# EVALUATION OF ARSENIC AND OTHER TOXIC METALS IN DRINKING WATER OF SAHIWAL DISTRICT USING DIFFERENT SPECTROSCOPIC TECHNIQUES (A CASE STUDY)

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**ABSTRACT:** Current study was carried out for the evaluation of concentrations of arsenic (As), chromium (Cr) and lead (Pb) in drinking water of district Sahiwal, Punjab, Pakistan. Samples were collected from various 20 locations. Sample sources were consisted of tubewell, filter plant, hand pump and tap water. Spectrophotometer was used for the evaluation of concentrations of As<sup>III</sup> and Cr<sup>VI</sup> while As total, Cr total and Pb levels were evaluated by using inductively coupled plasma-mass spectrometry (ICPMS). As <sup>III</sup> & As total were not detected (nd) in some tap water samples. The ranges of concentrations of As <sup>III</sup>, As total of Cr<sup>VI</sup>, Cr total and Pb in all types of water samples were nd (not detected) to 24.00 ppb, nd to 25.35 ppb, 4.57 to 6.36 ppm, 4.58 to 6.39 ppm and 2.11 to 22.76 ppb, respectively. Results obtained for As total of Cr total and Pb were compared with the maximum permissible limits of WHO, Pak EPA and USEPA. The levels of arsenic and lead were lower than Pak EPA guided values while chromium had crossed the standard limit of Pak EPA in all the water samples.

Keywords: arsenic, toxic metals, spectrophotometer, ICP-MS

### **1. INTRODUCTION**

The weight of toxic metals is greater than water about 4 to 5 times [1]. The properties of these elements are sustainability, toxicity and biological accumulation [2]. Toxic or nonessential and essential elements are the two divisions of these elements. Non-essential or toxic elements consist of arsenic, lead, silver, cadmium, nickel and aluminium whereas the 2<sup>nd</sup> division called essential elements include the elements like, chromium, cobalt, manganese, molybdenum, zinc, selenium, iron and copper. The concentration of elements such as Pb, Cr, As, Ag, Cd, Hg, Ba, Se and Zn may occur at µg/L level in groundwater. These metals become toxic when they cross the permissible limits of EPA and WHO [3]. Now-a-days their occurrence in groundwater is a health and environmental issue [4]. The entrance of these metals in groundwater is through various processes like agricultural sewage, industrial and municipal wastewater [5,6]. The discharging of these metals or their cations into the water and soil (environment) may result of their entrance in food chain. Thus the animals and plants health is affected [7]. Most of these metals have both beneficial and harmful effects (they have dual nature). Epidemiologically, the diseases like kidney problems, cancer, neurological problems and tooth degradation are interrelated with toxic metals [8].

Recently, arsenic contamination in water has created several threats i.e. skin, lung & bladder cancer [9]. Many health problems have been created due to toxic nature of arsenic. It is teratogenic, mutagenic and carcinogenic [3]. Its sources in water are either natural or anthropogenic. Natural sources of arsenic are ores and minerals dissolution, and percolation of rocks containing arsenic. Anthropogenically, it comes in water from preservatives, combusting fossil fuels and alloying agents. There are various species of inorganic arsenic out of which the two species arsenite (As <sup>III</sup>) and arsenate (As <sup>V</sup>) mostly occur in water. The species of organic arsenic are mostly present in seafood, are excreted by the body easily and are thus less toxic than inorganic species [3]. For arsenic evaluation, various methods are used, i.e. potentiometry [10], hydride generation-atomic absorption spectrophotometry (HGAAS) [11], voltammetry [12], inductively coupled plasma-mass spectrometry (ICPMS) [13] and spectrophotometry [14]. For quantitative measurement of arsenic, required detection limit is  $\leq 1 \ \mu g/L$  which is achievable only with ICP. So, arsenic measurement was carried out by using ICPMS due to its greater precision and accuracy. Since, ICP measures only As total, so As <sup>III</sup> was calculated by using spectrophotometer. The selection of spectrophotometric method was due to its easiness to operate, availability and low cost. As <sup>III</sup> can be determined spectrophotometrically with different reagents out of which leucocrystal violet method was selected because it is a direct method and does not require solvent extraction. Furthermore, it is sensitive, rapid, accurate, simple and selective [15].

Similarly, Cr  $_{total}$  was also calculated using ICPMS [13]. Out of 2 species of chromium (Cr  $^{III}$  and Cr  $^{VI}$ ), Cr  $^{III}$  is used in lipids & glucose metabolism while Cr  $^{VI}$  has toxic nature and causes dermatitis, kidney and lung cancer [16]. Chromium compounds are used in steel mills and leather industries, in procedures such as pigmentation, electroplating and catalysis. They come in water either through sewage or from industrial effluents [17], so their investigation especially Cr VI is necessary. Various methods are used for the evaluation of Cr <sup>VI</sup>, out of which spectrophotometric procedures are selected because they does not pollute climate and are low cost [18]. In this paper, the quantity of Cr <sup>VI</sup> was evaluated with 1,5diphenylcarbazide because the complexingagent and other reagents are available mostly in each laboratory [19]. Kidneys, circulatory, nervous and reproductive systems are affected by lead accumulation [1]. In water it is present at trace level, thus its determination was also carried out with ICPMS [13].

Arsenic contaminated water is investigated in various countries of Africa, Asia and America, thus it is a world problem [20]. Recently, trace elements including arsenic are calculated in different districts of Pakistan, i.e. in Lahore [21], Tharparkar [22], Faisalabad [23], Sheikhupura [24], Jamshoro [25], Karachi [26], Lahore and Kasur [27], Kohistan [28], Sialkot [5], Muzaffargarh [29], Kasur [30], Skardu [31], Islamabad [32], Tando Allayar [33] and Peshawar [34]. In past, arsenic, chromium and lead were not quantitatively determined in district Sahiwal. Current study was conducted to evaluate the levels of As, Cr and Pb in drinking water of different areas of district Sahiwal with the

following objectives :(i) to evaluate the concentrations of As, Cr &Pb and (ii) to compare them with WHO [35], Pak EPA [36] and USEPA [37] guided values.

# 2. EXPERIMENTAL

# 2.1. Materials

For As <sup>III</sup> detection, stock solution of arsenic was prepared by dissolving 173.33 mg sodium arsenite (analytical grade, Wako) in 100 ml demineralized water. From this stock, standard solutions were prepared. Aqueous solution of KIO<sub>3</sub> (potassium iodate, 1%, w/v, Merck), 2 M and 0.5 M aqueous solutions of sodium hydroxide (NaOH, Merck, analytical grade) and hydrochloric acid (HCl, Merck) were prepared. To prepare leucocrystal violet (LCV) solution, 250 mg LCV (Sigma, analytical grade), 200 ml demineralized water and 3 ml phosphoric acid (Merck, 85%, analytical grade) were added and shook in 1L flask. When dye dissolved, the flask was diluted to 1L.

For Cr<sup>VI</sup> evaluation, 0.25 g diphenylcarbazide (Merck) was dissolved in acetone (50%), it gave 0.25% solution of diphenylcarbazide. 3 M sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, Merck) and 0.0002 M potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Sigma) solutions were prepared. From this stock of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> other standards were prepared.

For ICPMS, reagent water, v/v nitric acid (HNO3, <2%, Fluka), v/v HCl (1%, Merck), ICPMS grade standard solutions (purity >99.99%, Analytika) were used.

### 2.2. Instruments

For the determination of Cr <sup>VI</sup> and As <sup>III</sup> spectrophotometer (UV-1900, BMS) was used while the levels of Pb, Cr  $_{\rm total}$  and As total were calculated by using ICP/MS (Agilent, 7700x).

# 2.3. Sampling

Polyethylene bottles used for sample collection were cleaned with HNO<sub>3</sub> (10%, Merck) and rinsed with demineralized water. Samples were collected by following the guidelines of American Public Health Association (APHA, 22<sup>nd</sup> edition). Four types of water sources were selected for sampling, i.e. tubewell, filter plant, tap and hand pump water. Forty labeled prewashed bottles were used for twenty different locations. Details of locations are given in table-I. From each location 2 samples were collected. The containers were rinsed with the drinking water sample before sampling, three times and 0.5 mL nitric acid (Suprapur) was added for the evaluation of toxic metals accurately, precisely and exactly. The obtained samples were preserved in refrigerator at 4°C. Divided the samples into 2 portions, each portion had 20 samples. One portion was sent to PCSIR research lab of Pakistan for the analysis of toxic metals on ICPMS. The 2<sup>nd</sup> portion was evaluated on spectrophotometer to measure the levels of Cr VI and As III.

Sr. No.	Location	Table-I: Details of Sampling Locations Detail				
1	SWLF1	Filter at Farid town (FT)				
2	SWLH1	Hand pump at FT				
3	SWLT1(I)	Tap water of Government Girls Higher Secondary School, FT				
4	SWLT1(II)	Tap water of Scheme No.2, FT				
5	SWLF2	Filter at Gulistan colony				
6	SWLH2	Hand pump at Gulistan colony				
7	SWLH3	Hand pump at Mohalla Salamat Pura				
8	SWLT3(I)	Tap water of Government High School, Mohalla Salamat Pura				
9	SWLT3(II)	Tap water of Mohalla Salamat Pura				
10	SWLF4	Filter at Fateh Shair colony				
11	SWLTW4	Tubewell at Fateh Shair colony				
12	SWLT5	Tap water of Muslim Bin Aqeel colony				
13	SWLTW5	Tubewell at Muslim Bin Aqeel colony				
14	SWLT6	Tap water of Shadman town				
15	SWLTW6	Tubewell at Shadman town				
16	SWLF7	Filter at Shadab town				
17	SWLT8(I)	Tap water of Government Technology College, Jahaaz ground				
18	SWLT8(II)	Tap water of Technical college, Jahaaz ground				
19	SWLT9	Tap water of Barkat town				

Tap water of Bashir colony

# 2.4. METHODS

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For the evaluation of As <sup>III</sup>, in a calibrated tube of 25 ml, small amount of sample having 4 to 40 ppb (0.004-0.04 ppm) arsenic was taken. KIO<sub>3</sub> (2 ml) was added followed by HCl solution (1 ml). After shaking the reaction mixture, LCV solution (1 ml) and 2 M NaOH solution (4-5 drops) were added. In a thermostat, the solution was kept for 5 min at 40°C. The solution was diluted with demineralized water upto 25 ml and the absorbance was measured at 592 nm against a reagent blank [15].

SWLT10

For Cr<sup>VI</sup> determination Vogel's textbook procedure [19] was adopted while for the determination of Cr total, As total and Pb the method 6020A of EPA/ICPMS (2007) was used.

# 3. RESULTS AND DISCUSSIONS

The results of As <sup>III</sup>, As <sub>total</sub>, Cr <sup>VI</sup>, Cr <sub>total</sub> and Pb in tubewell, filter plant, tap and hand pump water are given in Table-II and from Figure 1-5. The values of  $As_{total}$ ,  $As^{III}$  and Pb are expressed in ppb because they were detected at  $\mu g/L$  level while the values of Cr <sub>total</sub> and Cr <sup>VI</sup> are given in ppm because they were measured at mg/L level. Cr <sub>total</sub> As <sub>total</sub> and Pb mean concentrations were compared with the guided values of WHO, Pak EPA and USEPA (Table-III).

Average concentration of chromium was very high relative to standard value of Pak EPA but arsenic and lead average concentrations were lower than the permissible limits of Pak EPA. Similarly, the average concentration of lead was lower 20

than the recommended value of WHO while arsenic and chromium average concentrations were high relative to WHO guidelines.

9 locations had As total level >10 ppb while lead was found in 4 locations with the concentration >10 ppb. All the 20

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locations had chromium concentration >10 ppb. Similarly, it was also found that all the locations had As total and Pb levels <50 ppb while the level of Cr<sub>total</sub> was higher than 50 ppb in all the locations.

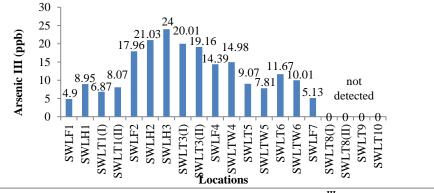
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Sr. No	Locations	As <sup>III</sup> (ppb)	As total (ppb)	Cr <sup>VI</sup> (ppm)	Cr total (ppm)	Pb (ppb)
1	SWLF1	4.90	5.23	5.63	5.64	6.72
2	SWLH1	8.95	9.03	4.65	4.67	5.94
3	SWLT1(I)	6.87	7.13	4.67	4.69	6.14
4	SWLT1(II)	8.07	8.79	6.36	6.39	3.91
5	SWLF2	17.96	18.02	6.02	6.04	5.01
6	SWLH2	21.03	21.17	5.41	5.43	7.03
7	SWLH3	24.00	25.35	5.58	5.61	14.27
8	SWLT3(I)	20.01	20.10	5.01	5.06	12.49
9	SWLT3(II)	19.16	20.14	5.23	5.23	22.76
10	SWLF4	14.39	15.07	5.92	5.95	3.67
11	SWLTW4	14.98	15.06	5.34	5.35	2.99
12	SWLT5	9.07	9.45	5.57	5.58	4.12
13	SWLTW5	7.81	8.09	5.33	5.35	3.76
14	SWLT6	11.67	12.02	5.91	5.95	12.47
15	SWLTW6	10.01	10.25	5.86	5.88	9.17
16	SWLF7	5.13	5.60	5.73	5.73	4.36
17	SWLT8(I)	nd	nd	6.16	6.17	7.19
18	SWLT8(II)	nd	nd	5.39	5.41	7.41
19	SWLT9	nd	nd	4.57	4.58	4.03

5.22

Table-II: Levels of Toxic Metals in Drinking Water of Sahiwal



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Figure-1: Comparison of values of As III

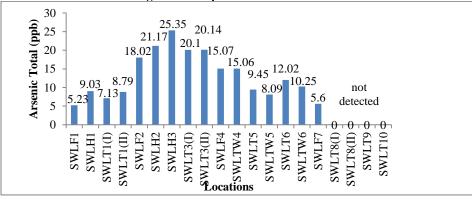


Figure-2: Comparison of values of As total

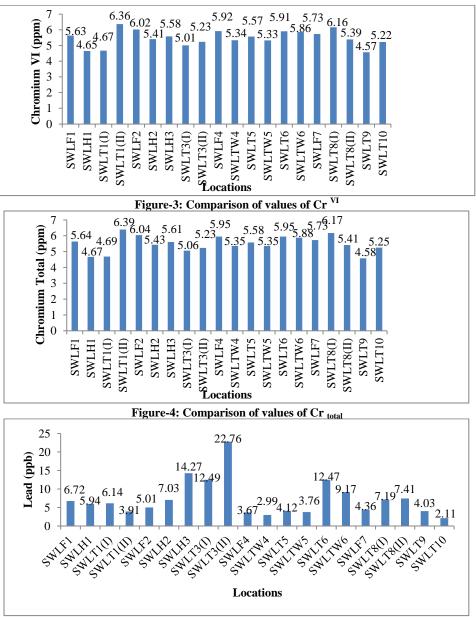


Figure-5: Comparison of values of Pb

Table-III: As total, Cr total and Pb Average Concentrations in Drinking Water of District Sahiwal and Their Comparison with WHO, Pak EPA, and USEPA.

Metals	Unit	Average Concentrations	WHO	Pak EPA	USEPA
As	Ppb	10.53	10	≤50	50
Cr	Ppm	5.50	0.05	≤0.05	0.10
Pb	Ppb	7.28	10	≤50	15

There are few leather factories in Sahiwal which discharge their wastes containing arsenic and chromium in resources of groundwater. That was the reason of high concentrations of As and Cr<sup>VI</sup> in drinking water of that area. The other drinking water As sources were the use of pesticides containing arsenic to increase the alkalinity and fertility of the soil. Arsenic produced by pollution, volcanic emissions and marine aerosols in the atmosphere was returned back to earth by wet & dry depositions which increase its concentration in drinking water. Since, calculated As concentration in all the regions was less than the permissible limit of Pak EPA of 50 ppb, so the water of those regions was 100% fit. Furthermore, the average concentration of As 10.525 ppb was 4.750 times smaller than the standard value of Pak EPA. As <sup>III</sup> range (nd to 24.00 ppb) was 0 to 1.056 times lower than the As <sub>total</sub> range (nd to 25.35 ppb) exhibiting that As <sup>III</sup> was the major contaminant in drinking water. In all the samples, Cr level was present above the permissible limits of USEPA, WHO and Pak EPA. So it should be constantly monitored. The average Cr concentration 5.498 ppm was 109.96 times higher than the Pak EPA standard value of 0.05 ppm for Cr. The ranges of Cr

 $^{\rm VI}$  and Cr  $_{\rm total}$  were 4.57 to 6.36 ppm and 4.58 to 6.39 ppm, respectively, indicating that Cr  $^{\rm VI}$  was 1.002 to 1.005 times higher than Cr total. It was observed that the major Cr contaminant present in water of the studied areas was Cr  $^{\rm VI}$ which is more toxic and can be converted by reduction into less toxic Cr III form. So, UNICEF, WHO, World Bank, UNDP and Pakistani government should sanction funds for reduction of Cr<sup>VI</sup> into Cr<sup>III</sup>. Lead was ranging from 2.11 to 22.76 ppb. The average Pb concentration 7.278 ppb was 1.374 times lower than WHO guided value of 10 ppb and 6.870 times smaller than Pak EPA limit of 50 ppb. It was also investigated that all the samples had Pb levels lower than the Pak EPA permissible limit of 50 ppb; only 4 samples had Pb levels greater than WHO guidelines of 10 ppb. So, according to local standard for Pb, the water of all the locations was fit. The reason for high levels of Pb at some locations could be anthropogenic or natural. Pb dissolves in drinking water from plumbing system, i.e. pipes, fittings and solders. Factors such as chloride, DO, pH, hardness and water standing time are responsible for its dissolution.

#### 4. CONCLUSION

In district Sahiwal, above mentioned drinking water locations had lead and arsenic levels below the national standard values. Their concentrations were also lower than WHO standard value of 10 ppb except few locations. The concentration of chromium was above the limits of local, WHO and USEPA standard values in all the regions.

Only the concentrations of arsenic, chromium and lead were calculated in selected areas, due to limited time duration. As there is variation in metal's concentration from site to site, thus it demands more experiments to calculate the concentrations of these metals and also of others. Epidemiologic association between these metals and cancer patients was not studied in this work. Therefore, experiments should be carried out to determine the levels of these metals in cancer patients.

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