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Analysis of arsenic from groundwater samples

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Key words: Groundwater, Arsenic, Electrical conductivity, Ghotki

Abstract

Total (100) samples of groundwater were taken from the various sources eighty (80) samples from hand-pumps, ten (10) from tube wells, and ten (10) from electric motors at sampling area in the different towns and villages of taluka Ghotki, district Ghotki, Sindh, Pakistan. The physico-chemical parameters were studied measuring electrical conductivity, pH and total dissolved salts for the evaluation of the quality of drinkable H_2O and the findings were checked by comparing them with the limits allowed by the WHO. pH values of 05 specimens were (6.12 - 6.4 pH) below permitted limit value. The electrical conductivity (EC) of 06 specimens were higher than the permitted limit. The total dissolved salts (TDS) in 13 specimens were higher than the permitted limit. The As kit method has been employed to examine As from samples of groundwater. It is a hand-held and user-friendly method for the analysis of As from ground H_2O. The permitted/safe limit of As given by WHO is 0.01mg/L or 10µg/L. The 34 (47.2%) arsenic containing water sampling were beyond the WHO permitted limit.

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Introduction

The use of water is a mandatory part of biological systems (Collins *et al.,* 2007). Groundwater is the most important and obligatory resource for humans to drink (Raessler, 2018) and used in industry and agriculture worldwide (Sarkar *et al.,* 2017). It has been calculated that about 1/3 of people worldwide drink groundwater (Bouderbala, 2017; Jain and Vaid, 2018; Li *et al.,* 2019). The preferred sources of water for drinking in the countryside, especially in developing countries, are groundwater (Katsanou and Karapanagioti, 2017), as its treatment, which includes disinfection, is frequently not necessary and the extraction systems can be located close to the people who drink it. Arsenic (As) contamination in potable water has became a serious global health problem (Rahman *et al.,* 2018; Tabassum *et al.,* 2019). Arsenic content found in potable water is either because of its natural existence in ground and surface water (Missimer *et al.,* 2018), or because of activities performed by humans like applications in industry (Daud *et al.,* 2017), leather and wood treatments (Schweitzer and Noblet, 2018), use of pesticides (García-Rico *et al.,* 2019).

Arsenic is a heavy and toxic metal which poses a severe risk to human health and the environment (Kempahanumakkagari *et al.,* 2017; Ravindra and Mor, 2019). Arsenic, water soluble, occurs in two main forms: arsenate (As^{+5}) and arsenite (As^{+3}) (Boruah *et al.,* 2019; Niazi *et al.,* 2018). These both types of arsenic produce chronic and acute toxicity to many different living things, even to human beings.

The humans exposure to As can occur by swallowing, inhaling or adsorption via skin (Mehta *et al.,* 2018); but swallowing is the dominant way of taking up arsenic. The exposure of inorganic arsenic at chronic level has a negative impact on health of humans (Jovanovic and Rašic-Milutinovic, 2017), causing skin disorders (Mandal, 2017), heart problems (Monrad *et al.,* 2017), neuropsychological disorders (Carroll *et al.,* 2017), genetic/reproductive diseases (Renu *et al.,* 2018), breathing problems (Li *et al.,* 2017), diabetes mellitus (Khan *et al.,* 2017; Wei *et al.,* 2018) and several kinds of tumors, such as pulmonary, skin, renal and urinary tract tumors (Gamboa-Loira *et al.,* 2017; Lynch *et al.,* 2017; Zhou and Xi, 2018).

According to the World Health Organization (WHO), the maximum permitted limit of As in drinking H_2O is $10\mu gL^{-1}$ (Chauhan *et al.,* 2017). Like other countries in South Asia, researchers and organizations like PCRWR and UNICEF in Pakistan have found As above 100 mg/L in groundwater (Baig *et al.,* 2010; Dev Brahman *et al.,* 2013). In many parts of the Punjab and Sindh provinces, As in drinkable H_2O was also found to be above the prescribed limits. In Punjab more than 20% of its populace are endangered by As contamination exceeding 10µg/L, while almost 3% are endangered by 50µg/L of As in drinking water. In Sindh, 16% and 36% of its population are endangered by As contamination of 50µg/L and 10µg/L respectively (Islam-Ul-Haq *et al.,* 2007). A number of conventional Instrumentation methods generally employed for the detection of arsenic including cathodic stripping voltammetry employing a mercury droplet hanging electrode (Khamkaew *et al.,* 2019), inductively coupled plasma mass spectrometry (Fırat *et al.,* 2017), atomic fluorescence spectrometry (Luo *et al.,* 2017), electrothermal atomic absorption spectrometry (Valdivia *et al.,* 2018), hydride generation atomic absorption spectrometry (dos Santos *et al.,* 2018), anodic stripping voltammetry (Garlaschelli *et al.,* 2017), etc. Even though the aforementioned procedures have small detection limits, their drawbacks like lacking on-site performance, expensive and the demand for highly qualified professionals restricts their implementations. The As kit is a hand-held and user-friendly method for detection of As from ground H_2O. It is inexpensive and easy to use and do not require maintenance.

Therefore we utilized the As kit for the detection of As. The physico-chemical parameters were studied measuring electrical conductivity, pH and total dissolved salts for the evaluation of the quality of drinkable H_2O and the findings were checked by comparing them with the limits allowed by the WHO.

Materials and methods

Sampling Area

Samples of groundwater were taken at random from the sampling area in the different towns and villages of Ghotki taluka, district Ghotki, Sindh, Pakistan as shown in Fig. 1. Total (100) groundwater samples were gathered from various sources at the Ghotki Taluka sampling sites. Eighty (80) samples from hand-pumps, ten (10) from tube wells, and ten (10) from electric motors were taken as shown in Table 1 from depths of approximately 50 to 120 ft. using plastic containers (capacity 1.0 L), with six to eight samples taken at every sampling site from April to July 2019.

Table 1. Assigning the ground water sample codes to the villages/mohalla's of taluka Ghotki District Ghotki, Sindh, Pakistan.

S. No	TC/UC	Villages / Mohall's	Tube well /Hand Pump Samples
1.	Hussain Beli	1. Faqeer CNG Ghotki	S1
		2. Village Mahmood Ali Gujar	S2
		3.Village Lashkar Bishti	S3
		4. Village Hussain Beli	S4
		5 Village Abdullah Ghoto	S5
		6Village Sardar Khan Ghoto	S6
		7. Village Jhungle Ghoto	S7
		8. Village Jalal Khan Ghoto	S8
		9. Sardar Shafi Muhammad Ghoto	S9
2.	Khuhara	10. Village Khuhara	S10
		11. Village Kauro Khan Langah	S11
		12.Village Mula Chutto Kalwar	S12
		13. Village Allah Dittao Lagahri	S13
		14.Village Rustum Kagahri	S14
		15. Village Azmat Khan Kolachi	S15
		16. Village Haji More Dayo	S16
		17.Village Achi Masjid	S17
		18.Village Bagh Channa	S18
3.	Adilpur	19. Village Baghdai	S19
		20. Village Arab kalwar	S20
		21. Kalwar Muhala Adilpur	S21
		22. Govt: High School Adilpur	S22
		23.Butani Muhala Adilpur	S23
		24. Muhla Gareebabad	S24
		25. Village Malook Shaikh	S25
		26.Village Malook Shaikh	S26
4.	Changlani	27. Village Ahmed Kalwar	S27
		28. Village R-B Kalwar	S28
		29.Village Wasand Kaladi	S29
		30. Village Sachedino Kalwar	S30
		31.Village Changlani	S31
5.	Berri	32. Village Tando Mahar	S32
		33. Villag Dhamaji	S33
		34.Village Mathelo Maomal-Ji-Mari	S34
		35.Village Sufi Rafique Arin	S35
		36. Village Berri	S36
		37.Village Wali Mohammad Burio	S37
		38. Village Zabardin Mahar	S38
6.	UC-Ruk	39.Village Haji Wassan Ruk	S39
		40.Village Taj Mohammad Ruk	S40
		41. Village Hai Abbasi	S41
		42. Village Sofi Anwar Shah Jahanpur	S42
7.	Khadwari	43.Village Haji Chanaser Ruk	S43
		44.Village Aayo Khan Shahani	S44
		45. Village Ali Bux Shahani	S45
		46 Village Rajib Khan Dhandho	S46
		47.Village Khadwari	S47
		48.Village Mohammad Ali Kalhoro	S48
		49..Village Sheikhani	S49
		50. Village Balach Khan Shahani	S50
		51. Village Jaffar Khan Shahani	S51
		52. Village Allah Warayo Shahani	S52
8.	Labano	53.Shahaid Public School Ghotki	S53
		54.Village Jewan khan Kolachi	S54

S. No	TC/UC	Villages / Mohall's	Tube well /Hand Pump Samples
		55.Village Soharo Kolachi	S54
		56.Village Rasool Nagar	S56
		57. Village Panjo Labano	S57
		58.ViIlage Central Jail Ghotki	S58
9.	Bhand	59.Village M.Azeem Menik	S59
		60.Village Hazoor Bux Gandani	S60
		61.Village Saifal Khan Kolachi	S61
		62.Village Puhoo Khan Waseer	S62
		63.Village Balach Khan Khoso	S63
		64. Village Naseer Khan Khoso	S64
		65.Village Jafar Khan Khoso	S65
		66. Village Nazeer Khan Kaladi	S66
10.	Ali Bagh	67.Village Raees Mohammad Phulpoto.	S67
		68.Village Dildar Mahar	S68
		69. Village Ramzan Mahar Derajo	S69
		70.Village Hussain Bhayo	S70
		71. Village Meehon Mahar	S71
		72. Village Attaullah Shah	S72
		73. Village Bahadur Soomro	S73
11.	UC-Atal Muradani	74. Village Atal Muradani	S74
		75. Village Sobo Shaikh	S75
		76. Village Ramzan Bhayo	S76
		77. Village Ali murad Mahar	S77
12.	Umar Draho	78. Muhala Shafiabad	S78
		79.Village Hafizabad	S79
		80.Lakhan Colony	S80
		81. Village Haseeja Mahar	S81
		82. Village lakho Khan Memon	S82
		83. Village Fatehpur	S83
		84. Village Atur Lolai	S84
13.	City-Ghotki (II)	85.Soomra Colony Rahmowali	S85
		86. Al-Madina Chowk Rahmovali	S86
		87. DC-School Ghotki	S87
14.	City- Ghotki (I)	88. Police Station Ghotki	S88
		89. Bismillah Hospital Ghotki	S89
		90. Shelton Hotel Ghotki	S90
		91. New Bus Stand Mathelo Road Ghotki	S91
		92.Shahi Bazar Ghotki	S92
		93. Dhong Muhala Ghotki	S93
		94. Anwar Abad Muhalla Ghotki	S94
		95. Soomra Colony Ghotki	S95
		96. Nahre Shah Ghotki	S96
15.	City-Ghotki (II)	97. Mirani Colony Ghotki	S97
		98. Shah Jamait Colony Ghotki	S98
		99. Kadria Factory Ghotki	S99
		100. Railway Station Ghotki	S100

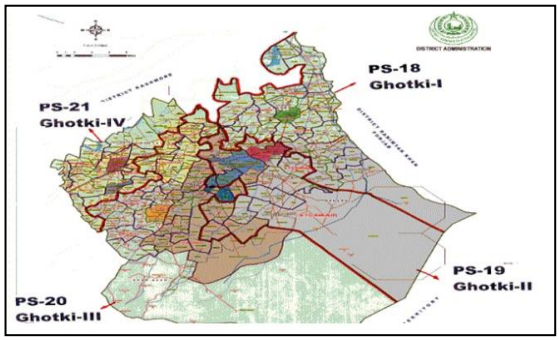

Fig. 1. Map of Taluka Ghotki.

Sample Preservation

The specimens were stored in plastic polyethylene flasks previously soaked in nitric acid at 10% for twenty-four hours and carefully rinsed using clean H_2O. The specimens were filtered using filter paper Whatman No. 42 in order to eliminate suspending solids and stored in the dark at 4°C. The list of groundwater specimens were coded by S 1 to S 100 of towns/villages of taluka Ghotki as shown in Table 2.

Fig. 2. Merck Arsenic Kit.

Preparation of the sample

The 500mL of specimens picked up in a beaker mixed with nitric acid concentrated a few droplets heated at about 75°C by putting them on a hot plate in order to reduce the volume near to dry. After that, the residuals were digested using HNO_3 2N by stirring with 33% addition of H_2O_2 further heated at 70°C to reduce to 20mL volume.

Table 2. Collection of Samples from Hand pump, Electrical motors & Tube well water.

Total U.C	14
Total number of samples	100
Hand pump	80
Electrical motors	10
Tube well water	10

Sample Analysis

Analysis of pH, total dissolved salts and electrical conductivity: pH was detected using a pH meter, electrodes immersed in samples of water. Conductivity was studied with the conductivity meter in the µS/cm unit. Conductivity meter electrodes were immersed in samples of water, displaying the TDS in mg/L unit.

Arsenic Kit method

The arsenic content was detected using Merck Arsenic Kit (0.01-0.5mg/L) (Merck K Ga A, 64271 Darmstadt, Germany) as shown in Fig. 2. utilizing method colorimetry with test strips in the laboratory within 48 hours of sampling. The reaction bottle of the arsenic kit was filled with 60mL of water sample up to the mark and analysis was performed as prescribed by the manufacturer of the kit.

Results and discussion

The pH of the 100 collected ground water samples was observed 6.2-8.5 pH. Out of these 06 samples were observed neutral having 7 pH values, 39 were acidic 6.2-6.98 pHs and 55 were basic 7.1-8.5 pHs as displayed in Table 3-7. pH values of 05 specimens such as S 25, S 40, S 68, S 90 and S 99 were (6.12-6.4 pH) below permitted limit value and remaining 95 specimens were within permissible limit suggested by WHO. Highest value of pH was detected 8.5 in 2 samples (S 36 and S 66) and lowest value of pH was detected 6.2 in S 25 sample as shown in Table 3-7.

The electrical conductivity (EC) of 100 collected ground water specimens was observed in range of 512-3194µS/cm. Out of these 06 specimens were higher than the permitted limit and 94 remaining specimens were within permissible limit suggested by WHO as displayed in Table 3-7.

Highest value of electrical conductivity was measured as 3194 µS/cm in S 24 sample and lowest value of electrical conductivity was measured as 512 µS/cm in S 90 sample as shown in Table 3-7.

Table 3. Analysis of ground water samples

WHO limit	6.5-8.5	2500 µS/cm	1000 mg/L	10 µg/L
Sample Codes	pH	EC µS/cm	TDS	As
S 1	7.1	1110	562	100
S 2	7	1792	791	0
S 3	6.88	764	556	25
S 4	7.1	1076	247	0
S 5	7.33	1005	486	5
S 6	7.41	1005	796	10
S 7	6.78	540	252	5
S 8	6.76	1180	504	5
S 9	6.83	1530	625	10
S 10	7	1056	523	5
S 11	7.05	520	264	100
S 12	6.58	844	442	100
S 13	6.86	1186	605	0
S 14	7.2	776	389	250
S 15	7.55	1502	759	10
S 16	7.16	1420	711	25
S 17	6.51	900	433	100
S 18	7.09	550	276	10
S 19	6.77	1046	521	0
S20	7.2	610	302	50

Table 4. Analysis of ground water samples.

WHO limit	6.5-8.5	2500 µS/cm	1000 mg/L	10 µg/L
Sample Codes	pH	EC µS/cm	TDS	As
S 21	6.79	1030	518	10
S 22	7.25	740	374	0
S 23	7.21	3150	1545	10
S 24	6.67	3194	1614	50
S 25	6.2	2200	1111	5
S 26	6.95	774	388	25
S 27	7.25	1385	628	5
S 28	6.81	1046	528	0
S 29	6.87	2326	1071	0
S 30	6.95	2266	1049	10
S 31	6.64	1478	745	10
S 32	7.14	1840	911	5
S 33	7.23	748	376	100
S 34	7.35	740	363	5
S 35	6.98	2090	1046	5
S 36	8.5	664	332	10
S 37	6.81	863	422	50
S 38	7.07	778	371	10
S 39	7	612	612	0
S 40	6.22	1214	720	0

Table 5. Analysis of ground water samples.

WHO limit	6.5-8.5	2500 µS/cm	1000 mg/L	10 µg/L
Sample Codes	pH	EC µS/cm	TDS	As
S 41	7.21	1720	823	0
S 42	7	1925	900	50
S 43	7.14	898	447	0
S 44	6.7	1158	580	0
S 45	6.96	1942	964	5
S 46	7.45	826	418	0
S 47	8.3	2817	1400	0
S 48	6.97	1600	748	50
S 49	6.62	1290	663	5
S 50	6.88	2600	1176	100
S 51	7.01	878	455	5
S 52	7.15	780	388	25
S 53	7.12	760	390	50
S 54	7	664	322	100
S 55	7.21	538	272	10
S 56	6.96	806	418	100
S 57	7.5	1301	625	100
S 58	7.1	1500	720	5
S 59	7.44	774	387	0
S 60	7.3	1052	529	10

Table 6. Analysis of ground water samples.

WHO limit	6.5-8.5	2500 µS/cm	1000 mg/L	10 µg/L
Sample Codes	pH	EC µS/cm	TDS	As
S 61	7.41	896	446	0
S 62	7.08	1100	538	50
S 63	6.5	1398	712	5
S 64	6.98	910	477	50
S 65	7.41	716	362	0
S 66	8.5	1500	740	5
S 67	7.65	2418	1222	0
S 68	7.85	2540	1300	10
S 69	7.65	2218	1096	0
S 70	7.11	802	397	50
S 71	7.31	1124	554	0
S 72	7.02	748	329	100
S 73	6.94	744	376	50

WHO limit	6.5-8.5	2500 µS/cm	1000 mg/L	10 µg/L
Sample Codes	pH	EC µS/cm	TDS	As
S 74	7.44	744	375	25
S 75	7.01	796	400	250
S 76	7.23	636	317	5
S 77	8.45	2390	1000	10
S 78	6.58	658	307	5
S 79	7.01	578	287	5
S 80	7	520	291	0

Table 7. Analysis of ground water samples.

WHO limit	6.5-8.5	2500µS/cm	1000mg/L	10 µg/L
Sample Codes	pH	EC µS/cm	TDS	As
S 81	6.88	944	464	5
S 82	7.1	936	459	0
S 83	7.58	1600	820	100
S 84	7.22	1100	526	10
S 85	6.9	784	393	5
S 86	7.41	1258	621	5
S 87	7.01	1080	550	25
S 88	6.18	1226	605	0
S 89	6.82	1236	610	50
S 90	6.12	512	288	0
S 91	6.64	2236	1114	0
S 92	6.81	1964	986	250
S 93	7.25	1830	915	100
S 94	7.23	1216	601	50
S 95	7.5	826	405	5
S 96	7.6	770	386	0
S 97	8.45	1964	526	0
S 98	6.82	1062	975	250
S 99	6.4	988	532	0
S 100	7.1	3172	1575	10

Table 3-7.

The total dissolved salts (TDS) in 100 collected ground water specimens were observed 247-1614mgL^{-1}. Out of these 13 specimens were higher than the permitted limit and 87 remaining samples were within permissible limit suggested by WHO as shown in Table 3-7. The highest total dissolved salts value was measured as 1614mg/L in S 24 sample and the lowest total dissolved salts value was measured as 247mg/L in S 04 sample as shown in Table 3-7. The As kit method has been employed to examine 100 samples of groundwater taken from taluka Ghotki district Gotki, Sindh, Pakistan. It is a hand-held and user-friendly method for the analysis of As from ground H_2O. The permitted/ safe limit of As given by WHO is 0.01mg/L or 10µg/L.

Out of 100 samples arsenic was absent in 28 samples and present in 72 collected ground water samples as shown in Table 3-7 and Fig. 3-7. And from 72 arsenic containing samples, 38 (52.8%) water sampling were in the range of the permitted limit, as suggested by WHO, while 34 (47.2%) water sampling was beyond the WHO permitted limit.

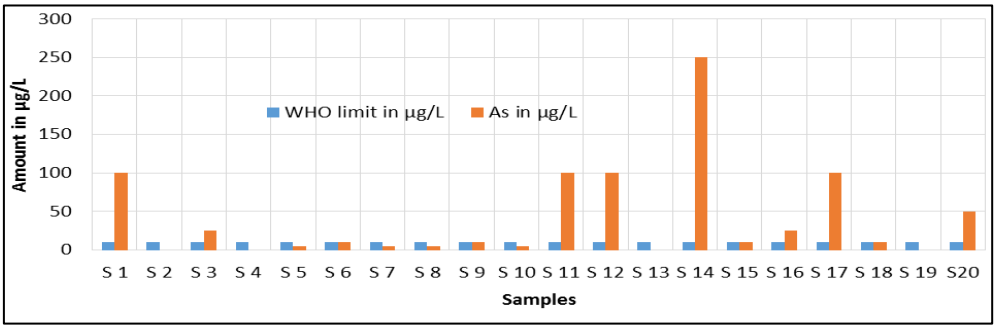

Fig. 3. Arsenic in ground water samples.

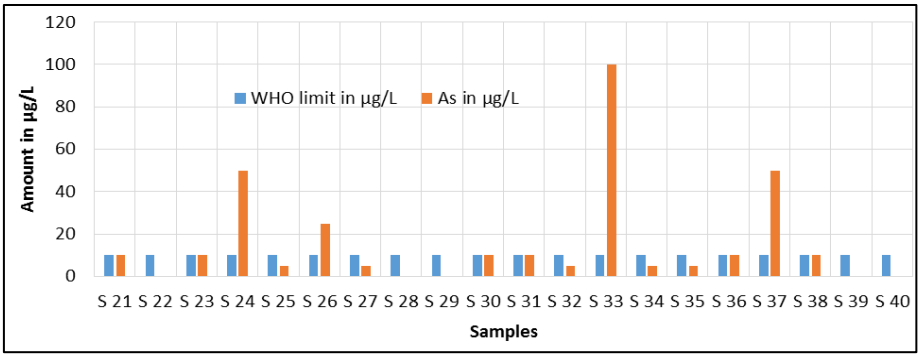

Fig. 4. Arsenic in ground water samples.

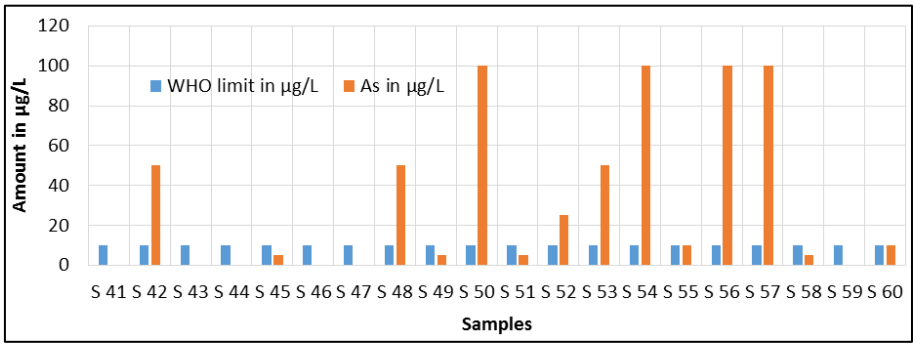

Fig. 5. Arsenic in ground water samples.

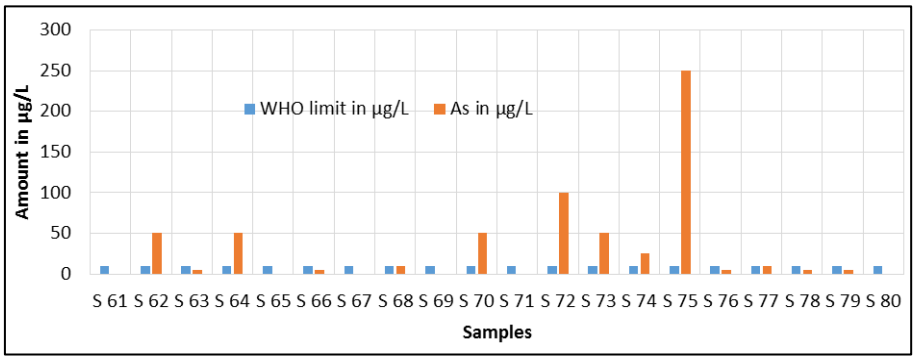

Fig. 6. Arsenic in ground water samples.

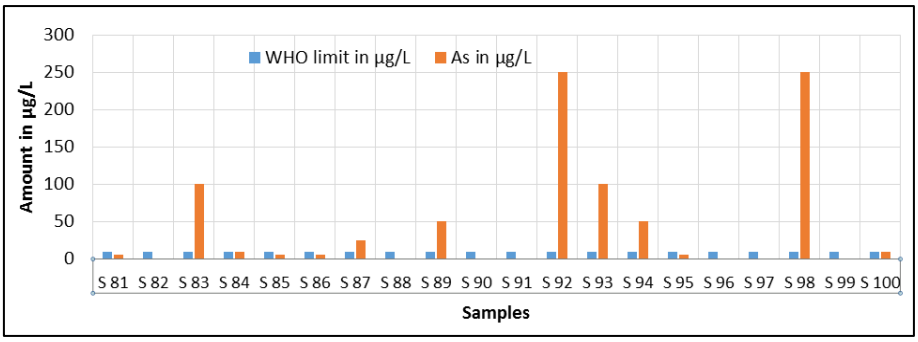

Fig. 7. Arsenic in ground water samples.

The highest value of arsenic was detected 250µg/L in the 4 samples (S 14, S 75, S 92 and S 98) and the lowest value of arsenic was found 5µg/L in 21 samples out of 72 ground water arsenic containing samples as shown in Table 3-7 and Fig. 3-7.

The results of As determination were validated by comparing the results of 20 samples analyzed by As kit were analyzed on inductive couple plasma (ICP), the results were with good comparison with both methods at 95% confidence limit.

Conclusion

It is concluded from our present research work that arsenic was present above permissible limit suggested by WHO in 34 (47.2%) ground water samples of taluka Ghotki and these are unsafe for drinking purpose without removal of arsenic.

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