Metal Contamination in Ground Water of Korangi Industrial Area, Karachi

S. NAEEM MAHMOOD, SITWAT NAEEM, ISHRATULLAH SIDDIQUI
AND FAROOQ AHMED KHAN
Environmental Studies Section,
PCSIR Laboratories Complex,
Karachi-75280, Pakistan

(Received 27th August, 1997, revised 25th May, 1998)

Summary: The levels of trace metals and major chemical constituents in 28 ground water samples of Korangi Industrial Area (KIA) and its adjoining areas were determined to assess the impact of uncontrolled disposal of industrial waste water on the quality of water. The concentration of metals viz. Zn, Mn, Fe, Cu, Pb, Cd, Cr, Co and Ni, were found to be excessive higher than the WHO recommended limits. The significantly higher concentration of major chemical constituents and trace metals in KIA water samples than the corresponding concentrations in the adjoining areas samples clearly indicated that the contamination in ground water of KIA was primarily due to percolation of industrial waste water into the acquifer of the area. The positive and high correlation co-efficient values (r) showed strong correlation among the metals and also suggested high and consistent trace metals concentration in the ground water under investigation.

Introduction

Karachi city is the largest industrial city of Pakistan having two planned industrial areas viz. Korangi Industrial Area (KIA) and Sind Industrial Trading Estate (SITE). SITE covers an area of about 16 Km^2 containing approximately 500 major industries, 60% of which are textile mills and the others are of diverse type dealing with chemicals, detergents, iron and steel, vegetable oils, beverages, food products etc. [1]. Korangi Industrial Area located in the district East, has a total area of 34.4 Km^2, having approximately 2000 various types of small and medium size industrial units [2]. However, leather industry (more than 100 units) and textile industry are the dominating industries of KIA which consume large volume of water [3]. The acute shortage of water due to the discrepancy between water supply and demand has forced many industrial units of KIA to meet their requirements from ground water source viz. wells, borings and hand pumps. In addition to the industrial use, the ground water of KIA is also being utilized for drinking and domestic purposes.

In our previous work [4], a small number of ground water samples were also collected from KIA. The analysis of the samples indicated the mixing of industrial waste water of the area with the ground water, hence it was thought worth-while to undertake a comprehensive study to assess the impact of the indiscriminate discharge/disposal of untreated industrial effluents on the chemical constituents of the ground water of KIA. Since the excessive levels of trace metals in water may adversely affect the quality of water and cause detrimental effects on human health [5,6], the concentrations of trace metals have also been determined in the ground water of KIA and its adjoining areas. This study is also intended to provide a data-base on the quality of ground water of the area and to help environmentalists and physiologist for establishing any possible correlation between water contaminants and prevalent health disorders in the local population.

Results and Discussion

Tables 1(a) and 1(b) give the concentration of major chemical constituents of the ground water samples collected from Korangi Industrial Area (KIA) and the areas adjoining KIA respectively.

pH of the water samples from KIA (Table-1a) ranges from 7.0 to 7.9, whereas pH of samples from the adjoining areas (Table 1b) ranges from 6.8 to 7.9 indicating that pH of the samples from the two locations vary within the narrow range and the waters are mostly weakly alkaline.

It would be observed from Table 1(a) that the waters contain high concentration of cations and anions.

Table-1(a): Chemical constituents of ground water of Korangi Industrial Area (mgl^{-1})

Sample No.	pH^+	Cl^-	SO_4^{--}	HCO_3^-	NO_3^-	Ca^{++}	Mg^{++}	Na^+	K^+	TDS
1	7.5	4517	1219	926	11	122	255	2900	55	10218
2	7.4	10576	2308	684	47	329	725	6200	113	21496
3	7.5	3892	982	600	29	206	345	2070	20	8256
4	7.6	5038	1439	768	64	184	280	3620	51	11536
5	7.5	3753	403	244	16	104	83	2472	45	7642
6	7.9	5308	464	996	13	76	61	3620	51	10786
7	7.4	4282	974	357	12	156	317	2483	37	8735
8	7.5	851	472	655	71	54	98	744	14	3015
9	7.6	2954	721	673	23	180	384	1535	12	6558
10	7.3	940	660	427	10	89	102	760	20	3230
11	7.5	895	490	720	15	92	150	671	18	3134
12	7.2	500	267	360	9	111	58	350	17	1682
13	7.4	493	453	720	8	69	79	550	30	2416
14	7.4	557	149	182	20	51	39	395	6	1440
15	7.3	347	510	136	15	62	57	294	30	1506
16	7.3	319	515	260	21	114	64	300	20	1640
17	7.2	285	372	168	18	123	42	165	47	1238
18	7.2	315	197	171	16	72	36	220	8	1552
19	7.0	347	111	512	23	76	41	284	31	1442
20	7.1	295	136	573	65	68	78	216	28	1489

*All values are in mgl^{-1} except pH.

Table-1(b): Chemical constituents of ground water of Korangi Industrial Area (mgl^{-1})

Sample No.	pH^+	Cl^-	SO_4^{--}	HCO_3^-	NO_3^-	Ca^{++}	Mg^{++}	Na^+	K^+	TDS
1	6.8	459	235	576	12	128	94	300	24	1838
2	6.9	931	560	528	7	125	142	650	14	2970
3	6.9	723	506	600	11	104	117	550	11	2234
4	7.9	413	453	178	12	69	76	315	52	1612
5	6.9	554	258	561	28	128	96	370	17	2110
6	7.3	605	220	481	16	119	62	439	34	2013
7	7.7	413	457	178	24	69	76	315	52	1612
8	7.4	612	378	130	29	85	60	414	40	1769

*All values are in mgl^{-1} except pH.

The levels of Na^+ and Cl^- are particularly high. Sodium ranges between 165 and 6200 mgl^{-1} and chloride between 285 and 10576 mgl^{-1}. Similarly the concentrations of other cations and anions are considerably high in the analysed samples. The mean values and ranges expressed in mgl^{-1} are: Ca^{++} 116.9 (51 - 329), Mg^{++}164.7 (36 - 725), K^+32.7 (6 - 113), SO_4^{--}624.1 (111 - 2308), HCO_3^-, 506.6 (136 - 996) and NO_3^- 25.3 (8 - 71). The concentration of total dissolved solids, which is mainly contributed by cations and anions is also high in the KIA samples (Table 1a) ranging from 1238 to 21469 mgl^{-1}. Out of 20 samples none has a TDS concentration of less than 1000 mgl^{-1}, whereas 11 samples have a concentration of more than 3000 mgl^{-1}.

A comparison of analytical data (Tables 1a and 1b) shows that the samples from the areas around KIA (Table 1b) have relatively low concentration of anions' and cations. The mean values and ranges expressed in mgl^{-1} are: Cl^-588.8 (413-931), SO_4^{--} 383.4(220-560), HCO_3^- 404(130-600), NO_3^- 174.(7-29), Ca^{++}103.4 (69-128), Mg^{++}90.4 (60-142), Na^+419.1 (300-650), and K^+30.5 (11-52). The concentration of total dissolved solids (1612-2970 mgl^{-1}) is also significantly lower than the KIA samples.

The soil of KIA is sandy to sandy loam in texture and since it is highly permeable in nature, it allows regular seepage of the industrial liquid effluents into the aquifer [7]. The samples from sector 7A of KIA (samples Nos. 1-7), where mostly tanneries are located, contain very high concentration of Na^+(2070 to 6200 mgl^{-1}) and Cl^- (3753 to 10576 mgl^{-1}). This clearly suggests that the high concentration of sodium chloride is mainly because of the seepage of tannery effluents into the ground water of the area.

Similarly, the chemical composition of the ground water of the whole area of KIA has been seriously deteriorated by the mixing of municipal and industrial waste water due to the inadequate drainage system and lack of treatment facilities for the industrial effluents of KIA.

Tables 2a and 2b show the concentration of trace metals in the ground water samples collected from KIA and its adjoining areas respectively. It would be noted that trace metals are widely distributed in all the analysed samples. However, the concentrations of trace metals in KIA samples (Table-2a) are significantly higher than those in the samples around KIA (Table-2b). The mean, median and extreme values (ranges) of trace metals in ground water samples of KIA and around KIA are listed in Tables 3a and 3b respectively. It is evident from the comparison of both the tables that the distribution of trace metals in KIA samples is wide spread and also accompanied by large variations.

Zn, an essential trace metal, is found in all ground waters but its level normally does not exceed 0.05 mgl^{-1}. No health-based guideline value has been proposed by WHO, however drinking water containing 3 mgl^{-1} Zn may not be acceptable to consumers [8]. The concentration of Zn in KIA samples is high, 8 samples (40%) contain more than 500 μgl^{-1} whereas none of the sample contains less than 400 μgl^{-1} (Table 2a). The extreme values, mean and median concentrations of Zn in the waters of the areas around KIA (Table 3a) are comparatively lower than those of KIA samples (Table 3b). The mean concentration in KIA water is 612.2 μgl^{-1} which is almost two fold of the one in the water around KIA (302.0 μgl^{-1}).

Fe is one of the most abundant metals in earth's crust and it is found in natural waters in the range of 0.5 to 50 mgl^{-1} [8]. The levels of Fe in KIA and its adjoining water samples range from 150.8 to 700.3 μgl^{-1} and from 165.5 to 224.5 μgl^{-1} having mean values of 322.9 and 190.3 μgl^{-1} respectively which are significantly high. No health-based guideline value for iron in drinking water is proposed by WHO, however water containing 300 μgl^{-1} Fe is likely to give rise to consumer complaints [8]. High Fe concentration imparts taste and colour to water and also encourages the formation of scales and slimes [8]. The iron present in the samples seems to be ferrous iron since no discolouration of waters was observed when collected from wells.

Mn usually occurs together with iron in ground waters. Although a provisional health-based guideline value of 0.5 mgl^{-1} in drinking water has been established by WHO, concentration of Mn exceeding 0.1 mgl^{-1} causes undesirable taste and stains laundry and sanitary wares [8]. Only four samples out of 20 from KIA contain more than 0.5 mgl^{-1} whereas all the sample from adjoining areas contain less than 0.5 mgl^{-1} of Mn (Tables 2a and 2b).

Copper is an essential element and is generally considered non-toxic for humans at usually low levels present in natural fresh waters. A provisional health-based guideline value of 2 mgl^{-1} has been recommended in drinking water by WHO, whereas more than 5 mgl^{-1} of Cu can give rise to taste and colour problems [8]. The mean and median values of Cu in KIA samples are 36.0 and 26.6 μgl^{-1}, while the corresponding values in the samples from adjoining areas are 7.6 and 8.2 μgl^{-1} which are about 4 times lower than the ones in KIA samples (Tables 3a and 3b). The increased Cu concentration in KIA samples also suggest the contribution of Cu to the ground water through percolation of industrial waste water.

Pb is a general toxicant and a cumulative poison which is present in water to some extent as a result of its dissolution from natural sources, but the excessive lead may be primarily from house hold plumbing. KIA ground waters contain 6.97 - 30.73 μgl^{-1} Pb with a mean value of 12.1 μgl^{-1} and adjoining areas water samples contain 2.38 - 5.94 μgl^{-1} Pb with a mean value of 4.5 μgl^{-1}. 5 samples of KIA (20%) contain Pb exceeding WHO health-based guideline value of 0.01 μgl^{-1} [8]. As explained earlier, the sources of this apparent contamination of Pb in KIA waters may be the indiscriminate discharges of untreated industrial and municipal waste waters.

Cd concentration in unpolluted natural waters are usually below 1 mgl^{-1} [9], but it is toxic to human beings even at low concentration. The Cd content of KIA waters ranges from 0.19 to 3.13 μgl^{-1} with 0.87 and 0.52 μgl^{-1} as the mean and median values respectively, whereas in the adjoining areas waters it ranges from 0.12 to 0.17 μgl^{-1} with 0.14 and 0.14 μgl^{-1} as the mean and median values respectively. The levels of Cd in KIA waters is higher than the ones in the adjoining areas (Tables 2a and 2b).

Table-2(a): Trace metals in the ground water of KIA (μgl^{-1})

Sample No.	Zn	Mn	Fe	Cu	Pb	Cd	Cr	Co	Ni
1	447.0	26.34	180.6	66.53	8.25	0.91	8.64	18.41	6.92
2	570.6	21.62	290.8	17.92	9.83	1.77	9.89	78.22	4.71
3	370.4	18.83	170.5	15.17	24.24	3.02	10.16	49.43	6.35
4	450.5	17.25	178.3	18.67	8.84	0.73	14.47	61.86	7.55
5	356.6	110.45	510.7	119.0	30.73	3.13	41.81	60.53	10.42
6	1168.0	218.64	574.8	30.64	7.58	0.62	10.66	24.30	12.33
7	363.4	21.52	224.6	14.52	7.61	0.54	7.83	12.23	6.94
8	930.2	20.31	700.3	127.83	24.52	0.51	6.69	9.93	5.48
9	430.4	24.62	150.8	17.55	8.96	0.43	4.08	13.62	5.32
10	510.6	19.73	230.6	16.39	25.47	1.32	5.52	11.45	6.13
11	360.9	70.82	190.4	31.62	8.69	1.15	4.16	10.22	5.26
12	1524.3	69.54	265.2	34.32	9.43	0.36	5.73	4.23	3.66
13	1466.5	20.67	230.4	20.63	14.54	0.39	6.41	4.47	7.19
14	351.2	17.57	325.6	29.54	7.46	0.31	3.73	1.13	2.23
15	526.6	47.0	328.8	34.81	8.52	0.38	4.41	1.72	3.15
16	458.3	19.68	394.5	28.47	7.24	0.32	3.82	1.05	2.83
17	582.1	32.34	280.3	39.62	8.85	0.26	5.86	1.7	2.72
18	496.8	22.63	588.0	12.58	7.59	0.87	6.84	1.68	4.06
19	379.6	19.22	346.6	24.73	6.97	0.28	3.62	1.24	2.53
20	498.5	18.75	296.3	19.64	8.23	0.19	3.74	1.57	3.41

Table-2(b): Trace metals in the ground waters adjoining KIA (μgl^{-1})

Sample No.	Zn	Mn	Fe	Cu	Pb	Cd	Cr	Co	Ni
1	335.6	16.28	194.4	7.05	3.22	0.15	2.62	1.13	3.84
2	286.2	12.43	165.5	6.86	2.38	0.14	2.13	1.32	4.11
3	315.0	5.04	170.7	2.13	4.32	0.12	2.96	1.25	2.23
4	319.4	15.63	224.5	7.38	5.69	0.17	0.92	0.58	2.57
5	194.4	7.25	186.2	8.92	5.68	0.14	1.95	0.92	2.88
6	298.5	12.46	198.6	9.64	4.35	0.14	1.97	1.15	2.52
7	343.8	13.71	196.9	9.13	5.94	0.13	0.73	1.33	3.27
8	323.5	14.0	185.8	9.84	4.87	0.13	1.21	0.29	3.6

However, except for the two samples of KIA, the levels are less than the WHO permissible limit of 3 μgl^{-1} [8].

Cr is a widely distributed metal in earth's crust, but its concentration is usually less than 1 μgl^{-1} in ground water [10]. The level of total Cr in all the samples is less than the WHO health-based provisional guideline value of 0.05 mgl^{-1}. However, the concentration of Cr in KIA samples is higher than that of adjoining areas samples. KIA samples contain 3.62-41.81 μgl^{-1} Cr with a mean value of 8.4 μgl^{-1}, whereas the samples around KIA contain 0.73-2.92 μgl^{-1} Cr with a mean value of 1.8 μgl^{-1}.

Cobalt is also found in water in very low concentration and is usually not detectable. Although no health-based guideline . value for Co is recommended by WHO, toxic side effects are observed in humans due to its excessive intake [11]. The concentration range, mean and median values of Co in KIA water samples are 1.05-78.22, 18.44 and 10.1 μgl^{-1} respectively (Table-3a) which are significantly higher compared with the corresponding values 0.29-1.33, 0.99 and 1.14 μgl^{-1} measured in the samples around KIA (Table 3b). The higher concentration of Co is indicative of seepage of industrial effluents into the sub soil water which may be attributed to indiscriminate discharge of industrial wastes in KIA.

Table-3(a): Mean, median and extreme values for trace metals in ground water of KIA (μgl^{-1})

Number of samples	Metal	Extreme values	Mean	Median
20	Zn	351.2 - 1524.3	612.2	477.5
20	Mn	17.25 - 218.6	41.9	21.6
20	Fe	150.8 - 700.3	322.9	285.5
20	Cu	12.58 - 127.8	36.0	26.6
20	Pb	6.97 - 30.73	12.1	8.8
20	Cd	0.19 - 3.13	0.87	0.52
20	Cr	3.62 - 41.81	8.40	6.1
20	Co	1.05 - 78.22	18.44	10.1
20	Ni	2.23 - 12.33	5.45	5.3

The concentration of Ni in the analysed samples is less than the WHO health-based guideline value of 0.02 mgl^{-1} [8]. The extreme, mean, and

Table-3(b): Mean, median and extreme values for trace metals in ground water adjoining KIA (μgl^{-1})

Number of samples	Metal	Extreme values	Mean	Median
8	Zn	194.4 - 343.8	302.0	317.2
8	Mn	5.04 - 18.62	12.4	13.1
8	Fe	165.5 - 224.5	190.5	190.3
8	Cu	2.13 - 9.84	7.6	8.2
8	Pb	2.38 - 5.94	4.5	4.6
8	Cd	0.12 - 0.17	0.14	0.14
8	Cr	0.73 - 2.92	1.8	1.96
8	Co	2.29 - 1.33	0.99	1.14
8	Ni	2.23 - 4.11	3.13	3.07

median values of Ni in KIA samples are 2.23-12.33, 5.45 and 5.3 μgl^{-1} respectively which are comparatively higher than the corresponding values of 2.23-4.11, 3.13 and 3.07 μgl^{-1} measured in the samples around KIA. However, samples (Nos. 1 to 7) collected from tannery area (Sect - 7A) mostly contain high levels of Ni.

The statistics to determine the behaviour of two related variables and the extent of their relationship is referred to as the correlation coefficient denoted by "r". An r value of -1 describes perfect negative correlation, whereas r = + 1 indicates perfect positive correlation and r = 0 shows no correlation between the two varieties.

In order to examine the relationship among various trace metals in the ground waters, correlation co-efficient values (r) have been calculated [12] and reported in Tables 4a and 4b. Since all the nine metals are detected in all the analysed samples, correlation co-efficient is calculated for each metal. In almost all the cases r values are positive and high showing strong correlation among the metals. A possible explanation for this observation may be that the wells do not flow and they take most of the metals from the bottom sediments and seepage of industrial waste water thus giving rise to a relatively high and constant metal concentration. Many soil minerals contain several metals simultaneously as their constituents at varied proportions, which are also likely to be leached and record high r values for their concentration in the ground water. The r values are also positive and high in the samples around KIA (Table 4b) which are comparatively less contaminated with industrial waste waters indicating that the soil minerals within the areas of location of the wells are also contributing the metal ions to some extent.

Table-4(a): Correlation co-efficient among trace metals concentrations in ground water of KIA

	Zn	Mn	Fe	Cu	Pb	Cd	Cr	Co
Mn	0.909							
Fe	0.959	0.872						
Cu	0.969	0.930	0.909					
Pb	0.969	0.897	0.969	0.896				
Cd	0.966	0.906	0.933	0.961	0.922			
Cr	0.812	0.97	0.809	0.861	0.796	0.826		
Co	0.981	0.898	0.982	0.922	0.989	0.941	0.912	
Ni	0.931	0.863	0.961	0.919	0.870	0.931	0.838	0.922

Table-4(b): Correlation co-efficient among trace metals concentrations in ground water adjoining KIA

	Zn	Mn	Fe	Cu	Pb	Cd	Cr	Co
Mn	0.916							
Fe	0.804	0.962						
Cu	0.987	0.893	0.813					
Pb	0.902	0.963	0.911	0.926				
Cd	0.788	0.913	0.947	0.803	0.766			
Cr	0.834	0.942	0.931	0.840	0.917	0.939		
Co	0.949	0.968	0.896	0.939	0.945	0.775	0.932	
Ni	0.783	0.935	0.934	0.811	0.947	0.947	0.988	0.886

The data on correlation co-efficient values clearly suggest that both industrial waste water and geochemical nature of the subsoil are the main causes of excessive metal concentration in the ground water of KIA. However, the absence of any base-line data for trace metals in the ground water of the areas under study, makes it quite difficult to assess the contribution of each factor separately. This study leads to the conclusion that the ground water of KIA has been highly contaminated primarily by the uncontrolled disposal of industrial waste water. The metal contamination has rendered the water unusable both for drinking and industrial purposes, it is therefore essential that effective and appropriate measures may be taken and necessary regulations may be adopted to prohibit the indiscriminate discharge and disposal of industrial effluents. Since water shortages in the large cities of Pakistan are causing the industries and people to utilize ground water sources, the protection of increasingly endangered ground water and mitigation of the contamination are the important fields in which considerable research must be undertaken.

Experimental

Sampling

20 ground water samples from Korangi Industrial area and 8 from the areas adjoining KIA were

collected in the months of June and July 1996. The water table in the area is at the depth of 6-12 meters. Except for a few samples which were collected from wells, most of the samples were collected in 1000 ml polyethylene screw-cap bottles. Before use the bottles were cleaned sequentially with a detergent wash, tap water rinse, 24 hrs soak in 1% HNO_3, and several high purity water rinses [13]. After cleaning operation, blanks for each bottle were prepared in high purity water in 1% ultrapure HNO_3 and the bottles having detectable levels of the trace metals of interest were rejected. The bottles were then dried at 100°C for 1 hr, cooled to room temperature, capped and labelled. 10 ml HNO_3, (1 ml acid/100 ml) was added to the samples which were used for the estimation of trace metals. Samples were immediately brought to the laboratory and refrigerated at 4°C.

Analytical procedure

Analytical grade (A.R.) chemicals were used in the preparation of reagents and standard analytical methods were employed for the determination of major chemical constituents [14,15]. Physiochemical analyses were performed for each sample in triplicate and the average values were recorded. pH was measured immediately, after collection of samples, using a portable digital pH meter and all other estimations were completed within two days after sampling.

SO_4 and TDS were determined by gravimetric methods, Cl by argentometric method, NO_3 by electrode method using a specific ion analyzer Orion-710, whereas HCO_3 was calculated by computing nomographically the alkalinity relationships. Ca and Mg were determined by EDTA titration method and Na and K were determined by flame photometer.

For the analysis of trace metals, reference standards were prepared from BDH Spectrosol AA standards (1000 ppm). Analyses were performed on Z 8000 Hitachi atomic absorption spectrophotometer with Zeeman effect background correction, equipped with a graphite furnace, a microprocessor and a built-in printer. Determinations of Cd, Co, Cr, Ni and Pb were carried out by flameless (ETAAS), and of Cu, Zn, Mn and Fe by flame (FAAS), atomic absorption spectrophotometry. In addition to the standard addition technique employed for the estimation of the trace metals, APDC - MIBK (Ammonium pyrrolidine dithiocarbamate - Methyl isobutyl ketone) method was also used to determine concentrations of Cd, Co, Cr, Ni and Pb. The detection limits, of Cu, Zn, Mn, Fe, Cd, Co, Cr, Ni and Pb were found to be 15, 6, 10, 25, 0.2, 2.4, 2.6, 3.5 and 2.5 μgl^{-1} respectively.

Analysis for each metal was carried out in triplicate to get representative results and the data reported in μgl^{-1}. Precision of the methods was determined from the co-efficient of variation (cv), calculated from triplicate analyses. All CV values were found to be below 10%. Indirect measure of the accuracy was obtained from recovery studies on 10 water samples spiked with each metal. Recoveries for the spiked samples were 100 ± 8%.

References

1. M.A.A. Beg, S. Naeem Mahmood and A.H.K. Yousufzai, *Pak. J. Sci. Ind. Res.*, **15**, 11 (1978).
2. A.H.K. Yousufzai, "Fourth National Symposium on Analytical and Environmental Chemistry" University of Peshawar, Bara Gali, (1995).
3. P. Driver, Rapid Assessment Survey of Industrial Pollution in Korangi Creek, Karachi, (W.S. Atkins International Surrey, (1987).
4. S. Naeem Mahmood, Sitwat Naeem, Ishratullah Siddiqui and Farooq Ahmed Khan, *J. Chem. Soc. Pak.* **19**, 42 (1997).
5. D.B. Louria, M.M. Joselow and A.A. Browder, *Ann. Intern. Med.*, **76**, 307 (1972).
6. J.R. Westendorf and A.C. Middleton, *Am. Water Works Assoc.* **71**, 417 (1979).
7. M.A.A. Beg, S. Naeem Mahmood and Sitwat Naeem, *Pak. J. Sci. Ind. Res.*, **33**, 431 (1990).
8. Guidelines for Drinking Water Quality, 2nd ed., Vol. 1, Recommendations, (World Health Organization, Geneva, 1993).
9. L. Friberg, G.F. Nordberg, and V.B. Vouk, Handbook of the Toxicology of Metals, Vol. 11, Elsevier, Amsterdam, (1986).
10. Guidelines for Drinking Water Quality, 2nd ed. Vol. 2, Health Criteria and other Supporting Information, (World Health Organization, CEHA, Amman, 1997).
11. R. Barbera, R. Farre and R. Montoro, *J. Assoc. off Anal. Chem.*, **68**, 511 (1985).
12. M.G. Godfrey, M.E. Roebuck and A.J.

Sherlock, "Concise Statistics", (Edward Arnold, London, 1988).
13. J.C. Meranger, K.S. Subramanian and C. Chalifoux, *J. Assoc. Off. Anal. Chem.*, **68**, 44 (1981).
14. W. Fresenius, K.E. Quentin and W. Schneider, Water Analysis, (Springer -Verlag Berlin Heidelberg, 1988).
15. Standard Methods for the Examination of Water and Wastewater, 17th Ed., (Amercian Public Health Association, Washington, D.C. 1989).