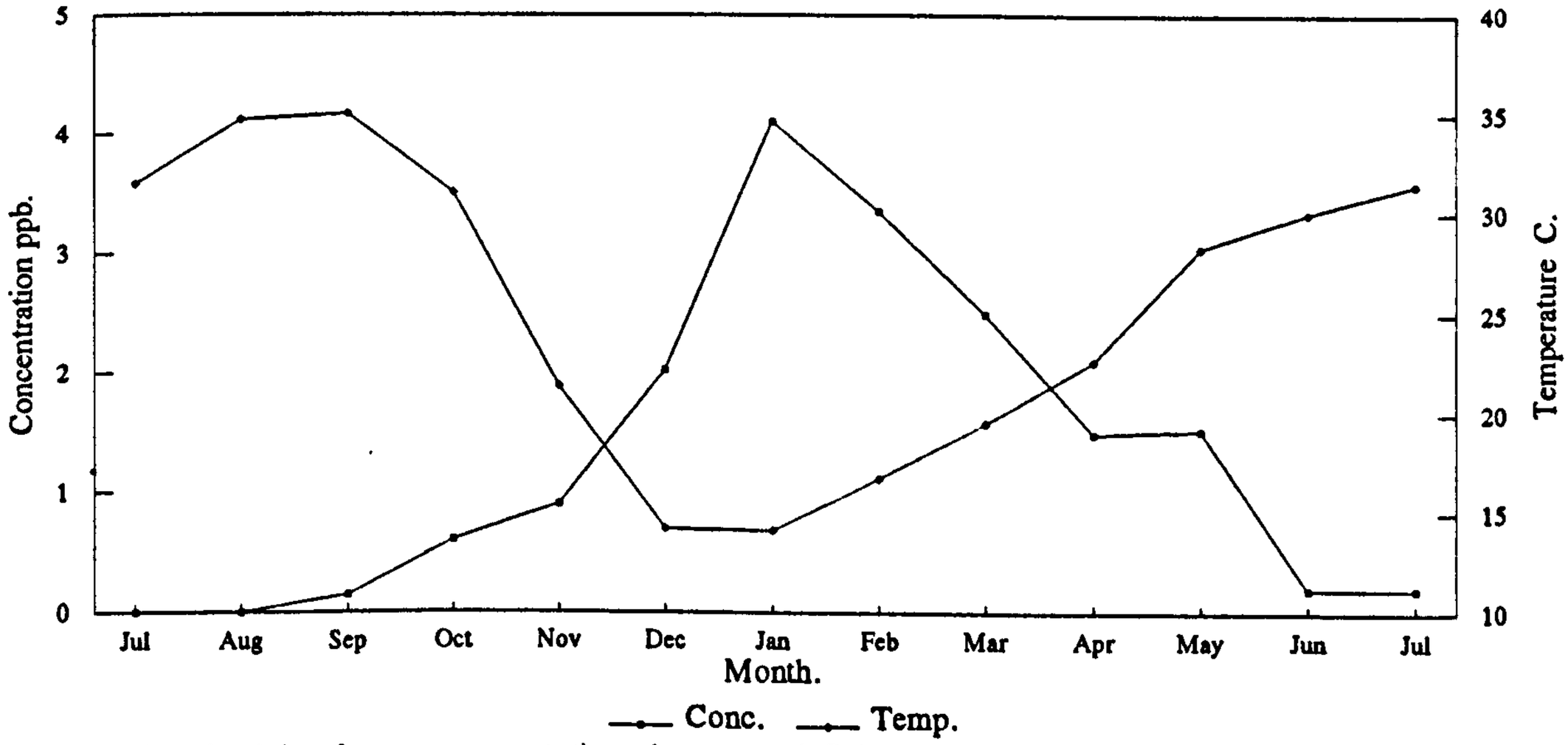

Fig. (22) Annual variation of manganese concentration and temperature in Doha seawater versus time.

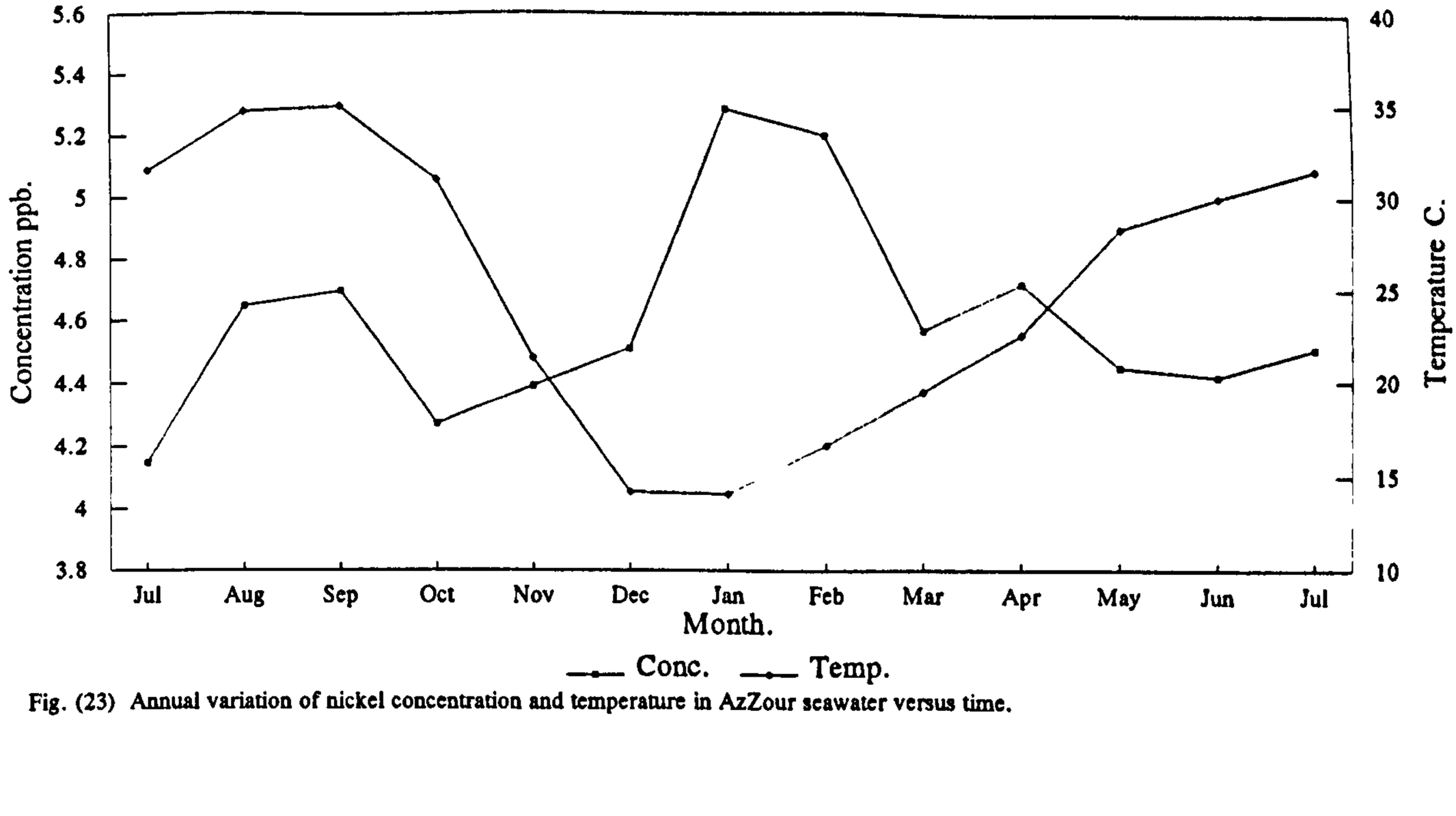

Fig. (23) Annual variation of nickel concentration and temperature in AzZour seawater versus time.

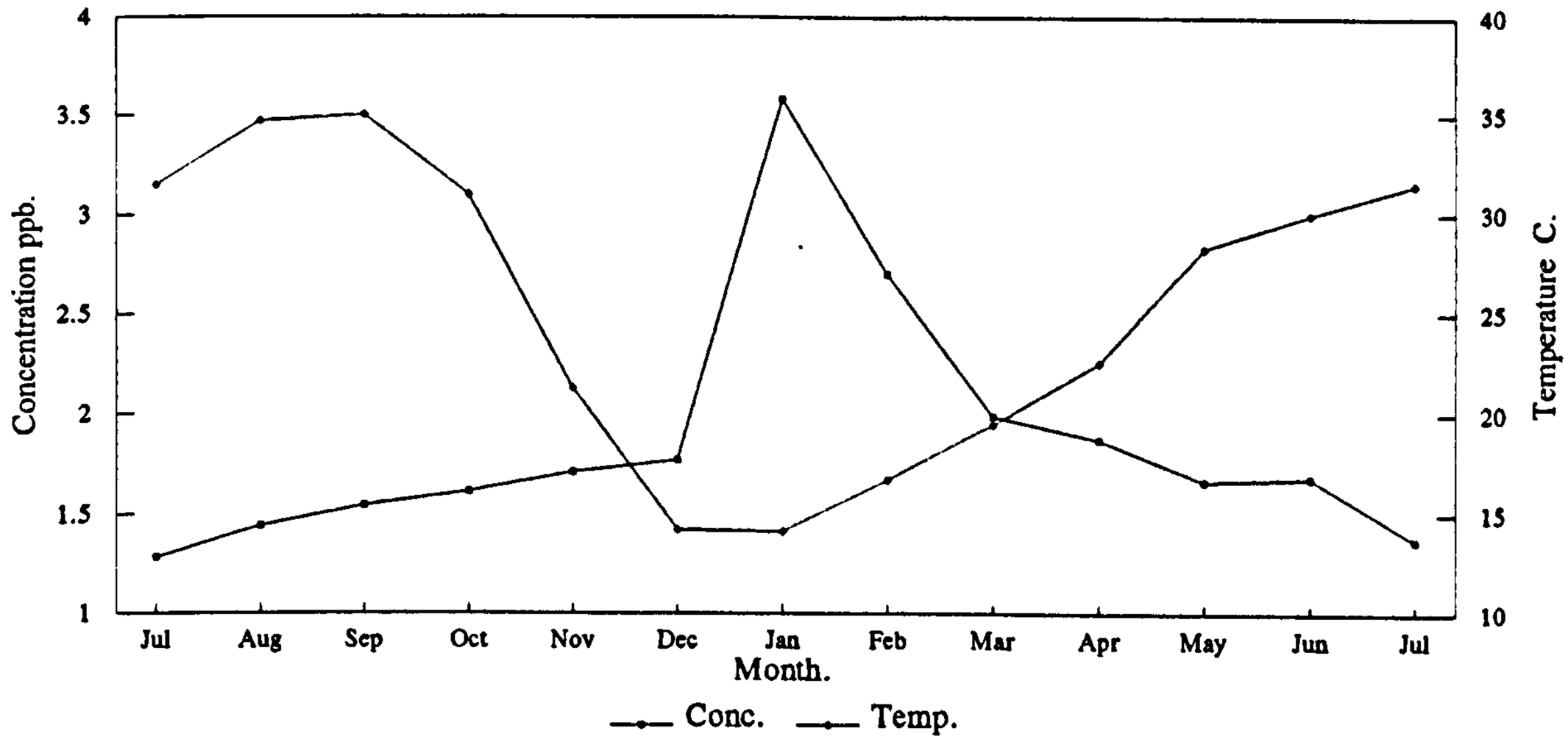

Fig. (24) Annual variation of nickel concentration and temperature in Shuaiba seawater versus time.

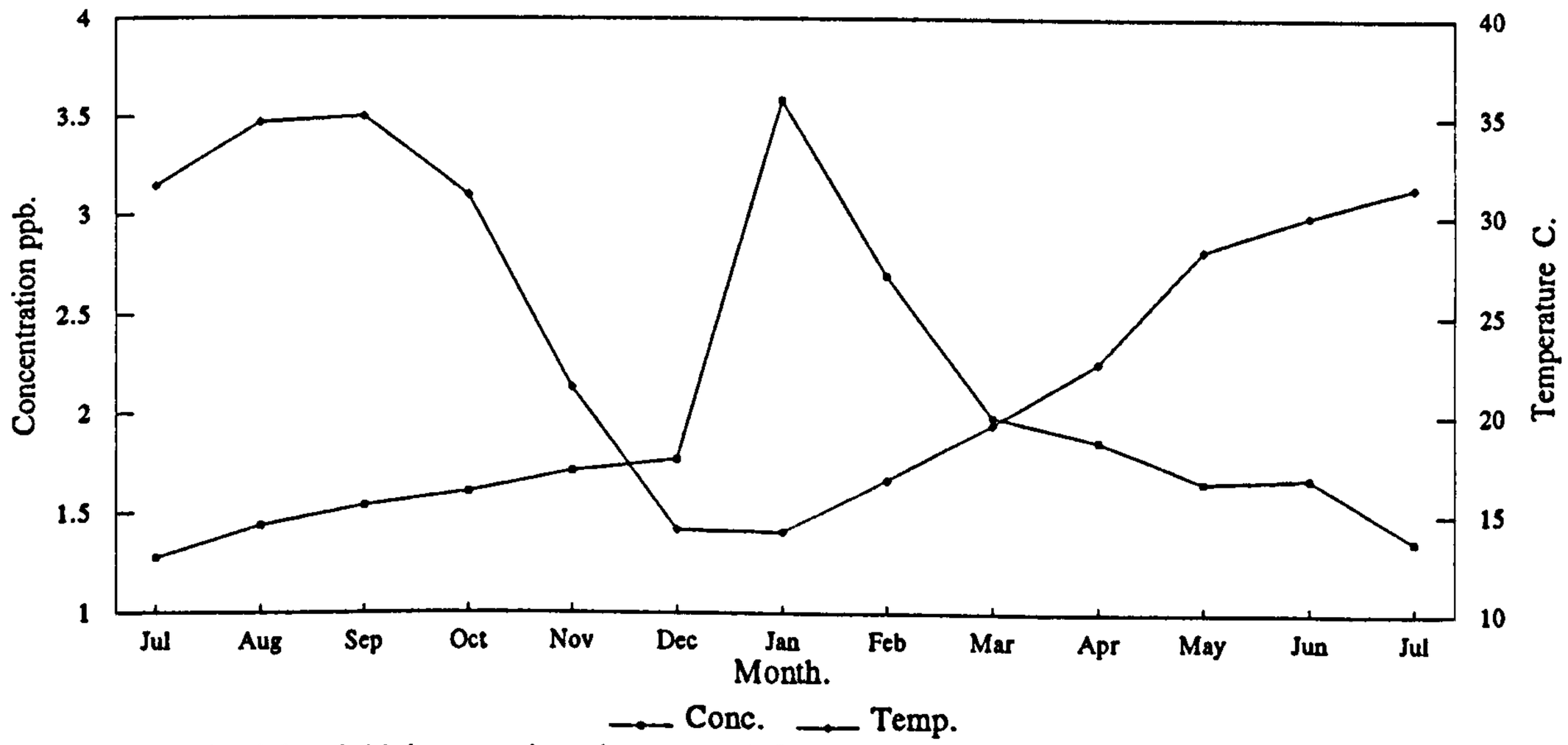

Fig. (25) Annual variation of nickel concentration and temperature in Doha seawater versus time.

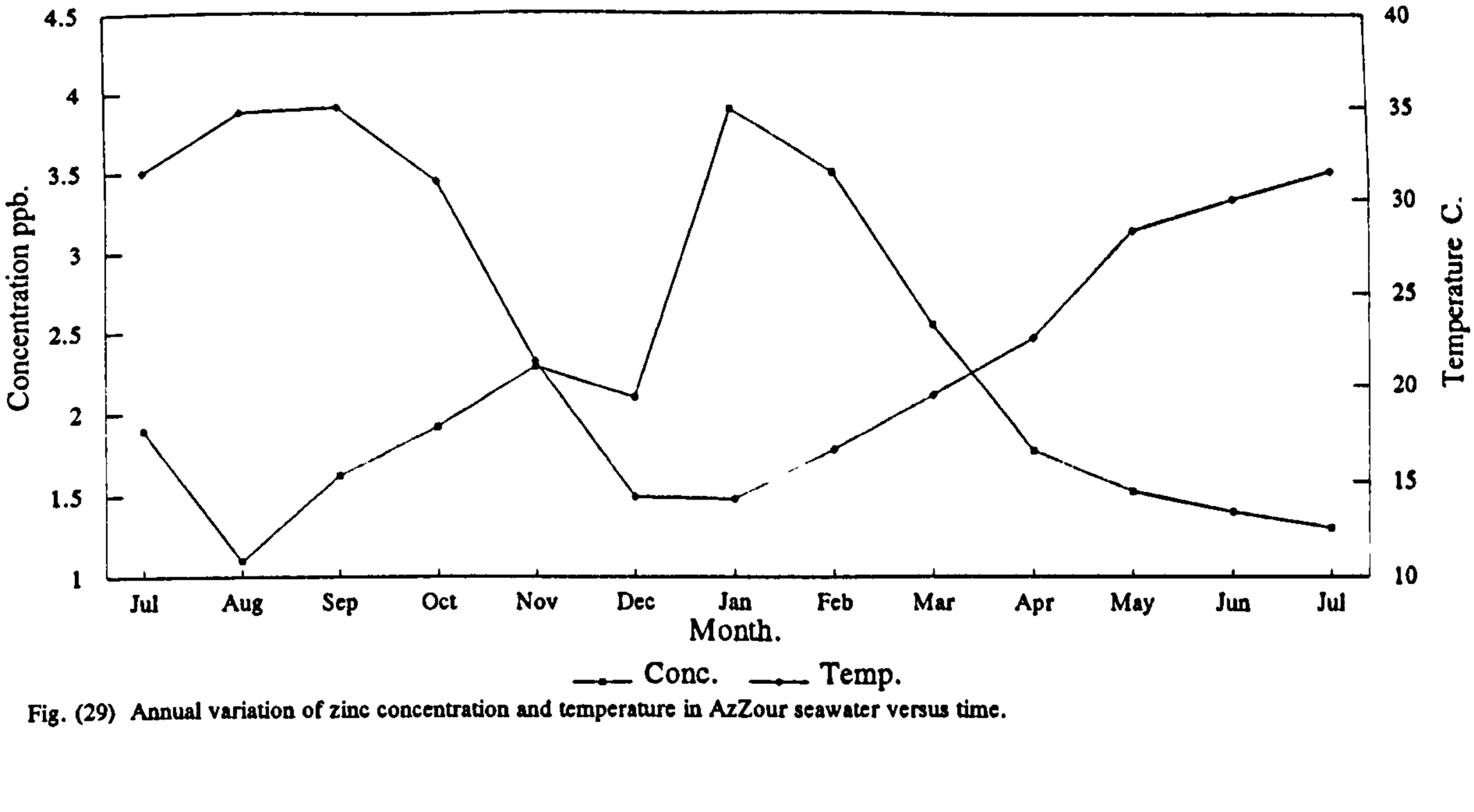

Fig. (29) Annual variation of zinc concentration and temperature in AzZour seawater versus time.

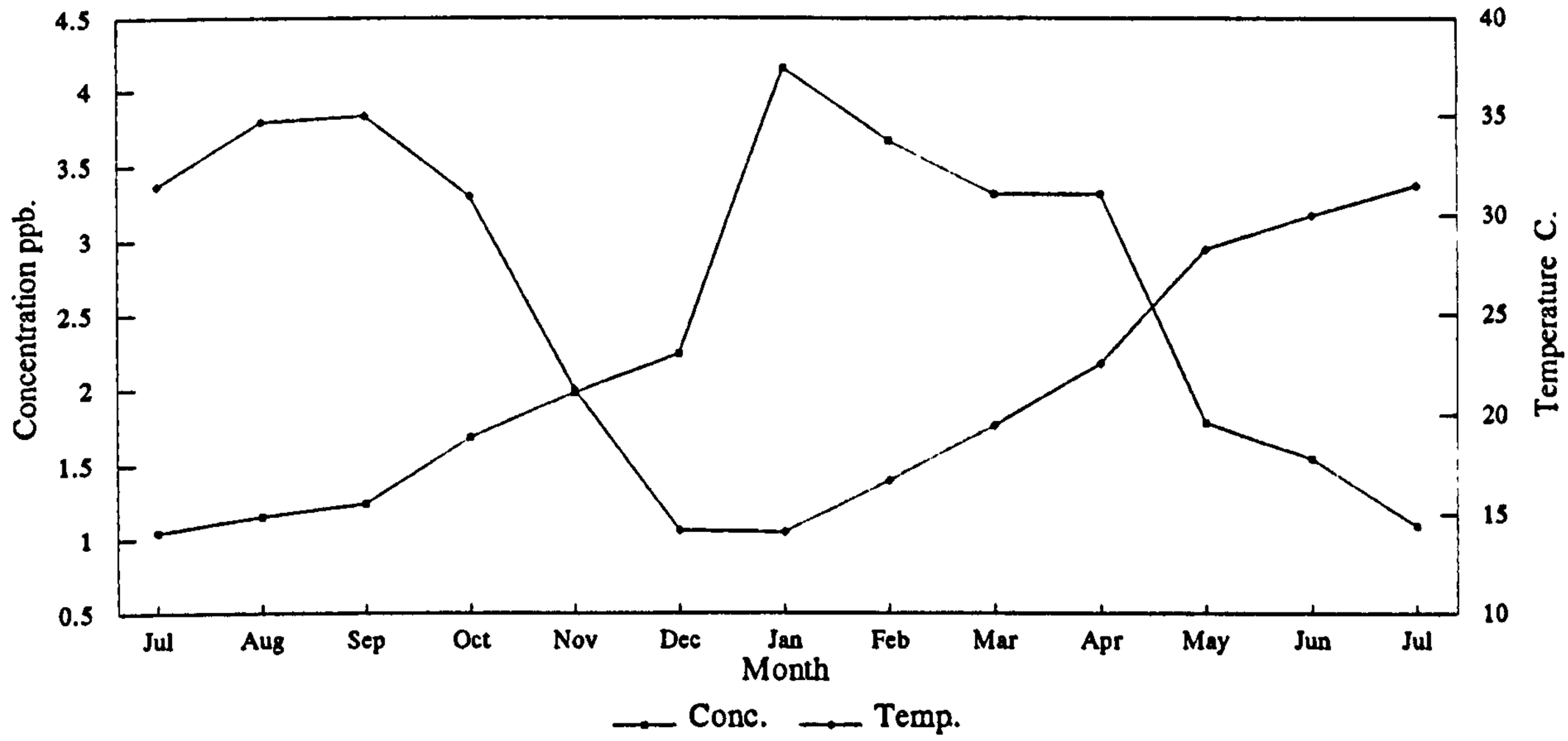

Fig. (30) Annual variation of zinc concentration and temperature in Shuaiba seawater versus time.

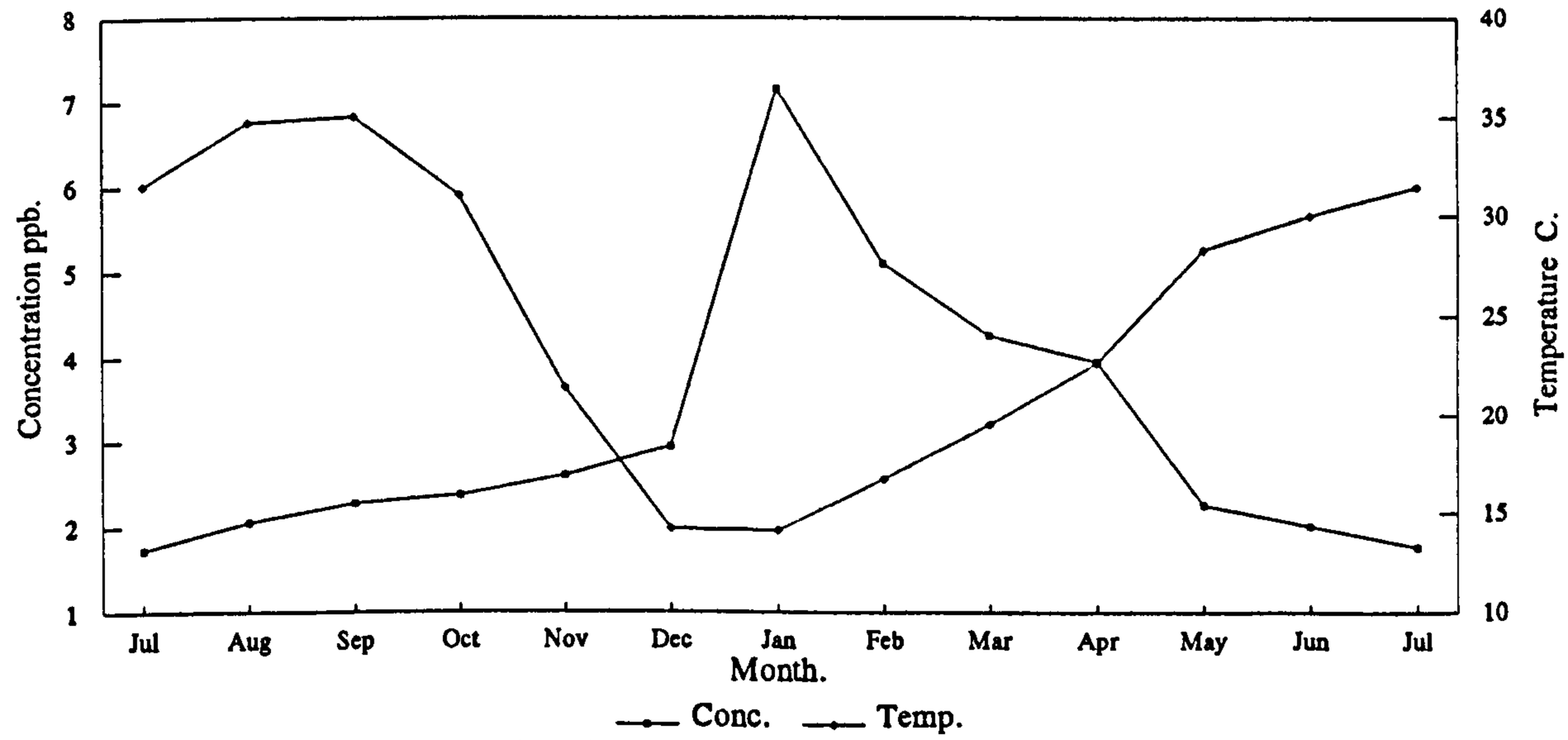

Fig. (31) Annual variation of zinc concentration and temperature in Doha seawater versus time.

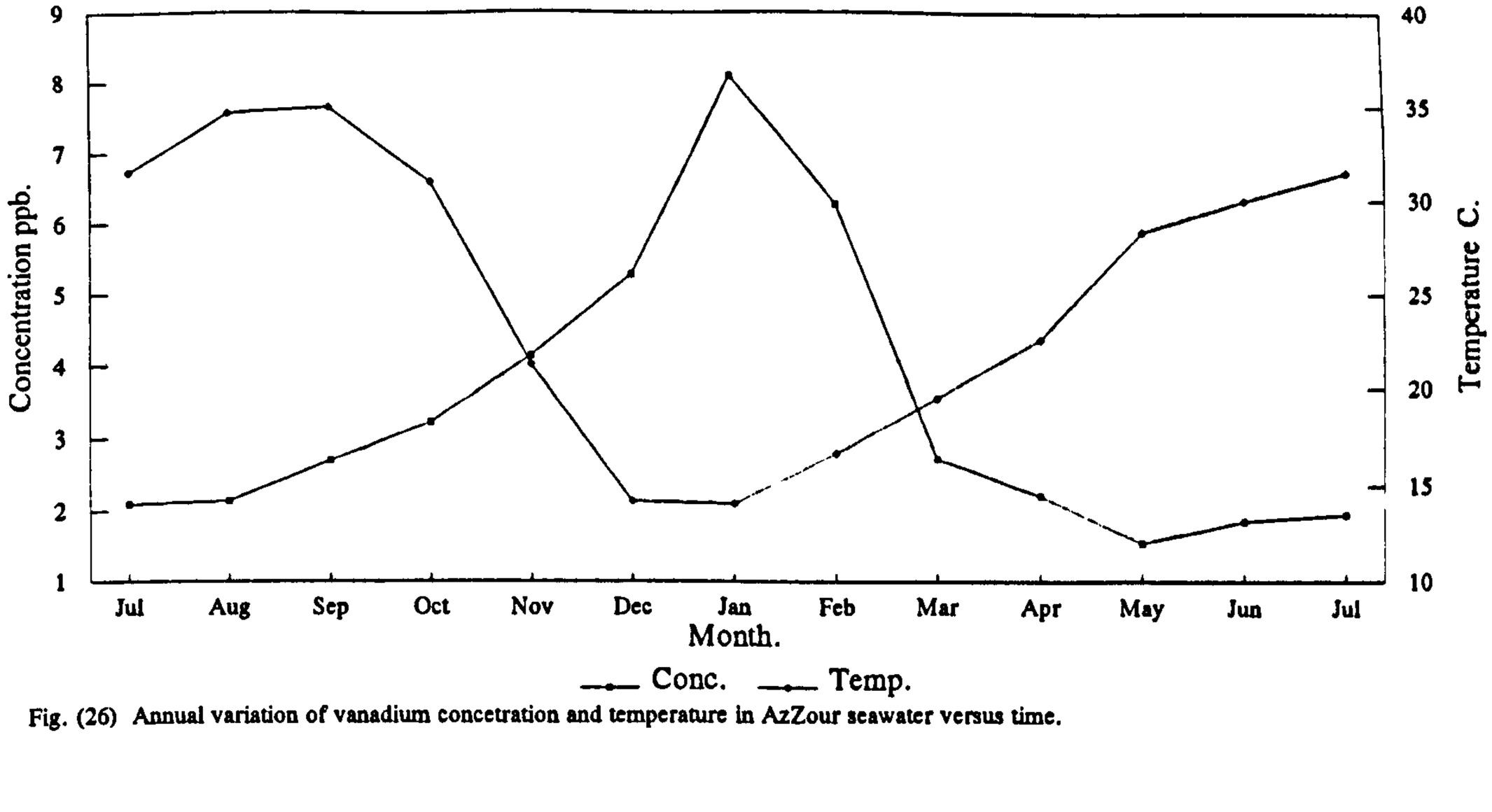

Fig. (26) Annual variation of vanadium concetration and temperature in AzZour seawater versus time.

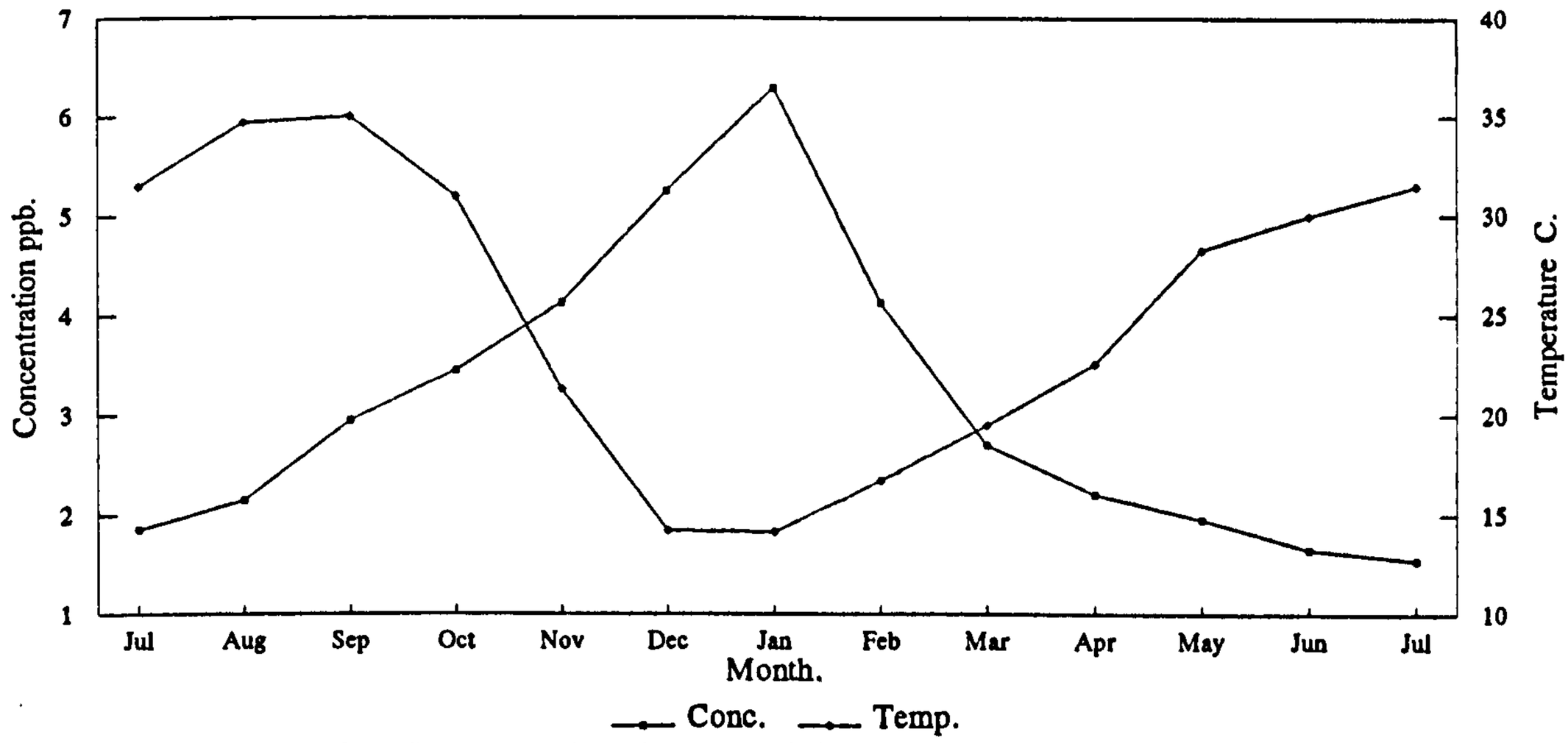

Fig. (27) Annual variation of vanadium concentration and temperature in Shuaiba seawater versus time.

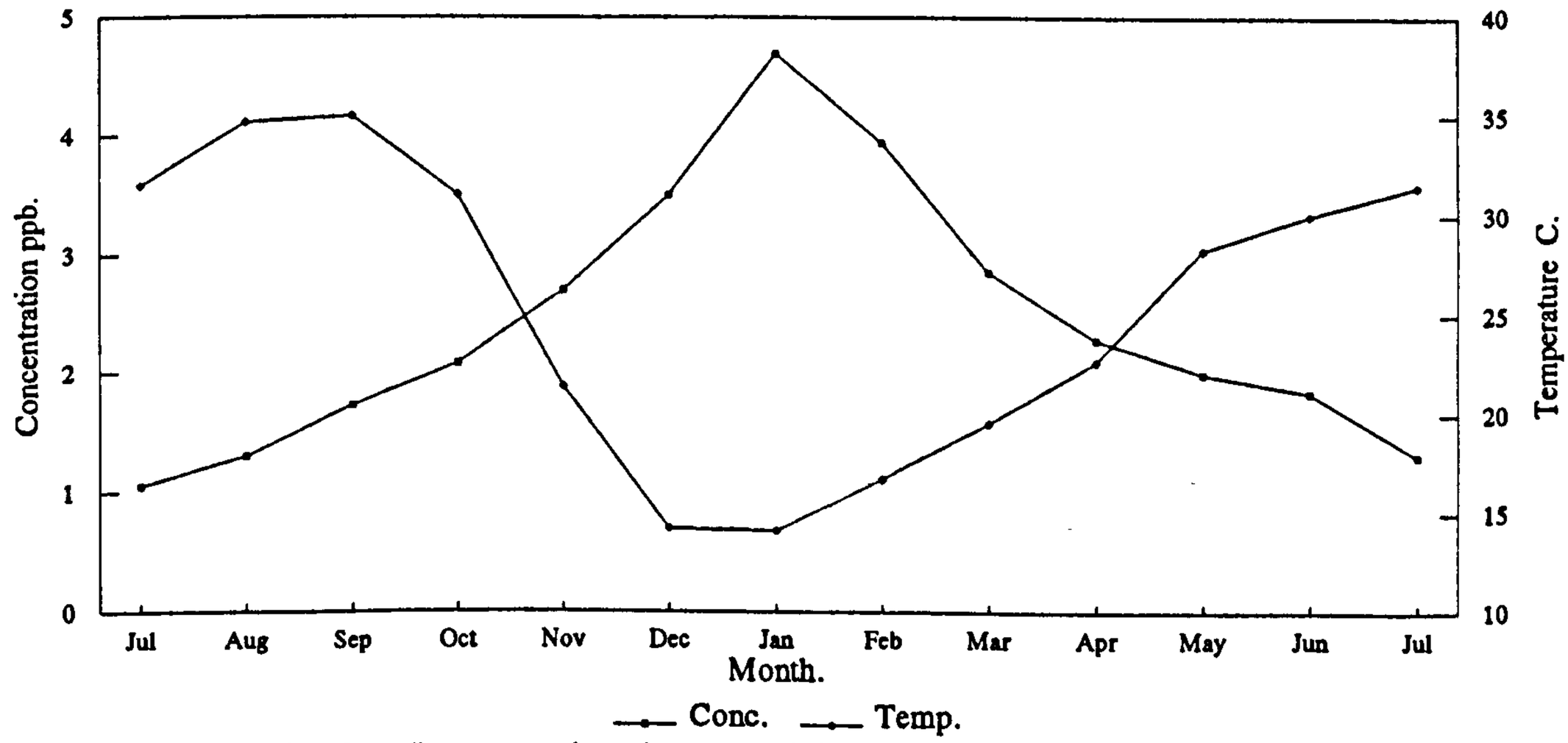

Fig. (28) Annual variation of vanadium concentration and temperature in Doha seawater versus time.

Table (49)

Solubilities of Inorganic Compounds in Water at Various Temperatures.

This table shows the amount of anhydrous substance which is soluble in 100 g of water at the temperature in degrees Celsius as indicated.

	SUBSTANCE	FORMULA	SOLID PHASE	0 C	10 C	20 C	30 C
1	Chromic oxide	CrO_3	.....	164.9	.....	.....	.....
2	Cupric chloride	$CuCl_2$	$2H_2O$	70.7	73.76	77.0	80.34
3	nitrate	$Cu(NO_3)_2$	$6H_2O$	81.8	95.28	125.1	.....
4	nitrate	$Cu(NO_3)_2$	$3H_2O$	.....	.....	.....	.....
5	sulphate	$CuSO_4$	$5H_2O$	14.3	17.4	20.7	25.0
6	Cuprous chloride	CuCl	.....	.....	.....	1.52 25	.....
7	Ferric chloride	$FeCl_3$	.....	74.4	81.9	91.8	.....
8	Ferrous chloride	$FeCl_2$	$4H_2O$	.....	64.5	.....	73.0
9	Ferrous chloride	$FeCl_2$	.....	.....	.....	.....	.....
10	nitrate	$Fe(NO_3)_2$	$6H_2O$	70.02	.....	83.8	.....
11	sulphate	$FeSO_4$	$7H_2O$	15.65	20.51	26.5	32.9
12	sulphate	$FeSO_4$	$1H_2O$	.....	.....	.....	.....
13	Lead acetate	$Pb(C_2H_3O_2)_2$	$3H_2O$	.....	.....	.....	55.04 25
14	bromide	$Pb\ Br_2$	.....	0.45544	.....	0.85	1.15
15	carbonate	$PbCO_3$	.....	.....	.....	0.00011	.....
16	chloride	$PbCl_2$	.....	0.6728	.....	0.99	1.20
17	chromate	$PbCrO_4$	.....	.....	.....	$7x10^{-6}$	.....
18	fluoride	PbF_2	.....	.....	0.060	0.064	0.068
19	nitrate	$Pb(NO_3)_2$	.....	38.8	48.2	56.5	66.0
20	sulphate	$PbSO_4$	.....	0.0028	0.0035	0.0041	0.00449
21	Manganous sulphate	$MnSO_4$	$7H_2O$	53.23	60.01	.....	.....
22	sulphate	$MnSO_4$	$5H_2O$	.....	59.5	62.9	67.76
23	sulphate	$MnSO_4$	$4H_2O$	.....	.....	64.5	66.44
24	Nickel chloride	$NiCl_2$	$6H_2O$	53.9	59.5	6.2	68.9
25	nitrate	$Ni(NO_3)_2$	$6H_2O$	79.58	.....	96.31	.....
26	nitrate	$Ni(NO_3)_2$	$3H_2O$	.....	.....	.....	.....
27	sulphate	$NiSO_4$	$7H_2O$	27.22	32.0	.....	42.46
28	sulphate	$NiSO_4$	$6H_2O$	.....	.....	.....	.....
29	Zinc chlorate	$ZnClO_3$	$6H_2O$	145.0	152.0	.....	.....
30	chlorate	$ZnClO_3$	$4H_2O$	.....	.....	200.3	209.2
31	nitrate	$Zn(NO_3)_2$	$6H_2O$	94.78	.....	118.3	.....
32	nitrate	$Zn(NO_3)_2$	$3H_2O$	.....	.....	.....	.....
33	sulphate	$ZnSO_4$	$7H_2O$	41.9	47.0	54.4	.....
34	sulphate	$ZnSO_4$	$6H_2O$	.....	.....	.....	.....
35	sulphate	$ZnSO_4$	$1H_2O$	.....	.....	.....	.....
36	Sodium chromate	Na_2CrO_4	$10H_2O$	31.17	50.17	88.7	.....
37	chromate	Na_2CrO_4	$4H_2O$	.....	.....	.....	88.7
38	chromate	Na_2CrO_4	.....	.....	.....	.....	.....
39	dichromate	$Na_2Cr_2O_7$	$2H_2O$	163.0	.....	177.8	.....
40	dichromate	$Na_2Cr_2O_7$	.....	.....	.....	.....	.....
41	vanadate (meta)	$NaVO_3$	$2H_2O$	.....	.....	15.3 25	.....
42	vanadate (meta)	$NaVO_3$	.....	.....	.....	21.1 25	.....

By N. A. Lange. Abridged from "Table of Solubilities of Inorganic Compounds in Water at Various Temperature" Lange, Handbook of Chemistry, 10th ed., McGraw-Hill, New York, 1961

Variations in concentrations of trace and heavy metals in the marine environment have been reported by several workers. Vazquez *et al*. (1990) studied the removal of trace metals by chemical changes and bioaccumulation, and concluded that the concentration of metals in the marine environment depends upon several factors: physiological conditions of marine organisms, salinity, temperature and pH. Stern and Grant (1981) emphasised the importance of several factors such as temperature, light levels and dissolved oxygen content on seasonal variation of trace metals. Ouseph (1992) suggested that the depletion of heavy metals are governed by pH, iron content and salinity of the water column.

Results presented by Boyle *et al*. (1981) showed a depletion of Cu in the surface seawater. Coale and Bruland (1988) also showed an increase in the dissolved Cu with depth. A similar conclusion was reached by Quinby-Hut and Wilde (1986-87) who reviewed the Cu levels in seawater and reported that Cu depletes near the surface. Cambell and Yeats (1981), and Emerson *et al*. (1979) found Cr concentrations slowly increased with depth. It is reported that heavy metals are required for normal growth function in many marine organisms such as plankton, oysters, and they are incorporated in the biological cycle [Sadiq (1992), Páez-Osuna *et al*. (1995)]. Sadiq and McCain (1993) pointed out that the metals bioaccumulated in clam, and have clear association with the biological cycle of these organisms. Brian *et al*. (1989) observed that a seasonal variation in trace metal concentrations occur at individual sites (the cycle of winter "peaks" and summer "lows"). Brian and coworker (1989) attributed their observation to the growth cycle of the algae where metal levels remain more stable during the period of low growth between September and the following February i.e. during the winter months when sea temperature is low and day-light hours are short.

The analysed samples were collected near the surface (1 meter depth), where the highest biological activities occur [Pelczar *et al*. (1977)]. Hence, the concentrations of the

studied elements will depend on competing processes such as coagulation, precipitation, complexation/chelation and sorption with dissolved organic and inorganic ligands [Moore (1984)].

Referring to the obtained results and the above citations, it can be concluded that the naturally occurring processes in the surface or near-surface seawater has a direct relationship with the temperature of the prevalent conditions. Heavy metal concentrations decrease with the increase of salinity. This behaviour was observed by Ouseph (1992), for Cu, Pb, Cd, Fe and Zn. Knowing that the salinity of seawater of Kuwait increases during summer and decreases during winter (47,000 mg/l ± 2000), the obtained results show similar behaviour with temperature.

As for the pH, results of Kuwait's seawater show very little variation of 8.2 ± 0.1 as shown in table (1) chapter (1). Hence, the pH effect on the studied metal concentration is expected to be minimal.

In conclusion, seasonal variations in temperature has a very profound effect on the concentrations of the studied metal ions in Kuwait's seawater. This effect is transmitted to the metal concentrations mainly through biological activities near the surface seawater. More important, reported concentrations of dissolved trace metals in seawater as shown in table (50), are misleading, since they vary drastically from worker to worker and, often are given without specifying the conditions. Trace metal ion concentrations in seawater, therefore, should be identified with; time, depth, location and temperature. However, if pH changes by a great amount, this variable also should be considered.

It is clear that ion concentrations in near-surface seawater vary from season to season and from one location to another. Hence, absolute concentrations for these metal ions in seawater can not be given without proper identification of the collected sample as pointed out by Mason (1966).

Table (50)

Concentrations of Dissolved Trace Metals in seawater as Reported in the Literature.

Element	Concentration µg/l							
	1[a]	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]	8[h]
Chromium	0.3	0.25	0.3	0.3	0.18	--	0.08	<1.0-2.36
Copper	0.5	1.0	0.5	0.1	0.79	0.2	0.3	3.67-9.33
Iron	2.0	--	2.0	2.0	0.1	0.5	1.0	23.29-33.83
Lead	0.03	0.004	0.03	0.003	0.04	<0.1	0.03	<0.05
Manganese	0.2	0.7	0.2	0.2	--	--	--	0.37-1.63
Nickel	0.5	0.6	1.7	0.2	--	--	--	1.84-4.55
Vanadium	2.0	2.4	2.5	2.5	--	--	--	2.37-3.77
Zinc	2.0	7.0	4.9	0.1	0.5	<10.0	0.03	2.11-3.24

a Drever (1982).
b Parker (1972).
c. Riley and Skirrow (1975).
d. Martin and Whitefield (1981).
e. Dames and Moore (1983).
f. Danielsson and Westlund (1980).
g. Jan and Young (1978a).
h. This study (1995).
-- No information available.

6.1.2. Ground Water.

The second source of contamination is identified as the brackish ground water which is added to the distillate to improve its quality and increase its quantity, as mentioned earlier. Three main blending/treatment plants are available in Kuwait, namely: AzZour, Shuaiba and Doha. The source of the ground water supplied to each plant comes from different ground water fields. AzZour blending plant is supplied from Um-Qudair ground water field , while Shuaiba and Doha blending plants are supplied from Shagaia and Sulaibiya ground water fields, respectively. The locations of these sites are shown on figure (11).

Representative ground water samples were collected from the three sources through respective ground level reservoirs. Table (51) shows the average of twenty samples collected in a year period. Each sample has been analysed in five replicates to findout the concentration of Cr, Cu, Fe, Pb, Mn, Ni, V and Zn, analysed using ICP-MS method.

Since, the three ground water fields are located in the same aquifer i.e. Dammam formation, the obtained results exhibited, as expected, similar levels of ion concentrations with very slight variation that could be attributed to a leaching effect due to long contact of water-strata inside the different locations of the formation.

Knowing the concentration of the respective metal ions in the ground water and the blending ratio of this water with the distillate, the potable water concentration of these ions can be calculated from the mass balance equation which will be addressed under the discussion of the potable water.

The source of contamination could be either from the oil spillage, or leached from the lower geological formations of oil wells as evident from table (52) which shows the trace metal ion concentrations in crude oil of Kuwait.

Data obtained from previous studies carried out in the Arabian Gulf Countries i.e. Saudi Arabia, Bahrain and Kuwait show the quality of ground water in the form of conductivity, pH, alkalinity, total hardness, sodium, potassium, chloride,

sulphate and fluoride. Concentrations of the trace metals were not emphasised [Turaihi (1978), Ahmed (1992), Ebrahim and Siwek (1992)].

Table (51)

Trace metal concentration (μg/l) in Kuwait's ground water.

Element	Sulaibiya	Shagaya	Um Qudair
Chromium	2.73	2.313	<1.0
Copper	20.57	24.27	20.18
Iron	36.62	34.92	25.83
Lead	0.36	1.584	2.45
Manganese	1.56	1.492	2.87
Nickel	4.60	2.190	3.58
Vanadium	24.11	26.41	20.08
Zinc	10.90	12.135	10.24

Table (52)

Trace metal concentration in Kuwait's crude oil.

Element	concentration (μg/g)
Chromium	1.0
Copper	0.1
Iron	0.5
Lead	<0.1
Manganese	0.1
Nickel	5.0
Vanadium	20
Zinc	0.2

Source: Kuwait Institute for Scientific Research (1982).

6.1.3. Distilled Water.

The typical analysis of distillate from the Kuwait multi-stage flash evaporation units shown in table (2) chapter (1), show that the distilled water is very soft and has a low pH value. It is transmitted to the potable water treatment sites via ductile-cement lined pipelines.

Table (53) represents average concentrations of the studied elements in distilled water. Twenty samples were collected through 13 months duration, and analysed in five replicates, using ICP-MS method.

Theoretically distillate should be devoid of all dissolved solids available in the seawater. However, detected concentrations in the distillate could be attributed to either, splash of droplets inside the distillation chambers or to contact with materials of construction, or both. In Kuwait, distillate contains salts in the range of 3-30 mg/l depending on the design and performance of the plant. This type of very "soft" water has a low buffer capacity and is considered quite aggresive to the materials that come into contact with it [Abdel-Jawad and Al Awadi (1984)]. Table (54) shows materials of construction used in multi-stage flash evaporator along with their chemical composition.

The sequence of distillate production starts with steam production passing through stainless steel (316L) demisters and in contact with the materials of the evaporation chambers (carbon steel) as shown in figure (2), chapter (1), the flow diagram of the MSF process. The evaporated steam is then condensed on the external side of the heat transfer tubes which are made of Cu/Ni (70/30) in the first two chambers of the heat recovery section and the three chambers of the heat rejection section. The remaining heat transfer tubes in the chambers numbers 3-23 are made of aluminium brass. The evaporated steam is condensed on the heat transfer tubes and accumulates in the distillate tray which is made from stainless steel 316L and pumped out through the distillate pump and distillate duct which both are also made of stainless steel 316L. Other materials that come into contact with the

process of distillate production are the ejector and the connecting tubes which are made of Cu/Ni 70/30.

From Table (53), it can be seen that the high concentrations of copper, iron, manganese, nickel and zinc are the result of distillate contact with material of construction used in MSF plants as evident from the chemical composition of these components as shown in table (54).

Table (53)

Trace metal concentration (μg/l) in Kuwait distilled water

Element	Doha	Shuaiba	AzZour
Chromium	<1.0	<1.0	<1.0
Copper	27.49	29.63	26.18
Iron	12.56	20.95	23.99
Lead	0.08	<0.05	<0.05
Manganese	0.34	0.19	0.30
Nickel	<1.0	1.59	1.63
Vanadium	<0.05	<0.05	<0.05
Zinc	10.26	10.66	10.37

Table (54)
Multi-Stage Flash evaporators; Material of construction.

Component	Material	Chemical Composition
1. External Stiffener. 2. Shell plate, Ceiling plate. 3. Brine and Distillate. 4. Flash Chamber. 5. Piping.	Carbon steel Carbon steel lined with 316L S.S. Carbon steel lined with 316L S.S. Carbon steel Carbon steel	<1.65% Mn, 0.06% Si, and 0.6% Cu
6. Distillation ducts, trays and condenser shell. 7. Demisters. 8. Venting and splashing baffle plates. 9. Deaerator packing support, nozzles and cross pipe assembly. 10. Brine heater. 11. Pumps. 12. Strainers. 13. Piping.	316L Stainless steel	0.08% C, 17% Al, 12% Ni and 2.5% Mo
14. Heat exchanger tube	Cupro.nickel	66% Cu, 30% Ni, 2% Fe and 2% Mn.
15. Vent and ejector condensers. 16. Pumping bearing, cooling coils and fittings.	70/30 copper/nickel	65-69% Cu, 28-32% Ni, 0.5-1.5% Nb, 0.25-1.5% Fe, 1.5% Mn, 0.5% Si, 0.15% C and 0.03 Pb.
17. Condenser tubes.	Aluminium brass	76% Cu, 22% Zn and 2% Al.

Continue table (54)

Component	Material	Chemical Composition
18. Water boxes. 19. Brine recirculating pumps.	mild steel	0.05-0.1% C, 0.25-0.5% Mn, 0.035% P and 0.04% S.
20. Piping.	90/10 copper/nickel	90% Cu and 10% Ni.
21. Plates and supports.	Naval brass	60.5% Cu, 1.0% Sn, 0.2% Pb, 38.7% Zn, and 0.1% Fe.

6.1.4. Potable Water.

As previously explained, (chapter 1), the potable water in Kuwait is produced from blending ground water with distilled water. At the time this work was carried out, the applied blending ratios of brackish with distilled water respectively, were as follows:

Doha site: 10% with 90%.

Shuaiba site: 12% with 88%.

AzZour site: 5% with 95%.

Based on these blending ratios, theoretical concentrations are calculated and presented in table (55). The concentrations are obtained using the mass balance equation:

$$C_1V_1 \text{ (distilled water)} + C_2V_2 \text{ (ground water)} = C_0V_0 \text{ (potable water)}$$

Where:

C = concentration.

V = volume.

Potable water samples were collected from the water installations of Kuwait and the studied elements were analysed. Results of samples collected from ground level reservoirs, pumping stations, elevated towers and lorry filling stations are presented in tables 56, 57, 58 and 59 respectively.

Comparing the obtained results with the theoretical estimation of the trace metal ion concentrations as shown in table (55), general agreement of the source of these metals can be understood. However, fluctuations in the obtained results can be attributed to corrosion of the components of the water installations due to the aggressiveness of the produced potable water as shown in table (2) chapter (1).

Chemical and physical analyses of the water produced in Kuwait indicate that it is suitable from the health point of view. The amount of dissolved oxygen is rather good, the alkalinity is low, the hardness is moderately low, chloride

view. The amount of dissolved oxygen is rather good, the alkalinity is low, the hardness is moderately low, chloride and sulphate ions are high compared to alkalinity, and free carbon dioxide is very low. In general bacteriological, physical, and chemical properties of the potable water distributed in Kuwait comply with the desirable limits of the international drinking water standards as shown in appendix I except for iron. The potable water after treatment shows no turbidity or colour. However, it seems that its quality deteriorates on its way to the consumer where it comes out of the tap turbid and coloured.

Although, Kuwait's distribution system is comparatively new, and most of its components are cement lined, corrosion problems in pumps, fittings, connections and consumers' service lines are encountered.

It is worth mentioning that colouring of the water by iron pickup (red water) stains laundry and bathroom fixtures but does not present the health hazard that excessive pickup of copper does, when corrosive water stagnates in iron and copper pipes, respectively.

Table (55)

Theoretical trace metal concentrations (μg/l)
in potable water network

Element	Doha	Shuaiba	AzZour
Chromium	<1.0	<1.0	<1.0
Copper	26.79	28.99	25.878
Iron	14.97	22.54	24.08
Lead	0.11	0.18	0.122
Manganese	0.46	0.39	0.433
Nickel	0.46	1.61	2.01
Vanadium	2.41	3.01	1.00
Zinc	10.32	10.71	10.367

Based on blending ratio of brackish water as indicated above with distilled water from the respective production site.

Table (56)

Trace metal concentration (μg/l) in potable water from reservoirs

Element	Doha	Shuaiba	AzZour
Chromium	<1.0	1.35	<1.0
Copper	27.66	23.72	28.72
Iron	30.47	30.05	60.28
Lead	0.15	0.08	<0.05
Manganese	1.22	1.22	0.90
Nickel	3.96	2.11	2.12
Vanadium	1.36	0.99	1.26
Zinc	17.80	12.12	13.21

Table (57)

Trace metal concentration (μg/l) in potable water from pumping stations

Element	Doha	Shuaiba	AzZour
Chromium	<1.0	1.53	<1.0
Copper	31.33	23.67	22.63
Iron	32.26	30.14	41.53
Lead	0.13	0.11	0.09
Manganese	1.07	1.20	0.70
Nickel	4.06	1.83	1.53
Vanadium	1.17	0.82	0.78
Zinc	11.23	11.07	10.40

Table (58)

Trace metal concentration (μg/l) in potable water from elevated towers

Element	Doha	Shuaiba	AzZour
Chromium	<1.0	1.47	<1.0
Copper	28.22	29.27	21.11
Iron	85.74	67.09	69.31
Lead	0.20	0.17	<0.05
Manganese	1.13	1.31	1.54
Nickel	3.89	2.29	2.24
Vanadium	1.22	1.29	1.19
Zinc	27.58	23.19	18.75

Table (59)

Trace metal concentration (μg/l) in potable water from lorry filling stations.

Element	Doha	AzZour
Chromium	<1.0	<1.0
Copper	28.28	21.06
Iron	92.68	54.21
Lead	0.21	<0.05
Manganese	1.49	1.45
Nickel	4.39	2.25
Vanadium	1.43	1.26
Zinc	23.54	18.75

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CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

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7.1 CONCLUSIONS.

Kuwait, being an arid coastal country, relies on seawater desalination to satisfy almost all its needs for potable water.

The quality of the produced water complies fully with the most stringent international standards for drinking water, except for its aggressiveness towards the materials of the storage and distribution facilities.

Generally speaking, trace metals are available in food and in water as a result of their natural occurrence on the earth, or as a result of the aggressiveness of the natural water towards the material which comes in contact with it. As the drinking water of Kuwait cannot be classified as purely natural and it contains trace metals, it was decided to investigate the source of certain trace metals available in the drinking water produced in Kuwait.

Chromium, copper, iron, lead, manganese, nickel, vanadium and zinc were selected for this investigation. The selection was based on the quality of the produced water, sources of its constituents, materials used in constructing the distillation plant, storage and distribution facilities, presence of oil near the ground water aquifers or in the seawater and presence of industrial contaminations in the seawater.

Trace metals may be determined satisfactorily by several instrumental methods. The concentrations of the dissolved and particulate of these trace metals are usually very low. Therefore, their determination requires a prior concentration step which ideally enriches the metal ions and frees them from interferences. Therefore, efforts were made to preconcentrate or separate these elements from their matrices prior to analysing them.

A solid-liquid extraction technique, using chelex-100 resin, was optimized to obtain satisfactory results. Optimum conditions were found at: pH = 6.7, flow rate = 3 ml/min, column height = 4 cm and resin = 100-200 mesh in the ammonium form. Under these conditions, the studied trace metals were successfully concentrated at very high recovery rates, with

minimum interferences, except for the chromium which was low (38% recovery). However, this technique required large quantities of ultra pure distillate, very pure chemical reagents and a very long time to accomplish.

Another technique using liquid-liquid extraction was investigated, Freon and methyl isobutyl ketone (MIBK) solvents were used, with and without back-extraction into nitric acid. It was found that without the back-extraction step, optimum recovery of the selected metals was achieved. However, due to the solubility of the MIBK with time and the precipitation of iron, analysis was performed immediately after the extraction. This technique required ultra pure chemical reagents and very clean surfaces of the extraction containers.

Atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) instruments were utilized to verify their suitability in analysing the trace metals under study. Although the obtained results indicate clearly that AAS has higher precision (0.0% - 1.18% coefficient of variation c.v.), compared to ICP-MS (1.08% - 4.47% c.v.), the latter instrument was adopted as it offers lower detection limits, is easier to use and faster to render results.

International standards for maximum recommended levels of the studied trace metals in drinking water are shown in table (60). It can be seen from tables 42 through 48, that results obtained from seawater samples are well below these recommended levels except for the iron (table 44) which slightly exceed the lower limit only during December and January. As for the brackish water samples, all the obtained results (table 51) are well below the maximium recommended levels for drinking water. Similarly all results obtained from analysing distillate samples (table 53) exhibited much lower values than the maximum recommended levels. Hence, it is axiomatic to expect low trace metal values in the blended stream of distillate and brackish water. The actual values (again except in the case of iron), are well below the maximum

Table (60)

Maximum recommended levels of the studied trace metals in drinking water*.

Element	EEC 1980	US EPA 1989	Canada	WHO 1993
Chromium	50	50	50	50
Copper	700-1500	200-1000	-	2000
Iron	300	50-300	300	-
Lead	50	50	50	10
Manganese	50	10-50	-	500
Nickel	50	-	-	20
Vanadium	-	-	-	-
Zinc	100-2000	5000	2000	-

* Concentrations in μg/l

recommended levels of the international standards as can be seen from tables 55 through 59. The high iron concentrations in the potable water samples are expected as the corrosive water is transmitted and distributed through iron pipes. It is worth mentioning that stabilization treatment of Kuwait's drinking water is in its final implementation stage. Water will be rendered non-corrosive and iron concentrations will be controlled.

Comparing the obtained results for the drinking water of Kuwait (table 56 through 59), with the theoretical blending values as found in the distillate and the ground water (table 55), general agreement of the source of these metals can be identified as follows:

Element	Most probable source
Chromium	ground water.
Copper	distillation plants.
Iron	distillation plants, ground water, and network.
Lead	ground water.
Manganese	ground water and network.
Nickel	distillation plants and ground water (oil)
Vanadium	ground water (oil)
Zinc	distillation plants and ground water

It is worth noting that the nickel and vanadium concentrations in both the ground water and the crude oil of Kuwait are of similar levels (table 51 and 52), which could indicate that both metals are coming from the same strata.

Results also indicate that sources of the studied trace metals are mainly the construction materials of the distillation plants, and/or the ground water. No direct relationship between the metal concentration in the seawater and the distillate could be deduced.

Although, the solubilities of the principal species of

the studied elements increase with temperature, their total concentrations in the Gulf seawater inversely changes with temperature. Their concentrations exhibited wide variations with seawater temperature. It was concluded that naturally occurring processes in the seawater surface or near-surface has a direct relationship with this observation. Most probably, this is due to the formation of organo-metallic complexes inter-related with the marine biological activities.

The highest concentrations of all the studied metals occurred during the lowest seawater temperature (January), whereas the lowest metal concentrations obtained during the highest seawater temperature (August). The fluctuation in concentrations of these metals with temperature varies from metal to metal and from one location to another. Chromium and nickel fluctuate in concentration two to two and half times in general over the year. Copper, iron, vanadium and zinc fluctuate four to five times over the same period. Manganese shows great fluctuation ranging from 10 to 27 times, with the higher biological activities as expected near the outfall of the great rivers (Tigris and Euphrates). A similar trend was noticed with nickel and zinc, both showed higher fluctuation near the north area. The remaining metals did not show significant difference in fluctuation between the north and the south of Kuwait. Since the metal concentrations in the seawater vary mainly with temperature, location and level of collecting the water samples, reported absolute metal concentrations in various seas should be revised and more meaningful data should be specified.

7.2. SUGGESTIONS FOR FURTHER WORK.

Through this work, concentrations of certain trace metals in the Gulf seawater have been determined. The technique showed that with the highest seawater concentration in the world, minute concentrations of the trace elements can be measured with an acceptable degree of accuracy and reproducibility. Also, through this work, great variations in trace metal concentrations, mainly with temperature have been observed. Analysing ground water samples show certain trace metal concentrations, these metals may be brought from elsewhere by wind, at least; the aerial deposition of cadmium and lead, water (rain). During transport and deposition on the soil surface, particles were sorted according to mineralogical composition. Of course, these metals transported through the soil and leached into the ground water.

Based on this work, the following further work can be suggested:

1- Other trace metals in Kuwait seawater and ground water such as aluminium, arsenic, cadmium, mercury, molybdenum, selenium, tin and titanium should be investigated.

2- Trace metal concentrations in various seas, at different levels and temperature should be revised.

3- As the seawater temperature varies widely in the Gulf (between 15-35 °C), work should be pursued to determine the relationship between the trace metal concentration and the aquatic biological activities, with special emphasis during the months of January and August.

4- Desalination brine, industrial and municipal effluents are discharged to the sea. Trace metal concentrations in these streams and near the outfalls, should be determined and the in-situ aquatic life should be investigated.

5- Further work is also needed to determine the source of the trace metals in Kuwait's ground water.

6- Work is needed to determine the trace metal contents in soil at different levels; mainly the area around the ground water wells.

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APPENDIX I

INTERNATIONAL DRINKING WATER STANDARDS

INTERNATIONAL DRINKING WATER STANDARDS

Substances or Parameters	W.H.O. 1984	W.H.O. 1993		U.S.E.P.A. 1989		European Community 1980	
	G.V.	G.V.	Complaint value	M.C.L.G	M.C.L.	G.V.	M.A.C.
1. Organoleptic Parameters							
Colour	15 TCU		15 TCU			1 mg/l Pt/Co scale	20 mg/l Pt/Co scale
Turbidity	5 NTU		5 NTU			1 mg/l SiO_2 0.4 Jackson units	10 mg/l SiO_2 4 Jackson unit
Odour	Inoffen sive		Accept- able			Dilution number: 0	2 @ 12°C 3 @ 25°C
Taste	Inoffen sive		Accept- able			Dilution number: 0	2 @ 12°C 3 @ 25°C
2. Physiochemical Parameters							
Temperature (°C)			Accept- able			12	25
pH	6.5-8.5		<8.0 recommen ded			6.5-8.5	
Conductivity µS/cm @20°C						400	

INTERNATIONAL DRINKING WATER STANDARDS

Substances or Parameters	W.H.O. 1984	W.H.O. 1993		U.S.E.P.A. 1989		European Community 1980	
	G.V.	G.V.	Complaint value	M.C.L.G.	M.C.L.	G.V.	M.A.C.
Chloride	250		250			25	
Sulphate	400		250			25	500
Calcium						100	
Magnesium						30	50
Sodium	200		200			20	150-175
Potassium						10	12
Aluminium	0.2		0.2			0.05	0.2
Hardness	500						30 mg/l Ca minimun
Alkalinity							30 mg/l HCO_3 minimum
Total Dissolved Solids 180°C	1000		1000			1500	

INTERNATIONAL DRINKING WATER STANDARDS

Substances or Parameters	W.H.O. 1984	W.H.O. 1993		U.S.E.P.A. 1989		European Community 1980	
	G.V.	G.V.	Complaint value	M.C.L.G.	M.C.L.	G.V.	M.A.C.
3. Parameter for Substances Undesirable in Excessive Amounts							
Nitrate (as NO_3)	44.3	50		44.3	44.3	25	50
Nitrite (as NO_2)		3.0 (P)		3.3	3.3		0.1
Boron		0.3				1.0	
Iron	0.3						
Copper	1.0	2.0 (P)	1.0	1.3	OCC	0.1	3.0
Zinc	5.0		3.0			0.1	5.0
Fluoride	1.5	1.5		4.0	4.0		1.5 (12°C) 0.7 (25°C)
Cobalt							

INTERNATIONAL DRINKING WATER STANDARDS

Substances or Parameters	W.H.O. 1984	W.H.O. 1993		U.S.E.P.A. 1989		European Community 1980	
	G.V.	G.V.	Complaint value	M.C.L.G.	M.C.L.	G.V.	M.A.C.
Barium		0.07		5.0	5.0	0.1	
Silver		U					0.01
Manganese	0.1	0.5 (P)	0.1			0.02	0.05
4. Parameters Concerning Toxic Substances							
Arsenic	0.05	0.01 (P)		0.0	0.03		0.05
Beryllium		NAD					
Cadmium	0.005	0.003		0.005	0.005		0.005
Cyanide	0.1	0.07 (P)					0.05
Chromium	0.05	0.05 (P)		0.1	0.1		0.05
Lead	0.05	0.01					
Mercury	0.001	0.001		0.002	0.002		0.05

The following general points should be noted:

1. **W.H.O. standards.** The 1993 edition shows major and significant changes from 1984. In particular, many parameters are no longer assigned guideline values, but instead are listed as "Substances and Parameters in Drinking Water that may give rise to complaints from Consumers". These parameters, where applicable, are listed as "Complaint Values" in the table. **G.V.** (Guideline Values) are listed where applicable. Some parameters appear in the 1993 lists in both columns, indicating that a parameter may give rise to complaints at levels below the health-based guideline values.

2. **U.S.E.P.A. Primary Drinking Water Regulations.** At the time the reference went to press, most Regulations were still in "Proposed" status. These proposed values are underlined. Regulations are shown under two headings: **M.C.L.G.** (Maximum Contaminant Level Goals), and **M.C.L.** (Maximum Contaminant level).

3. **European Community Standards.** Some parameters have not yet been assigned values. These are indicated in the table by shaded blank squares. Parameters are listed as **G.V.** (Guideline Values) and **M.A.C.** (Maximum Admissible Concentration).

4. Unless otherwise stated, all concentrations are shown in **mg/l.**

5. An unshaded blank square in the table indicates that no value is assigned to the parameter.

Additional Notes.

NAD: No Adequate Data to recommend a health-based Guideline Value.

OCC: Optimal Corrosion Control.

(p): Provisional Guideline Value.

U: Unnecessary. It is not necessary to recommend a Guideline Value for these substances, because they are not hazardous to human health at the concentrations normally found in drinking water.

APPENDIX II

STANDARD CONDITIONS OF ATOMIC ABSORPTION AND INDUCTIVELY COUPLED PLASMA SPECTROSCOPY FOR Cr, Cu, Fe, Mn and Ni ANALYSIS.

STANDARD PROGRAM

for:
Element: Chromium Matrix: 2M Nitric Acid

5000 PROGRAM FORM

ELEMENT	Cr
ABS/CONC/EM	ABS
AA/AA-BBG/BG	AA
GAIN	
CONT/HOLD/HT/AREA	HT
REC DUPL	
REC ABS (tc)	+
AVG	2
CV	
LAMP#	
LAMP MA	
SLIT HIGH	
SLIT LOW	0.7
λ PEAK (nm)	
λ SLOW (nm)	357.9
SCAN	
t (sec)	6.0

HGA 500 PROGRAM

STEP	1	2	3	4	5	6
TEMP	120	1000	2700	2700		
RAMP TIME	5	5	0	2		
HOLD TIME	50	25	5	2		
REC			-5			
READ			1			
BASELINE		10				
INT FLOW	300	300	80	300		
INT ALT						
EXT ALT						

STANDARD PROGRAM

for:
Element: Copper Matrix: 2M Niric Acid

5000 PROGRAM FORM

ELEMENT	Cu
ABS/CONC/EM	ABS
AA/AA-BBG/BG	AA
GAIN	
CONT/HOLD/HT/AREA	HT
REC DUPL	
REC ABS (tc)	+
AVG	2
CV	
LAMP#	
LAMP MA	
SLIT HIGH	
SLIT LOW	0.7
λ PEAK (nm)	
λ SLOW (nm)	324.7
SCAN	
t (sec)	6.0

HGA 500 PROGRAM

STEP	1	2	3	4	5	6
TEMP	120	600	2500	2700		
RAMP TIME	5	5	0	2		
HOLD TIME	50	25	5	2		
REC			-5			
READ			1			
BASELINE		10				
INT FLOW	300	300	80	300		
INT ALT						
EXT ALT						

STANDARD PROGRAM

for:
Element: Iron Matrix: 2M Nitric Acid

5000 PROGRAM FORM

ELEMENT	Fe
ABS/CONC/EM	ABS
AA/AA-BBG/BG	AA
GAIN	
CONT/HOLD/HT/AREA	HT
REC DUPL	
REC ABS (tc)	+
AVG	2
CV	
LAMP#	
LAMP MA	
SLIT HIGH	
SLIT LOW	0.2
λ PEAK (nm)	
λ SLOW (nm)	248.3
SCAN	6.0
t (sec)	

HGA 500 PROGRAM

STEP	1	2	3	4	5	6
TEMP	120	600	2500	2700		
RAMP TIME	5	5	0	2		
HOLD TIME	50	25	5	2		
REC			-5			
READ			1			
BASELINE		10				
INT FLOW	300	300	80	300		
INT ALT						
EXT ALT						

STANDARD PROGRAM

for:
Element: Manganese Matrix: 2M Nitric Acid

5000 PROGRAM FORM

ELEMENT	Mn
ABS/CONC/EM	ABS
AA/AA-BBG/BG	AA
GAIN	
CONT/HOLD/HT/AREA	HT
REC DUPL	
REC ABS (tc)	+
AVG	2
CV	
LAMP#	
LAMP MA	
SLIT HIGH	
SLIT LOW	0.2
λ PEAK (nm)	
λ SLOW (nm)	279.5
SCAN	
t (sec)	6.0

HGA 500 PROGRAM

STEP	1	2	3	4	5	6
TEMP	120	1000	2200	2700		
RAMP TIME	5	5	0	2		
HOLD TIME	50	20	5	2		
REC			-5			
READ			1			
BASELINE		10				
INT FLOW	300	300	80	300		
INT ALT						
EXT ALT						

STANDARD PROGRAM

for:
Element: Nickel Matrix: 2M Nitric Acid

5000 PROGRAM FORM

ELEMENT	Ni
ABS/CONC/EM	ABS
AA/AA-BBG/BG	AA
GAIN	
CONT/HOLD/HT/AREA	HT
REC DUPL	
REC ABS (tc)	+
AVG	2
CV	
LAMP#	
LAMP MA	
SLIT HIGH	
SLIT LOW	0.2
λ PEAK (nm)	
λ SLOW (nm)	232.0
SCAN	
t (sec)	6.0

HGA 500 PROGRAM

STEP	1	2	3	4	5	6
TEMP	120	1000	2700	2700		
RAMP TIME	5	5	0	2		
HOLD TIME	50	20	5	2		
REC			-5			
READ			1			
BASELINE		10				
INT FLOW	300	300	100	300		
INT ALT						
EXT ALT						

APPENDIX III

THE ENHANCED CONDITIONS OF ATOMIC ABSORPTION SPECTROSCOPY FOR THE ANALYSIS OF Cu and Ni.

STANDARD PROGRAM

for:
Element: Copper Matrix: Freon

5000 PROGRAM FORM

ELEMENT	Cu
ABS/CONC/EM	ABS
AA/AA-BG/BG	AA
GAIN	
CONT/HOLD/HT/AREA	HT
REC DUPL)	
REC ABS (tc)	+
AVG	3
CV	
LAMP #	
LAMP MA	
SLIT HIGH	
SLIT LOW	0.7
λ PEAK (nm)	
λ SLOW (nm)	324.7
SCAN	
t (sec)	6.0

HGA 500 PROGRAM

STEP	1	2	3	4	5	6
TEMP.	110	900	2300	2700		
RAMP TIME	5	10	0	3		
HOLD TIME	20	10	3	1		
REC			-5			
READ			1			
BASELINE		10				
INT FLOW	300	300	0	300		
INT ALT						
EXT ALT						

STANDARD PROGRAM

for:
Element: Nickel Matrix: Freon

5000 PROGRAM FORM

ELEMENT	Ni
ABS/CONC/EM	ABS
AA/AA-BG/BG	AA
GAIN	
CONT/HOLD/HT/AREA	HT
REC DUPL	
REC ABS (tc)	+
AVG	3
CV	
LAMP #	
LAMP MA	
SLIT HIGH	
SLIT LOW	0.2
λ PEAK (nm)	
λ SLOW (nm)	232.0
SCAN	
t (sec)	6.0

HGA 500 PROGRAM

STEP	1	2	3	4	5	6
TEMP	110	400	1100	2500		
REMP TIME	5	10	0	3		
HOLD TIME	20	10	3	1		
REC			-5			
READ			1			
BASELINE		10				
INT FLOW	300	300	0	300		
INT ALT						
EXT ALT						

APPENDIX IV

DETAILED RESULTS OF ANALYSIS

Chromium concentration at Doha area.

DOHA E.S.	DOHA W.S.W	D.W.	B.W.	P.W.P.S.	P.W.F.S.	P.W.Res.	P.W.E.T.
1.47	1.98	0.00	3.80	0.00	0.00	1.23	0.00
1.70	2.14	0.00	2.50	0.00	1.40	1.24	0.00
1.55	2.16	0.00	2.10	0.00	0.00	1.27	0.00
1.68	2.14	0.00	3.40	0.00	0.00	1.12	1.10
1.68	2.25	0.00	4.00	1.10	0.00	0.00	0.00
1.67	2.26	0.00	2.50	0.00	1.10	1.23	0.00
2.49	4.10	0.00	1.29	0.00	0.00	0.00	1.90
2.90	3.23	0.00	4.26	1.20	1.00	0.00	0.00
2.09	2.14	0.00	3.14	0.00	1.30	0.00	0.00
2.20	1.98	0.00	4.30	2.30	0.00	1.27	0.00
2.20	1.73	0.00	3.70	1.80	0.00	1.09	1.09
1.95	1.59	0.00	3.93	2.00	0.00	1.10	0.00
1.67	1.42	0.00	2.30	0.00	2.60	1.10	0.00
1.67	1.87	0.00	1.38	0.00	0.00	0.00	1.60
1.87	2.06	0.00	1.30	0.00	0.00	1.60	1.50
2.09	2.19	0.00	2.10	0.00	1.50	1.17	0.00
2.12	2.76	0.00	3.18	1.30	0.00	0.00	1.30
3.57	3.85	0.00	1.50	0.00	0.00	0.00	0.00
3.22	3.06	0.00	1.17	0.00	1.30	1.90	0.00
Chromium	0 = <1.0ppb						
n=20	n=20		n=20				
2.09000	2.36000	<1.0	2.73000	<1.0	<1.0	<1.0	<1.0
0.58	0.72		1.10				

Copper concentration at Doha area.

DOHA E.S.	DOHA W.S.W	D.W.	B.W.	P.W.P.S.	P.W.F.S.	P.W.Res.	P.W.E.T.
7.56	3.8	22.5	14.9	33	21.8	18.6	26.70
7.67	3.6	25.1	35.1	29	16.8	27.8	30.90
9.74	4.6	23.5	32.2	28	36.9	42.3	30.00
10.5	5.9	41.7	14.2	57	26.9	25.4	38.00
12.2	5.8	35.3	17.83	51.6	24.9	26.6	26.00
11.5	7.6	24	17.7	34	31.9	27.5	28.90
13.5	9.6	20.9	27.69	34.9	15	20.3	31.50
12.4	9.1	32.3	28.9	27.2	25.1	28.5	29.40
10.7	7.6	19.9	13.7	23.4	17.8	39.3	38.10
9.9	5.9	17.8	18.45	43.4	38.8	26.6	34.20
8.9	5.9	40.6	18.5	36.4	27.7	27.1	14.70
7.56	5.5	28.6	21.3	25.9	31.3	26.5	20.60
7.01	4.33	23.30	21.60	26.80	36.30	27.60	31.30
6.84	3.70	24.80	21.60	26.10	35.60	26.00	36.30
4.69	4.15	30.50	18.50	26.90	29.40	24.60	21.40
5.97	4.89	29.50	21.20	27.80	20.40	31.40	21.90
7.25	7.86	31.70	20.70	36.50	31.90	39.10	26.40
9.83	10.87	23.30	20.60	30.90	34.10	26.60	28.30
12.85	13.30	23.00	10.70	34.90	31.30	30.60	24.70
10.10	8.30	31.50	16.10	38.80	31.70	25.40	31.30
n = 20	n = 20	n = 20	n = 20	n = 18	n = 20	n = 19	n = 17
9.33	6.62	27.49	20.57	31.33	28.28	27.66	28.22
2.46	2.63	6.58	6.22	5.40	7.03	5.02	4.41

The shaded numbers were not included in the calculation.

Iron concentration at Doha area.

DOHA E.S.	DOHA W.S.W	D.W.	B.W.	P.W.P.S.	P.W.F.S.	P.W.Res.	P.W.E.T.
22.40	23.20	30.40	39.50	47.70	50.02	25.90	111.00
22.80	24.00	12.60	23.30	42.20	63.00	25.50	94.50
23.40	29.50	10.80	38.60	30.10	59.20	42.20	83.40
25.87	23.20	12.30	39.70	35.50	85.50	23.50	95.20
27.70	30.70	13.90	40.10	33.20	126.00	33.30	67.10
63.30	69.50	13.40	46.40	21.50	124.00	23.60	65.40
59.90	61.50	12.00	39.10	19.90	98.00	47.00	85.20
51.10	33.90	6.20	21.70	14.50	79.00	34.00	95.00
45.70	33.70	13.00	28.90	27.30	72.00	44.30	97.10
33.40	31.00	24.20	57.50	33.80	85.00	21.30	67.30
29.40	30.70	6.70	43.30	34.20	119.00	23.20	129.00
23.40	25.60	10.60	36.40	39.30	118.00	45.90	92.70
17.30	23.90	31.40	18.20	16.70	97.00	29.80	69.80
13.40	19.80	8.90	11.20	32.90	109.00	27.50	84.50
12.60	17.60	9.70	10.90	31.50	64.00	26.90	76.90
15.60	19.60	8.90	39.60	31.60	96.00	25.70	85.40
18.90	23.90	15.60	28.80	34.30	98.00	24.50	69.70
29.70	34.30	12.00	53.70	31.90	115.00	28.07	80.90
60.90	65.60	0.95	34.40	29.80	118.00	28.90	80.20
58.70	55.40	13.50	50.90	39.50	77.90	28.40	84.50
n=20	n=20	n=16	n=17	n=19	n=20	n=20	n=20
32.77	33.83	12.56	36.62	32.26	92.68	30.47	85.74
17.20	15.91	3.65	9.84	7.49	23.50	8.05	15.72

The shaded numbers were not included in the calculation.

Lead concentration at Doha area.

DOHA E.S.	DOHA W.S.W	D.W.	B.W.	P.W.P.S.	P.W.F.S.	P.W.Res.	P.W.E.T.
0	0.00	0.00	0.31	0.18	0.23	0.12	0.23
0.00	0.00	0.09	0.19	0.28	0.24	0.18	0.21
0.00	0.00	0.00	0.50	0.29	0.19	0.19	0.21
0.00	0.00	0.00	0.38	0.12	0.21	0.15	0.22
0.00	0.00	0.00	0.43	0.13	0.22	0.12	0.21
0.00	0.00	0.00	0.70	0.18	0.19	0.11	0.23
0.00	0.00	0.08	0.28	0.19	0.18	0.18	0.21
0.00	0.00	0.00	0.61	0.11	0.18	0.12	0.18
0.00	0.00	0.00	0.26	0.10	0.24	0.19	0.18
0.00	0.00	0.09	0.37	0.12	0.24	0.15	0.28
0.00	0.00	0.00	0.18	0.08	0.24	0.14	0.21
0.00	0.00	0.00	0.28	0.12	0.21	0.11	0.17
0.00	0.00	0.54	0.31	0.13	0.23	0.12	0.21
0.00	0.00	0.09	0.27	0.15	0.21	0.15	0.17
0.00	0.00	0.22	0.34	0.12	0.18	0.12	0.18
0.00	0.00	0.00	0.66	0.18	0.17	0.18	0.19
0.00	0.00	0.00	0.49	0.12	0.17	0.11	0.19
0.00	0.00	0.00	0.10	0.11	0.19	0.13	0.21
0.00	0.00	0.00	0.43	0.09	0.18	0.19	0.17
0.00	0.00	0.43	0.56	0.11	0.21	0.18	0.18

Lead 0= <0.05ppb

n=20	n=20	n=20	n=17	n=18	n=20	n=20	n=20
<0.05	<0.05	0.08	0.36	0.13	0.21	0.15	0.20
			0.13	0.03	0.03	0.03	0.03

The shaded numbers were not included in the calculation.

Manganese concentration at Doha area.

DOHA E.S.	DOHA W.S.W	D.W.	B.W.	P.W.P.S.	P.W.F.S.	P.W.Res.	P.W.E.T.
0.00	0.00	3.60	1.02	1.04	2.90	0.00	1.08
0.00	0.00	0.00	1.46	2.20	2.10	0.00	1.30
0.30	0.00	1.80	1.50	0.90	1.90	1.54	1.00
0.80	0.40	0.00	1.40	1.30	1.97	0.99	1.07
1.10	0.70	0.00	1.32	1.20	1.45	1.76	1.57
2.15	1.90	1.60	3.10	0.89	0.85	0.85	0.97
3.90	4.30	2.40	2.50	1.80	0.96	1.50	1.10
3.10	3.60	0.00	2.40	0.98	1.61	1.10	0.98
2.70	2.90	0.00	2.60	0.96	0.95	2.10	1.00
2.28	2.28	0.00	1.80	1.20	1.20	1.09	1.80
2.10	0.90	1.10	1.40	1.10	1.88	1.89	1.20
0.20	0.20	0.00	1.50	1.30	1.14	1.16	1.18
0.20	0.20	2.40	1.20	0.99	1.94	1.06	0.94
0.00	0.00	2.60	1.44	0.91	1.91	1.32	1.14
0.40	0.50	0.00	1.30	0.78	1.59	0.79	0.79
1.10	0.90	0.00	1.20	0.67	1.03	0.69	0.84
1.90	1.90	0.00	3.50	0.99	1.10	1.11	0.95
2.80	3.60	0.00	1.50	1.09	1.09	1.09	1.10
4.20	4.90	0.45	2.16	1.06	1.89	0.85	1.27
3.40	3.50	0.47	1.40	1.10	1.74	0.99	1.30
Manganese	0=<0.05ppb						
n=20	n=20	n=16	n=17	n=19	n=19	n=18	n=20
1.63	1.63	0.34	1.56	1.07	1.49	1.22	1.13
1.40	1.63	0.61	0.42	0.24	0.43	0.39	0.24

The shaded numbers were not included in the calculation.

Nickel concentration at Doha area.

DOHA E.S.	DOHA W.S.W	D.W.	B.W.	P.W.P.S.	P.W.F.S.	P.W.Res.	P.W.E.T.
1.32	1.23	0.00	1.09	3.42	3.40	3.71	3.67
1.54	1.34	0.00	1.00	5.10	3.49	4.40	3.41
1.60	1.48	1.20	2.01	6.30	5.10	3.48	3.73
1.69	1.52	0.00	2.35	3.35	4.60	3.90	3.68
1.71	1.71	0.00	2.92	4.80	3.05	4.45	3.91
1.74	1.80	0.00	1.00	4.50	5.20	3.75	4.80
3.57	3.59	5.40	6.90	8.90	5.15	4.35	4.21
2.20	3.20	0.00	3.40	3.45	5.67	3.36	2.91
1.89	2.10	0.00	6.97	3.65	5.60	3.39	2.89
1.84	1.90	0.00	6.70	8.80	4.95	4.27	3.90
1.80	1.53	0.00	6.40	5.90	3.58	4.02	3.93
1.45	1.90	0.00	4.03	4.60	5.12	3.98	6.70
1.33	1.40	3.35	6.60	3.54	5.09	3.99	3.62
1.31	1.30	4.33	6.92	4.35	5.60	3.71	5.09
1.10	1.09	1.09	3.50	2.90	3.71	3.60	4.65
1.32	1.20	0.00	2.37	3.19	3.90	4.36	4.21
1.50	1.55	0.00	4.80	4.26	3.36	4.45	3.68
1.61	1.74	0.00	5.01	3.45	3.45	4.09	3.91
1.90	1.98	2.09	2.94	2.90	4.30	3.58	4.16
2.70	3.90	2.10	4.30	3.48	3.48	4.40	3.60

Nickel 0=<1.0ppb

n=20	n=20		n=17	n=18	n=20	n=20	n=19
1.67	1.78	<1.0	4.60	4.06	4.39	3.96	3.89
0.56	0.79		1.83	0.99	0.90	0.37	0.56

The shaded numbers were not included in the calculation.

Vanadium concentration at Doha area.

DOHA E.S.	DOHA W.S.W	D.W.	B.W.	P.W.P.S.	P.W.F.S.	P.W.Res.	P.W.E.T.
1.10	0.99	0.00	28.50	1.35	1.26	2.09	0.86
1.40	1.20	0.00	28.70	0.86	0.00	1.21	0.00
1.90	1.55	0.00	23.90	0.81	0.00	1.04	0.00
2.09	2.06	0.00	22.20	1.10	1.50	1.32	1.06
2.70	2.69	0.00	22.50	1.21	0.00	0.00	0.00
3.15	3.86	0.00	29.80	1.30	1.40	2.09	0.95
4.58	4.79	0.00	22.70	1.05	1.90	1.30	1.79
3.90	3.98	0.00	28.80	1.80	1.08	0.08	0.99
2.70	3.02	0.00	27.10	1.20	1.80	1.49	0.00
1.95	2.63	0.00	18.40	1.06	0.00	1.19	1.48
1.85	2.15	0.00	33.40	0.55	0.53	1.65	1.12
2.01	1.67	0.00	28.50	1.50	0.00	0.00	1.30
1.65	0.99	0.00	28.90	1.69	1.50	1.13	0.97
1.10	1.05	0.00	23.50	1.62	1.50	1.02	1.61
0.98	1.10	0.00	22.20	1.15	0.09	1.89	1.09
1.54	1.10	0.00	25.09	0.69	1.11	1.10	1.54
2.21	1.86	0.00	13.50	0.89	1.64	1.19	1.67
3.15	2.90	0.00	16.90	1.35	1.56	1.32	1.49
5.35	4.35	0.00	15.80	1.30	1.35	1.08	0.97
2.90	3.54	0.00	20.48	0.90	0.99	0.98	0.66
Vanadium	0=<0.05ppb						
n=20	n=20		n=18	n=20	n=13	n=17	n=16
2.41	2.37	<0.05	24.11	1.17	1.43	1.36	1.22
1.17	1.23		4.38	0.33	0.27	0.36	0.33

The shaded numbers were not included in the calculation.

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Zinc concentration at Doha area.

DOHA E.S.	DOHA W.S.W	D.W.	B.W.	P.W.P.S.	P.W.F.S.	P.W.Res.	P.W.E.T.
2.31	1.15	8.75	12.10	13.15	18.69	15.00	**39.10**
2.44	1.66	9.65	9.80	10.25	27.80	20.00	31.60
2.41	2.15	**16.00**	10.35	10.79	24.15	16.65	34.60
2.20	2.53	7.98	**14.15**	10.95	21.20	19.90	35.80
2.60	2.61	10.80	**14.80**	10.90	20.17	**28.30**	24.30
2.60	3.28	10.79	9.88	13.55	26.99	19.90	**39.50**
8.15	6.16	9.75	9.85	11.25	20.19	22.00	37.40
6.20	4.00	10.55	11.56	**17.50**	28.30	17.55	**38.00**
4.83	3.70	8.99	12.50	11.25	**39.90**	23.50	23.50
4.41	3.50	11.40	10.90	10.55	23.55	16.30	21.20
2.09	2.42	10.70	11.65	10.25	**39.50**	21.15	23.40
1.54	2.50	12.50	11.00	**19.20**	20.50	19.50	21.30
1.24	2.30	11.70	**16.00**	**14.00**	21.25	**26.00**	29.80
1.34	1.00	9.35	9.88	**22.00**	25.55	16.50	24.60
1.17	1.09	12.20	11.75	12.50	23.75	12.25	24.55
1.69	1.95	6.99	10.89	10.85	**39.85**	11.59	23.50
2.68	2.96	11.70	10.55	11.65	26.55	10.65	**39.50**
3.36	3.73	8.90	10.60	10.85	25.85	17.52	25.49
6.45	6.18	10.60	10.90	10.69	22.19	19.25	25.95
5.06	5.64	11.69	11.05	10.25	**39.50**	21.25	34.25
Zinc	0=<1.0ppb						
n=20	n=20	n=19	n=17	n=16	n=16	n=18	n=16
3.24	3.03	10.26	10.90	11.23	23.54	17.80	27.58
1.96	1.55	1.50	0.82	1.01	3.05	3.64	5.45

The shaded numbers were not included in the calculation.

Chromium concentration at Shuaiba area.

ShuaibaS.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.
0.00	1.40	5.37	1.29	1.20	1.24
0.00	0.00	2.27	1.40	1.30	1.50
0.00	0.00	1.73	1.10	1.19	1.55
0.00	0.00	1.83	1.20	1.09	1.11
0.00	1.30	2.64	1.20	1.07	1.23
0.00	0.00	1.88	1.09	1.10	1.15
1.10	0.00	3.15	2.60	1.09	1.61
0.00	1.10	3.40	1.30	3.08	1.78
0.00	0.00	3.18	1.80	1.05	1.50
0.00	0.00	1.57	1.90	1.21	1.45
0.00	0.00	2.95	2.30	3.49	1.61
0.00	0.00	1.03	1.70	1.11	1.63
0.00	0.00	1.84	1.65	1.20	1.62
0.00	1.07	1.94	1.46	2.82	1.78
0.00	0.00	1.29	1.25	1.25	1.47
0.00	0.00	3.93	1.52	1.10	1.54
0.00	0.00	1.17	1.43	1.15	1.36
0.00	0.00	2.55	1.40	1.07	1.55
1.15	1.30	2.19	1.45	1.55	1.55
0.00	0.00	3.40	1.55	1.09	1.25

Chromium 0=<1.0ppb

		n=19	n=20	n=19	n=20
<1.0	<1.0	2.31	1.53	1.35	1.47
		0.84	0.37	0.58	0.19

The shaded numbers were not included in the calculation.

Copper concentration at Shuaiba area.

ShuaibaS.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.
1.10	61.06	15.20	28.30	25.80	25.10
1.50	31.40	22.50	35.50	27.60	30.80
2.25	25.80	28.20	23.20	25.80	31.80
3.55	30.40	31.16	25.60	25.70	26.70
5.15	56.60	29.70	25.60	25.40	29.40
6.35	20.90	18.80	21.60	15.80	38.70
7.05	20.70	31.20	19.20	30.90	22.90
4.62	22.10	22.60	12.40	25.16	27.30
3.65	39.70	14.60	26.40	25.80	24.20
3.15	32.20	20.40	26.60	25.20	31.40
2.75	31.20	31.20	22.90	21.30	30.50
2.43	25.50	20.20	25.15	24.60	27.60
2.09	32.15	23.20	25.70	22.50	23.70
1.90	21.50	14.60	31.40	25.60	34.60
2.90	27.90	24.50	23.40	21.30	31.40
3.68	35.35	25.55	22.20	21.60	31.50
3.54	35.50	28.15	21.40	21.50	31.60
5.22	26.70	27.60	19.75	20.60	30.60
6.25	31.80	31.50	18.80	21.20	30.40
4.35	42.60	24.60	18.90	20.25	34.60
n=20	n=18	n=20	n=18	n=18	n=19
3.67	29.63	24.27	23.67	23.72	29.27
1.68	6.34	5.65	3.48	2.35	3.48

The shaded numbers were not included in the calculation.

Iron concentration at Shuaiba area.

ShuaibaS.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.
9.40	23.90	37.50	39.20	37.30	82.60
10.30	23.40	39.15	26.50	26.50	94.50
12.20	23.80	33.60	28.50	32.90	92.90
13.20	18.20	38.10	28.70	29.70	57.50
17.50	25.50	49.00	26.70	26.30	62.70
28.60	24.25	35.50	24.40	26.40	40.90
62.70	11.50	39.50	27.50	29.50	64.20
40.90	16.45	35.00	27.70	34.20	44.70
29.10	26.30	34.20	27.50	39.10	95.50
24.30	29.60	36.80	43.70	28.60	56.20
23.10	16.80	27.60	33.90	23.10	55.10
19.10	15.60	32.30	26.40	26.30	90.10
13.79	17.10	31.40	26.50	31.40	64.60
9.80	21.70	31.40	37.30	34.90	72.50
10.60	20.90	32.50	34.60	34.60	54.60
12.90	20.20	34.60	34.50	35.60	60.90
23.40	22.50	35.15	36.50	29.70	52.60
30.70	22.60	32.60	29.80	29.80	55.40
59.60	22.50	32.60	26.70	29.80	51.90
51.60	16.10	29.80	29.80	31.60	66.15
n=20	n=20	n=19	n=19	n=18	n=19
25.14	20.95	34.17	30.14	30.05	67.09
16.56	4.40	3.16	4.40	3.51	16.14

The shaded numbers were not included in the calculation.

Lead concentration at Shuaiba area.

ShuaibaS.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.
0.00	0.00	2.55	0.09	0.00	0.15
0.00	0.00	2.25	0.09	0.00	0.15
0.00	0.00	3.65	0.09	0.09	0.21
0.00	0.00	0.90	0.15	0.09	0.16
0.00	0.00	0.70	0.15	0.09	0.10
0.00	0.00	0.88	0.10	0.10	0.11
0.00	0.00	1.40	0.10	0.10	0.26
0.00	0.00	0.39	0.10	0.10	0.09
0.00	0.00	1.40	0.10	0.09	0.19
0.00	0.00	0.38	0.10	0.10	0.22
0.00	0.00	0.84	0.10	0.07	0.05
0.00	0.00	1.30	0.09	0.07	0.25
0.00	0.00	0.07	0.10	0.07	0.27
0.00	0.00	1.35	0.10	0.09	0.05
0.00	0.00	3.40	0.18	0.07	0.06
0.00	0.00	0.75	0.16	0.10	0.18
0.00	0.00	0.99	0.10	0.10	0.17
0.00	0.00	1.36	0.10	0.10	0.14
0.00	0.00	2.40	0.10	0.09	0.16
0.00	0.00	2.75	0.10	0.07	0.15

Lead 0=<0.05ppb

		n=20	n=20	n=20	n=17
<0.05	<0.05	1.49	0.11	0.08	0.17
		1.01	0.03	0.03	0.05

The shaded numbers were not included in the calculation.

Manganese concentration at Shuaiba area.

ShuaibaS.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.
0.00	0.19	2.80	1.11	1.53	1.23
0.00	0.13	1.60	1.10	1.20	1.37
0.10	0.00	0.00	0.00	0.00	0.00
0.20	0.30	1.20	1.60	1.08	1.04
0.23	0.10	1.90	1.80	1.02	1.34
0.49	0.00	2.12	1.11	0.16	0.20
1.07	0.18	1.69	2.67	2.16	1.97
0.66	0.00	1.70	0.00	0.00	0.00
0.51	0.00	1.20	0.00	0.51	0.00
0.40	0.14	2.50	2.60	0.10	1.20
0.40	0.19	2.30	1.60	1.30	1.61
0.20	0.23	0.00	1.32	1.60	2.10
0.00	0.00	0.00	1.05	1.11	1.65
0.00	0.43	0.73	0.92	1.17	1.60
0.00	0.19	1.30	1.20	1.30	1.60
0.20	0.00	1.40	0.99	1.20	1.12
0.50	0.43	1.80	0.98	1.20	1.15
0.73	0.35	2.50	1.10	1.30	0.95
0.99	0.47	1.70	0.99	1.50	1.15
0.85	0.45	1.40	1.10	0.00	0.92

Manganese 0=<0.05ppb

n=20	n=20	n=16	n=15	n=14	n=14
0.37	0.19	1.82	1.20	1.22	1.31
0.34	0.17	0.50	0.26	0.27	0.30

The shaded numbers were not included in the calculation.

Nickel concentration at Shuaiba area.

ShuaibaS.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.
1.28	1.15	1.69	1.18	1.35	2.55
1.44	1.05	1.52	2.15	1.25	2.56
1.54	1.68	1.51	2.45	2.56	2.40
1.61	1.25	1.21	2.25	2.55	2.30
1.71	1.33	1.51	2.25	2.45	2.15
2.77	2.33	1.55	1.88	2.60	2.24
3.58	1.30	1.69	1.60	2.05	1.99
2.70	2.55	1.90	1.75	2.50	2.50
1.99	1.35	1.31	1.82	2.30	1.89
1.87	1.35	1.72	1.62	2.08	1.79
1.66	1.60	1.50	1.95	1.90	2.35
1.68	2.15	1.80	1.96	2.36	2.55
1.37	1.85	2.45	2.35	1.85	2.45
1.30	1.75	3.87	2.90	1.16	2.55
1.45	1.82	1.77	1.90	1.55	2.64
1.55	1.73	2.65	1.45	2.45	1.98
1.79	2.85	1.66	1.25	2.85	1.77
2.15	1.74	4.74	1.82	2.45	1.89
3.95	1.98	4.15	1.55	2.60	2.55
2.70	1.29	3.80	1.65	2.65	2.60

Nickel	0=<1.0ppb				
n=20	n=18	n=16	n=19	n=18	n=20
2.00	1.59	1.72	1.83	2.11	2.29
0.74	0.36	0.37	0.35	0.49	0.30

The shaded numbers were not included in the calculation.

Vanadium concentration at Shuaiba area.

ShuaibaS.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.
1.85	0.00	23.90	0.89	0.98	1.24
2.14	0.00	22.50	1.09	0.99	1.24
2.95	0.00	27.70	0.40	0.87	1.43
3.45	0.00	28.70	0.87	0.86	1.24
4.13	0.00	25.90	0.85	0.87	1.25
5.25	0.00	24.50	0.91	0.85	1.35
6.29	0.00	35.20	0.95	0.89	1.45
4.13	0.00	26.40	0.91	1.16	1.44
2.70	0.00	23.50	0.10	1.12	1.29
2.20	0.00	28.10	0.68	1.15	1.33
1.95	0.00	26.10	0.61	1.05	1.16
1.65	0.00	36.10	0.72	0.89	1.22
1.55	0.00	26.50	2.37	0.86	1.25
1.20	0.00	29.90	2.15	2.29	1.44
2.32	0.00	21.60	0.86	2.23	1.23
2.75	0.00	21.20	0.55	1.09	1.13
3.94	0.00	22.50	0.93	1.21	1.33
4.45	0.00	25.90	0.79	0.89	2.35
6.55	0.00	27.50	0.89	0.99	1.23
5.15	0.00	24.40	0.69	1.15	1.25

Vanadium 0=<0.05ppb

n=20		n=17	n=16	n=18	n=19
3.33	<0.05	25.11	0.82	0.99	1.29
1.59		2.32	0.14	0.13	0.10

The shaded numbers were not included in the calculation.

Zinc concentration at Shuaiba area.

ShuaibaS.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.
1.05	11.85	13.60	7.98	19.70	20.40
1.15	10.55	10.50	9.57	10.90	20.20
1.24	10.40	12.40	20.30	19.60	26.70
1.68	10.75	11.25	9.56	11.60	23.40
1.98	10.65	12.50	9.55	10.20	26.20
2.24	10.42	12.40	8.94	12.25	21.10
4.16	11.30	13.40	8.69	16.25	22.70
3.67	9.55	14.25	9.70	11.20	20.80
3.31	11.45	11.60	8.90	10.70	27.20
3.31	11.60	12.50	9.40	17.30	22.10
1.78	11.65	9.30	12.50	12.25	26.55
1.54	10.45	19.25	14.20	15.25	24.25
1.09	10.23	13.51	15.20	13.70	27.40
1.05	10.43	14.30	15.90	11.20	20.56
2.25	12.60	9.96	10.40	12.50	21.60
2.35	9.85	10.50	11.10	11.25	20.60
2.68	9.88	10.55	16.50	12.70	22.90
2.94	9.85	10.23	13.40	12.45	22.54
4.27	9.96	9.99	13.50	13.25	22.40
3.55	9.85	10.70	12.50	12.50	24.25
Zinc	0=<1.0ppb				
n=20	n=20	n=14	n=16	n=16	n=20
2.36	10.66	11.03	11.07	12.12	23.19
1.07	0.82	1.08	2.15	1.27	2.45

The shaded numbers were not included in the calculation.

Chromium concentration at AzZour area.

AzZourS.W	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.	P.W.F.S.
1.06	0.00	0.00	0.00	0.00	0.00	0.00
1.11	0.00	0.00	0.00	0.00	0.00	0.00
1.12	0.00	0.00	0.00	0.00	0.00	0.00
1.06	0.00	0.00	0.00	0.00	0.00	0.00
1.21	0.00	0.00	0.00	0.00	0.00	0.00
1.37	0.00	0.00	0.00	0.00	0.00	0.00
3.06	0.00	0.00	0.00	0.00	0.00	0.00
2.98	0.00	0.00	0.00	0.00	0.00	0.00
2.40	0.00	1.38	0.00	0.00	0.00	0.00
2.07	0.00	1.30	0.00	0.00	0.00	0.00
1.80	0.00	0.00	0.00	0.00	0.00	0.00
1.26	0.00	2.10	0.00	0.00	0.00	0.00
1.20	0.00	0.00	0.00	0.00	0.00	0.00
1.09	0.00	0.00	0.00	0.00	0.00	0.00
1.67	0.00	0.00	2.00	1.00	0.00	0.00
1.78	0.00	3.80	1.00	0.00	0.00	0.00
1.91	0.00	1.50	2.40	1.90	0.00	0.00
1.93	0.00	1.17	0.00	1.60	0.00	0.00
3.42	0.00	0.00	0.00	1.50	0.00	0.00
3.22	0.00	0.00	0.00	0.00	0.00	0.00
1.84	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

Chromium 0=<1.0ppb

Copper concentration at AzZour area.

AzZourS.W	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.	P.W.F.S.
4.15	29.00	22.00	20.00	19.60	**36.80**	20.60
4.00	23.00	18.00	26.00	27.80	28.60	15.40
5.10	30.00	30.00	20.00	21.10	28.50	20.40
4.90	25.00	19.00	31.00	29.70	27.90	13.90
5.00	**40.90**	21.70	22.70	38.50	25.10	20.50
8.30	21.20	32.10	20.80	34.10	12.60	35.60
13.30	22.10	10.70	16.60	34.00	14.70	28.60
7.00	29.60	10.30	33.10	38.20	**35.00**	24.90
6.40	20.40	16.30	14.90	37.80	30.00	**10.20**
5.50	23.60	18.20	16.70	22.60	12.40	19.60
4.20	27.80	**39.00**	30.40	27.20	12.20	13.00
3.20	31.40	23.20	**41.20**	24.40	14.20	**46.00**
3.10	**39.20**	10.60	28.20	21.80	12.30	17.60
2.92	28.20	18.10	16.10	**12.30**	11.70	14.80
2.99	28.90	32.00	**10.70**	27.10	28.50	20.10
4.06	29.40	26.00	20.60	21.70	29.10	24.50
6.28	23.30	22.00	26.10	29.50	22.00	28.00
7.23	24.80	15.60	20.70	28.10	23.40	22.10
10.95	23.00	18.00	22.80	34.20	22.20	19.20
10.10	30.50	19.70	20.60	28.20	24.50	20.20
n=20	n=18	n=19	n=18	n=19	n=18	n=18
5.93	26.18	20.18	22.63	28.72	21.11	21.06
2.86	3.58	6.52	5.41	6.04	7.16	5.70

The shaded numbers were not included in the calculation.

Iron concentration at AzZour area.

AzZourS.W	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.	P.W.F.S.
14.90	50.00	16.20	37.90	83.10	78.00	47.70
20.20	23.00	12.90	46.40	40.00	85.00	49.30
20.70	30.00	19.50	60.00	71.00	61.30	38.50
18.50	19.00	55.00	37.40	78.00	84.10	42.50
16.50	19.00	14.00	31.90	51.10	72.70	81.00
20.40	16.00	36.00	21.90	48.00	56.90	83.10
32.30	11.00	38.00	24.00	62.40	83.00	48.00
43.20	20.00	14.70	21.60	47.70	85.30	62.40
29.30	39.00	16.40	85.80	38.60	61.00	74.30
28.70	24.00	49.80	80.20	81.00	48.60	81.00
28.50	54.00	28.50	74.30	46.20	56.20	70.70
19.30	40.40	56.80	27.10	86.00	60.90	40.10
17.40	56.00	14.70	63.40	86.00	49.90	53.50
10.30	21.20	19.90	53.20	54.30	36.80	82.20
12.60	26.10	22.90	65.40	62.40	74.90	61.20
14.90	19.70	29.50	51.70	58.60	86.10	57.80
18.20	41.50	41.70	61.00	49.10	79.40	64.10
28.40	21.90	27.80	43.50	46.50	67.30	62.70
41.30	16.70	27.00	31.70	42.70	72.30	48.90
30.20	19.70	35.50	27.90	71.90	86.40	45.60
n=20	n=17	n=18	n=17	n=16	n=20	n=16
23.29	23.99	25.83	41.53	54.28	69.31	54.21
9.07	8.77	10.89	15.29	11.92	14.70	10.85

The shaded numbers were not included in the calculation.

Lead concentration at AzZour area.

AzZour S.	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.	P.W.F.S.
0.00	0.00	2.19	0.60	0.00	0.20	0.00
0.00	0.00	4.50	0.82	0.00	0.00	0.23
0.00	0.00	2.61	0.00	0.00	0.00	0.00
0.00	0.00	1.30	0.10	0.00	0.13	0.14
0.00	0.00	3.14	0.00	0.00	0.00	0.00
0.00	0.00	1.75	0.00	0.00	0.00	0.00
0.00	0.00	0.31	0.25	0.18	0.00	0.07
0.00	0.00	2.50	0.00	0.00	0.00	0.00
0.00	0.00	3.57	0.53	0.61	0.00	0.05
0.00	0.00	3.70	0.00	0.00	0.00	0.00
0.00	0.00	2.17	0.00	0.00	0.00	0.00
0.00	0.00	1.49	0.00	0.00	0.00	0.00
0.00	0.00	3.08	0.69	0.68	0.10	0.00
0.00	0.00	1.32	0.00	0.00	0.00	0.00
0.00	0.00	1.47	0.00	0.00	0.00	0.00
0.00	0.00	1.66	0.00	0.00	0.00	0.00
0.00	0.00	2.90	0.24	0.28	0.00	0.10
0.00	0.00	3.34	0.15	0.16	0.00	0.00
0.00	0.00	2.40	0.18	0.13	0.13	0.00
0.00	0.00	1.37	0.00	0.00	0.07	0.00

Lead 0= <0.05ppb

		n=19	n=16	n=18		
<0.05	<0.05	2.45	0.09	0.04	<0.05	<0.05
		0.94	0.15	0.08		

The shaded numbers were not included in the calculation.

Manganese concentration at AzZour area.

AzZourS.W	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.	P.W.F.S.
0.00	0.37	1.00	0.73	0.93	1.90	1.51
0.00	0.29	1.00	0.71	0.89	1.30	1.55
0.10	0.38	1.63	0.83	1.14	1.61	1.84
0.20	0.26	5.20	0.87	0.79	1.79	1.63
0.23	0.16	3.81	0.59	1.17	1.50	1.83
0.49	0.34	3.90	0.55	0.46	2.61	1.19
0.60	0.19	3.70	0.79	0.65	1.21	1.54
1.07	0.29	2.51	0.78	1.30	1.80	1.91
0.51	0.43	3.56	0.75	1.41	1.10	1.17
0.40	0.31	3.30	0.72	0.90	1.80	1.19
0.40	0.27	3.00	1.40	0.85	1.30	1.27
0.00	0.26	4.50	0.72	1.08	2.80	1.81
0.00	0.37	3.27	0.78	0.97	1.80	1.05
0.00	0.43	4.27	0.55	0.64	1.03	1.12
0.00	0.21	1.63	0.28	0.56	1.67	1.53
0.18	0.27	2.16	0.54	0.71	1.68	1.48
0.38	0.32	3.01	0.29	0.63	1.37	1.68
0.64	0.19	2.51	0.57	0.34	1.61	1.13
1.10	0.41	2.19	0.31	0.89	2.01	1.52
0.67	0.35	1.27	0.74	0.69	1.30	1.09

Manganese 0=<0.05ppb

n=20	n=20	n=20	n=16	n=18	n=18	n=20
0.33	0.29	2.87	0.70	0.90	1.54	1.45
0.34	0.08	1.20	0.11	0.24	0.29	0.28

The shaded numbers were not included in the calculation.

Nickel concentration at AzZour area.

AzZourS.W	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.	P.W.F.S.
4.15	1.52	4.10	1.78	2.15	2.83	2.49
4.65	1.64	3.76	1.39	1.24	2.51	1.67
4.70	1.49	5.22	1.90	2.35	2.64	1.84
4.27	1.82	3.49	1.64	1.80	2.69	1.93
4.39	1.67	3.16	1.52	2.32	2.57	1.64
4.51	1.73	2.98	1.15	1.40	3.46	2.67
5.29	1.46	3.58	1.38	2.44	2.25	2.78
5.20	1.93	3.90	1.64	1.80	2.10	1.90
4.57	1.81	5.10	1.49	2.10	1.90	2.40
4.72	1.45	3.86	1.78	2.90	2.53	1.50
4.45	1.73	3.10	2.13	2.70	2.38	2.40
4.42	1.38	3.50	1.12	2.15	2.24	2.13
4.51	1.29	4.10	1.60	2.32	2.15	1.80
4.17	1.81	3.93	1.90	2.10	1.93	1.81
3.89	1.62	5.42	1.39	1.50	2.40	2.70
4.09	1.46	3.91	1.48	1.96	1.90	2.56
4.19	1.84	3.64	1.71	1.70	1.59	2.08
4.37	1.46	3.19	1.09	1.65	1.60	2.90
5.55	1.73	3.24	1.51	1.40	2.03	2.80
4.95	1.82	3.49	1.08	1.29	1.17	2.90

Nickel	0=<1.0ppb					
n=20	n=20	n=17	n=20	n=16	n=18	n=20
4.55	1.63	3.58	1.53	2.12	2.24	2.25
0.43	0.18	0.36	0.29	0.38	0.36	0.47

The shaded numbers were not included in the calculation.

Vanadium concentration at AzZour area.

AzZourS.W	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.	P.W.F.S.
2.09	0.00	13.80	0.89	1.15	1.61	1.16
2.14	0.00	13.80	0.69	1.18	1.10	1.44
2.70	0.00	21.20	1.05	1.29	1.29	1.19
3.22	0.00	10.00	0.78	1.52	1.09	1.25
4.13	0.00	23.10	0.93	1.23	1.15	1.35
5.28	0.00	25.20	0.79	1.17	2.04	1.23
8.10	0.00	22.40	0.84	0.97	1.32	1.25
6.29	0.00	32.60	0.79	1.56	1.32	1.44
2.70	0.00	34.90	0.92	1.45	1.76	1.48
2.20	0.00	13.50	0.86	1.52	1.32	1.67
1.54	0.00	27.40	0.59	1.30	1.18	1.53
1.85	0.00	18.40	0.95	1.29	1.04	1.30
1.94	0.00	28.40	1.01	1.13	1.17	1.07
1.92	0.00	19.90	0.77	1.32	1.06	1.23
2.21	0.00	15.20	0.52	1.13	1.09	1.23
3.15	0.00	22.50	0.61	1.09	1.08	1.09
4.17	0.00	27.20	0.49	1.32	1.26	1.13
5.35	0.00	13.50	0.83	1.08	1.21	1.36
8.19	0.00	10.60	0.73	1.25	1.34	1.13
6.28	0.00	15.80	0.57	1.70	1.18	1.11

Vanadium 0=<0.05ppb

n=20	n=20	n=16	n=20	n=19	n=17	n=19
3.77	<0.05	20.08	0.78	1.26	1.19	1.26
2.11		5.37	0.16	0.19	0.10	0.14

The shaded numbers were not included in the calculation.

Zinc concentration at AzZour area.

AzZourS.W	D.W.	B.W.	P.W.P.S.	P.W.Res.	P.W.E.T.	P.W.F.S.
1.90	10.10	8.90	6.70	14.10	15.50	20.90
1.10	9.55	9.10	8.90	13.79	29.30	19.90
1.63	9.73	9.70	9.90	14.60	23.30	18.60
1.92	8.94	9.60	8.60	12.80	21.30	19.60
2.29	10.16	9.80	9.20	13.40	32.40	20.28
2.10	9.32	9.50	11.00	12.20	17.90	20.66
3.90	12.20	10.30	13.10	12.70	23.80	19.40
3.50	9.51	9.90	8.70	13.86	24.50	18.50
1.55	9.82	11.00	9.40	12.80	29.90	19.80
1.51	11.70	12.10	13.40	12.12	24.50	17.95
1.52	10.80	10.90	13.90	12.71	20.10	16.63
1.40	11.68	11.52	8.61	12.38	34.30	19.22
1.30	11.40	10.60	12.20	13.32	21.20	15.45
1.49	10.70	11.55	7.25	13.69	21.60	17.40
1.67	9.91	9.60	8.99	12.89	25.30	17.30
1.96	10.50	9.40	11.30	13.45	24.60	21.90
2.14	10.06	10.60	10.75	12.65	25.40	16.60
2.29	12.08	10.55	10.65	14.12	25.50	19.56
3.92	10.26	10.36	10.80	13.70	29.40	18.50
3.08	9.06	9.80	11.23	12.86	21.50	16.70

Zinc	0=<1.0ppb					
n=20	n=20	n=20	n=17	n=20	n=16	n=18
2.11	10.37	10.24	10.40	13.21	24.45	18.75
0.84	0.99	0.86	1.54	0.70	3.04	1.40

The shaded numbers were not included in the calculation.