

# Evaluation and Quantification of Some Trace Elements in Drinking Water by ICP-OES

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## Abstract

Trace amount of elements are common in water, some of these elements may be hazardous to human health and others may be vital to human body. Using inductively coupled plasma-optical emission spectrometry (ICP-OES) technique after 10-fold pre-concentration and acid digestion, the concentrations of 10 trace elements samples (TEs) Ba, Cu, Cr, Ni, V, Mn, Mo, Ag, P and Si were determined in drinking water in Turabah Province (Saudi Arabia). The concentrations of Cu, Cr, Ni, V, Mn, Mo, Ag and P in the samples of local and national factories were found to be below the maximum level that that recommended by World Health Organization (WHO) and Saudi Arabia Standards Organization (SASO). While, the concentrations of Ba was above and below the maximum level that recommended by WHO and SASO according to the sample source. The concentrations of Ba, Cu, Cr, Ni, V, Mo, Ag, and P in the wells samples were below the maximum level, while the concentrations of Mn was above the maximum level. The analysis method was validated in terms of accuracy, precision, limit of detection (LOQ) and limit of quantification (LOD) and confirmation reliability. The recovery percent was found to be 97.5 -99.7%.

**Keywords:** Trace elements; Drinking water; Wells water; ICP-OES

## Introduction

Water is an essential component for life and an important source of intake of trace elements in humans. Therefore, its quality is of great importance to human health. In Turabah province (Saudi Arabia) Local factories of water treatment are small simple units consist usually of sand filters, carbon filters and ion exchange resin. The resource of the water for these local factories is wells in the valley of Turabah. No daily quality control tests for following up the quality of water in these factories, most of the people used the water produced by local factories in cooking, were some of them used it for drinking. The quality of drinking-water is a powerful environmental determinant of health; groundwater which the source of the drinking water in Turabah province contains major ions of the trace metals and other toxic pollutants [1]. All TEs are toxic if consumed at sufficiently high levels for long enough periods. The difference between toxic intakes and optimal intakes to meet physiological needs for essential trace elements is great for some elements but it is much smaller for others. According to their biological activity some of the trace elements are classified as essential trace elements which are required in very small amounts, they play a very important role in keeping the body working effectively; on the other hand numbers of trace elements are not classified as essential trace elements due to the human nutrition and their toxicity. For example Ba is not considered to be an essential element for human nutrition [2], The health effects of barium depend on the level of exposure, at high concentrations, it causes vasoconstriction by its direct stimulation of arterial muscle, peristalsis as a result of the violent stimulation of smooth muscles, convulsions and paralysis following stimulation of the central nervous system, the acute toxic oral dose of Ba is between 3 and 4 g [2]. Copper is one of a relatively small group of metallic elements which are essential to human health, it is combines with certain proteins to produce enzymes that act as catalysts to help a number of body functions. Copper necessary for the development of connective tissue, nerve coverings, and bone, it acts as a reductant in the enzymes, and required for the proper functioning of many important enzyme systems [3]. On the other hand, lack of Cu intake causes anemia, growth inhibition, and blood circulation problems [4,5]. According to study in Chile by Olivares et al. the observed level of Cu

in drinking-water which has no effect was to be 2 ppm [4]. Manganese is an essential element for many living organisms, including humans, for example, some enzymes require manganese, while adverse health effects can be caused by in adequate intake or over exposure of Mn. At the median drinking-water level of 10 ppm determined in the national inorganic and radionuclide survey, the intake of Mn would be 20 µg/day for an adult, assuming a daily water intake of 2 litres [5]. Large doses of Mn cause headaches, apathy, irritability, insomnia, and weakness of the legs. Long-term heavy exposure to Mn may result in a nervous system disorder [5-7]. Nickel is considered to be probably essential trace element to human health, because it might play a role in the regulation of many enzymes, but a high toxicity of element is observed during high exposure that can produce diverse health effects [5,8]. Chromium is an example of an essential nutrient to humans that potentiates insulin action and thus influences carbohydrates, lipid and protein metabolism [5,9]. Molybdenum is considered as essential metal in both animals and humans, safe and adequate intake levels have been suggested for various segments of the population, it was found to be for infants 0.015-0.04 mg/day, for children aged 1-10 was 0.025-0.15 mg/day and for all individuals above the age of 10 was 0.075-0.25 mg/day [10]. Silicon is major constituent of the mammalian diet derived from cereals and cereal-based products, natural water contain soluble silicates (mostly orthosilicic acid) generally at 1-20 ppm [11]. Silicon plays a role in bone matrix formation and bone mineralization, the main known biological actions of Si are related with collagen, elastine and proteoglycans [12], silicon can affect the concentration of Al in drinking water, the significant correlation between Al and Si concentrations suggests that

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Si can eliminate Al in water, and probably in the body it might do the same [13]. Silver average concentrations in USA in natural waters are 0.2–0.3 µg/L, in Canadian tap water, only 0.1% of the samples contained more than 1-5 ng/L of Ag [13].

Elsheikh et al. [14] studied the concentration of 12 TEs Na, K, Ca, Mg, Fe, Zn, B, Al, Pb, Cd, As and Sr, in drinking water of Turabah Province, they found that the concentration of some TEs are below the maximum level recommended by WHO and SASO while others elements concentrations are above the maximum level. Electrochemical method was used for determination the concentration of Pb, Cd, Cu, Zn, Fe, Se in the tap water of Jeddah city (Saudi Arabia), the obtained results were lower than the average range of these elements in the maximum concentration as they were allowed to be by WHO [15]. Trace elements such as Al, B, Ba, Cd, Cr, Cu, Mn, Pb and Zn were studied by Momen et al. [16] in human blood samples from occupants of urban populations of Taif city (Saudi Arabia), the results of the study showed that the mean concentrations of the Al, B, Ba, Cd, Cu and Pb in human blood of diabetic mellitus and hypertensive patients were higher than the corresponding values of normal subjects. Zahid [17] studied the quality of drinking water in Riyadh city (Saudi Arabia) The results show that the most of the elements concentrations are in standard range of WHO and SASO. Tayyeb et al. studied the concentrations of Zn, Cr and Cd in the commercially available drinking water in Makkah and Jeddah cities (Saudi Arabia), they found that the concentration of these elements are within the maximum permissible levels for the drinking water recommended by WHO and SASO [18].

Different Techniques have been developed for the analysis of trace elements to increase the accuracy of the low amount in matrices. Some factors affect the choice of an analytical technique, including susceptibility to matrix effects, the range of elements covered the detection limits and suitability for the matrix of interest. The usefulness of an analytical method for TEs analysis also depends on the range of elements covered and the order of magnitude of its DL for the elements at the top and bottom of its sensitivity range. Detection limits will not be the same for all elements, so that simultaneous multielements determination will require compromises in experimental conditions that will affect the accuracy and precision of at least a few elements [7].

Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES) has become the technique of choice in many analytical laboratories for providing the accurate and precise measurements with large linear dynamic range. It is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, and can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation [19,20]. Some trace elements present in very low concentration, this is depending on the type of the sample and its source. In this case pre-concentration is necessary to reach the low DL.

The present study aimed to determine and evaluate the concentration of trace elements including Ba, Cu, Cr, Ni, V, Mn, Mo, Ag, P and Si in drinking water samples of local (LF), national (NF) factories and wells from Turabah Province (Saudi Arabia) by using ICP–OES, and to compare the obtained values with those values that recommended by WHO and SASO.

## Materials and Methods

### Reagent and glassware's

The reagents and chemicals were obtained from Merck (Darmstadt, Germany, www.merck.de), are analytical grade. De-ionized doubly

distilled water (DDDW) and nitric acid (69-72% (m/m),  $d=1.41-1.51 \text{ kg l}^{-1}$ ) was used. Acid-washed polyethylene bottles were used for preparing and storing solutions. All solutions were stored in the refrigerator until needed for analysis. Polyethylene storage bottles, glassware and the auto sampler cups were cleaned by soaking in 5 mole  $\text{l}^{-1}$   $\text{HNO}_3$  for about 24 hrs, rinsing five times with DDDW, dried, and stored in a class-100 laminar-flow hood.

### Samples collection and preparation

Forty tow samples were collected from six wells, three local factories and two national factories (1000  $\text{cm}^3$  of each). The samples kept in polyethylene storage bottles (metal free containers) after soaking the bottles in dilute nitric acid (5 mole  $\text{l}^{-1}$   $\text{HNO}_3$ ) overnight and washed with DDDW and then washed three times with the collected water sample before taken. The samples were filtrated through a 0.45 µm pore diameter membrane filter at the time of collection and the pH of each sample was measured then maintained in the refrigerator.

One hundred  $\text{cm}^3$  of each well sample was transferred into 250  $\text{cm}^3$  conical flask, while five hundred  $\text{cm}^3$  of each sample of local factories and national factories was transferred into 1000  $\text{cm}^3$  conical flask. 5  $\text{cm}^3$  of 5.0%  $\text{HNO}_3$  was added to it and then evaporated to about 10  $\text{cm}^3$  by using adjustable hot plate (95°C). The sample was cooled and transferred to 50  $\text{cm}^3$  volumetric flask. The residue was washed with 5  $\text{cm}^3$  of 5.0%  $\text{HNO}_3$  and with DDDW, and the volume was completed with DDDW to the mark. All prepared samples were maintained in the refrigerator until needed for analysis.

### Instrumentation and conditions

The concentrations of the standards and trace elements, Ba, Cu, Cr, Ni, V, Mn, Mo, Ag, P and Si were analyzed by using A Varian 725-ES inductively coupled plasma-optical emission spectrometer (ICP-OES), with radial viewing configuration (Perkin Elmer, USA). The ICP-OES operating conditions were well optimized and carefully selected in order to maximize the sensitivity for the desired elements and to obtain the best precision and accuracy. Details of the operating conditions are summarized in Table 1. The LOD and the LOQ from 1%  $\text{HNO}_3$  for the determined element are shown in Table 2.

### Statistical analysis

The results were statistically evaluated by Student *t*-test and ANOVA test ( $p=0.05$ ). The Microsoft Excel and Origin software's were also used to assess the significance of the differences between the variables investigated in well, local and national factories samples. The concentration values obtained were expressed as mean value  $\pm$  standard deviation ( $p=0.05$ ). All statistical analyses were based upon triplicate measurements of all standards and sample solutions.

## Results and Discussion

The results were expressed as  $x \pm s$ , where  $x$  is a mean values and  $s$  is standard deviation. The method was validated in terms of accuracy, precision, LOD, LOQ and confirmation reliability [21,22]. The recoveries percentage (%) was found to be 97.5-99.7%. The LOD and the LOQ from 1%  $\text{HNO}_3$  for the determined elements was shown in Table 2. The relative standard deviations (RSDs) for the samples were show in Tables 3A and 3B. The method was validated from the results of recoveries%, LOD, LOQ and RSDs, and it found to be reliable, accurate and precise.

The pH of the all samples were found to be within the recommended range (pH=6.5-8.5). The concentrations values of P, Cu, Mo, Cr and Ba

Parameters	Conditions
Power (KW)	1.20
Plasma flow rate (L/min)	15.0
Auxiliary Flow (L/min)	1.50
Viewing height (mm)	10
Nebulizer Pressure (KPa)	250
Replicate read time (s)	7
Sample uptake delay (s)	30
Pump rate (rpm)	20
Rinse time (s)	25
Replicates	3

TEs=Trace Elements

Table 1: ICP-OES operating parameters for determination of selected TEs.

Element	Wavelength (nm)	LOD	LOQ
P	213.618	0.014014	0.03685
Cr	267.716	0.0013	3.37246
Cu	327.395	0.0013	3.11014
Mo	379.825	0.0051	13.4007
Ti	334.941	0.0006	1.3958
V	292.401	0.0016	4.2951
Ni	231.604	0.0053	12.4232
Si	288.158	0.00858	0.01951
Ba	455.403	0.0005	1.1847
Ag	338.289	0.0035	8.90134

LOD=Limit of Detection; LOQ=Limit of Quantification

Table 2: LOD and LOQ for determination of selected TEs.

RSD					Element
National factories samples		Local factories samples			
2	1	3	2	1	
2.8	ND	8.88	8.33	1.41	P
ND	ND	ND	7.69	3.44	Cu
5.41	ND	2.94	3.57	9.09	Mo
ND	ND	ND	ND	11.11	Cr
1.90	6.41	0.97	3.35	8.00	Ba
ND	ND	ND	7.14	ND	Mn
ND	ND	ND	5.56	6.25	Ni
10	ND	5.88	5.88	10	Ti
ND	ND	6.25	ND	ND	V
ND	ND	ND	4.35	8.70	Ag
5.90	5.63	2.15	1.37	1.07	Si

ND=Not Detected

Table 3A: The relative standard deviation (RSD) for the factories samples.

of the local factories and the national factories samples were shown in Tables 4A and 4B (Figures 1A and 1B). The results show that all the concentrations were below the maximum level that recommended by WHO and SASO (Table 5). However, the concentration of Ba of national factory (1) are below the maximum level that recommended by SASO but it is above the maximum level that recommended by WHO, while it is concentrations values of the local factory(3) and national factory(2) (Table 4A) are above the maximum level that recommended by WHO and SASO. The concentrations values of Ba of the local factory(3) was  $5.1354 \pm 0.05$  ppm which seems to be higher than the maximum concentration found in groundwater in the Netherlands 2.5 ppm, in drinking-water in Canada 0.086 ppm, in water supplies of cities in the USA 0.043 ppm, and in drinking-water in Norway was to be 0.09 ppm[2]. The higher Ba concentration could affect the human's health and for long-term exposure may cause death.

The concentrations values of the elements Mn, Ni, Ti, Ag and Si of the all factories samples were shown in Table 5 (Figures 1C and 1D), the results show that all the concentrations were below the maximum level that recommended by WHO and SASO. However; Figure 1D show the high concentrations values of Si, which have no limit listed by WHO and SASO.

Tables 6A and 6B (Figures 2A and 2B) show the concentrations values of wells samples of the elements Ba, P, Cu, Mo, Cr, Ti, V and Ag, the results show that all the concentrations are below the maximum level. Table 6C (Figures 2C and 2D) show the concentrations values of Mn and Si of wells samples, The results show that the concentrations of Mn are above the maximum level that recommended by WHO and SASO, as mentioned before Mn in large doses and Long-term heavy exposure could affect the human health, An epidemiological study was conducted in Greece to investigate the possible correlation between long-term (i.e., more than 10 years) Mn exposure from water and neurological effects in elderly people [6].

Figure 2D show the high concentrations values of Si, as mentioned before, in drinking water no limit listed by WHO and SASO, but Si is considered as an essential element, and it has significance effect in dialysis patients. In these patients Si concentrations were significantly higher than those noted in subjects with normal renal function as well as in patients with chronic renal failure not yet in dialysis and patients treated by continuous ambulatory peritoneal dialysis [23]. However, human health risk in some patients could relate to high Si concentrations in drinking water.

## Conclusions

According to the drinking water guide line recommended by WHO and SASO, the concentrations obtained of TEs of the local and national factories samples are below the maximum level recommended, except Ba which in a some samples is above the maximum level recommended by SASO. More over the results obtained of the some wells samples of trace element Mn are above the maximum level recommended by both WHO and SASO. Silicon was detected in all samples, in some samples with high concentrations so intensive study on it is toxicity, human risk and formula is recommended.

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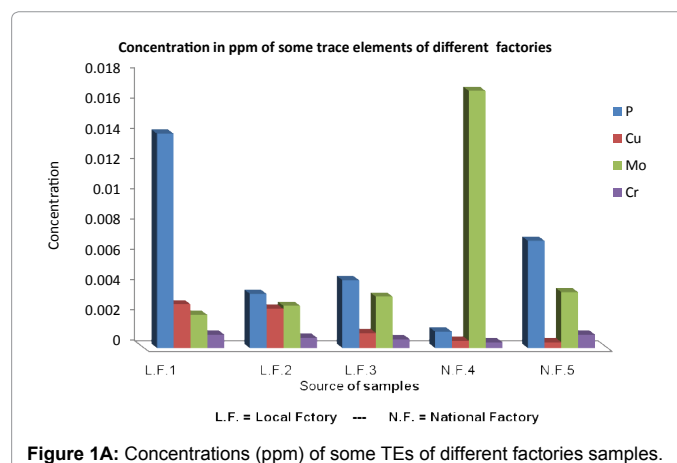


Figure 1A: Concentrations (ppm) of some TEs of different factories samples.

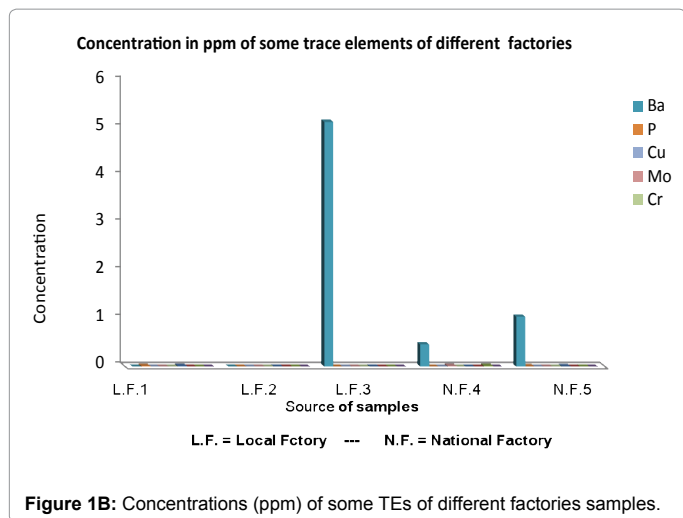


Figure 1B: Concentrations (ppm) of some TEs of different factories samples.

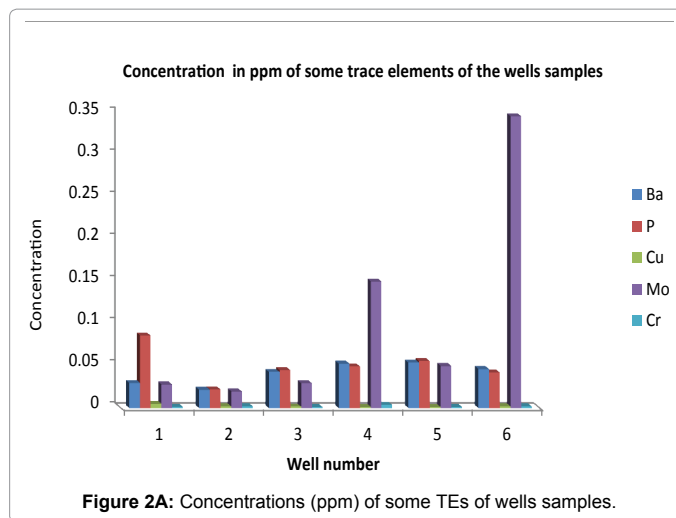


Figure 2A: Concentrations (ppm) of some TEs of wells samples.

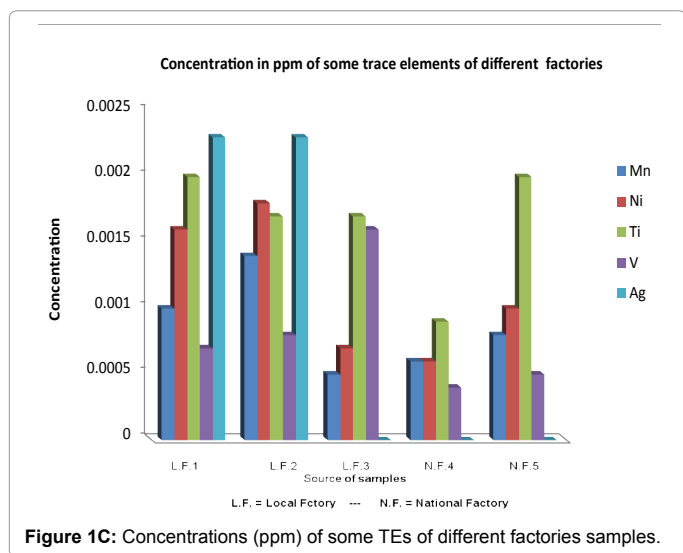


Figure 1C: Concentrations (ppm) of some TEs of different factories samples.

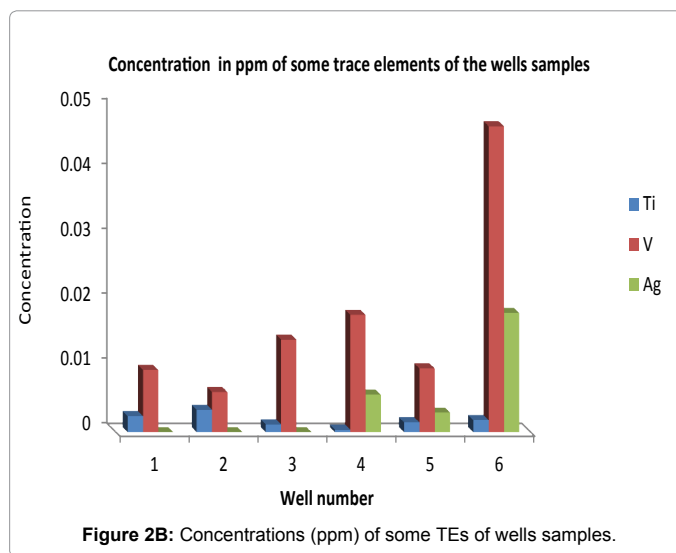


Figure 2B: Concentrations (ppm) of some TEs of wells samples.

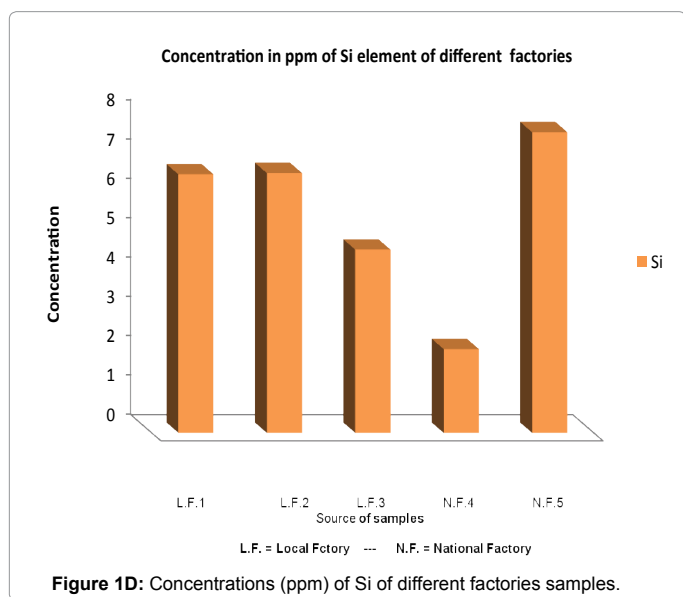


Figure 1D: Concentrations (ppm) of Si of different factories samples.

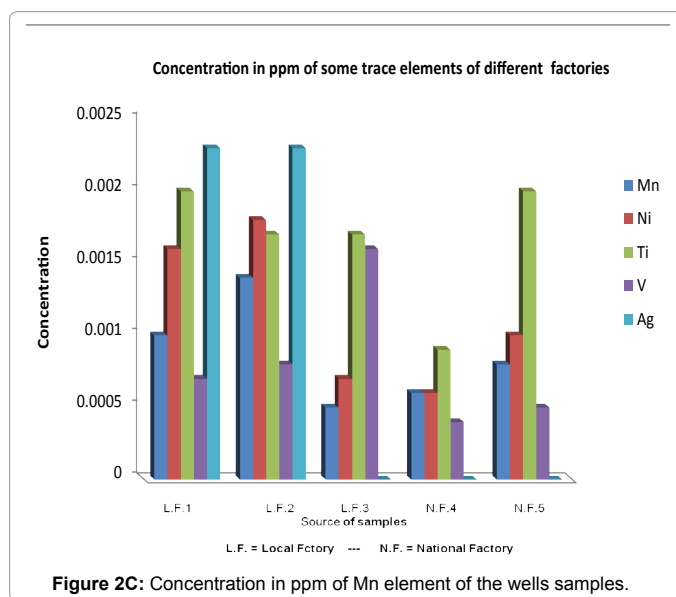


Figure 2C: Concentration in ppm of Mn element of the wells samples.

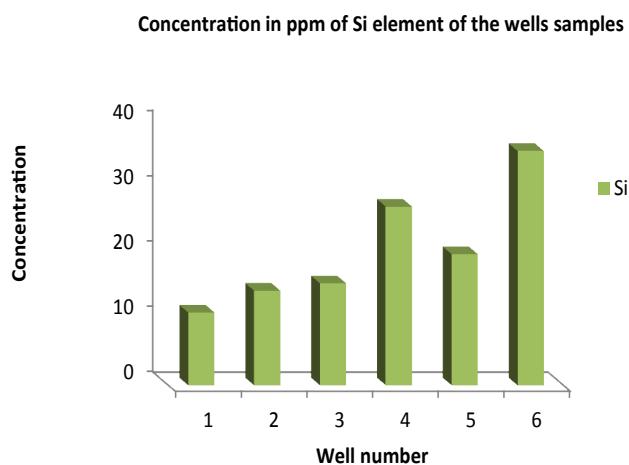


Figure 2D: Concentration in ppm of Si element of the wells samples.

Element	RSD					
	Wells samples					
	1	2	3	4	5	6
Ba	9.97	9.07	6.98	7.54	7.38	6.42
P	5.80	4.46	2.21	4.04	3.57	7.03
Cu	7.65	4.50	ND	ND	ND	8.23
Mo	7.07	9.98	6.67	6.65	5.97	8.67
Cr	5.43	ND	ND	4.95	ND	4.57
Ti	3.98	8.65	8.13	ND	6.41	5.29
V	6.24	4.81	7.00	5.53	3.05	4.25
Ag	ND	ND	ND	6.92	9.80	4.90
Mn	2.10	1.53	4.81	8.50	1.59	7.47
Si	7.17	7.59	8.33	6.59	8.98	5.86

ND=not detected

Table 3B: The relative standard deviation (RSD) for the wells samples.

Element	Concentration (ppm)				
	Local factories samples			National factories samples	
	1	2	3	1	2
P	0.01417 ± 0.0002	0.0036 ± 0.0003	0.0045 ± 0.0004	0.0011 ± 0.00	0.0071 ± 0.0002
Cu	0.0029 ± 0.0001	0.0026 ± 0.0002	0.001 ± 0	0.0005 ± 0	0.0004 ± 0
Mo	0.0022 ± 0.0002	0.0028 ± 0.0001	0.0034 ± 0.0001	0.017 ± 0	0.0037 ± 0.0002
Cr	0.0009 ± 0.0001	0.0007 ± 0	0.0006 ± 0	0.0004 ± 0	0.0009 ± 0
Ba	0.0025 ± 0.0002	0.0046 ± 0.0002	5.1354 ± 0.05	0.468 ± 0.03	1.0517 ± 0.02

a: a mean value ± standard deviation (n=3)

Table 4A: Concentration (ppm) of the TEs in different factories.

Element	Concentration (ppm)				
	Local factories samples			National factories samples	
	1	2	3	1	2
Mn	0.001 ± 0.000	0.0014 ± 0.0001	0.0005 ± 0.0000	0.0006 ± 0.0000	0.0008 ± 0.0000
Ni	0.0016 ± 0.0001	0.0018 ± 0.0001	0.0007 ± 0.0000	0.0006 ± 0.0000	0.001 ± 0.0001
Ti	0.002 ± 0.0002	0.0017 ± 0.0001	0.0017 ± 0.0001	0.0009 ± 0.0000	0.002 ± 0.0002
V	0.0007 ± 0.0000	0.0008 ± 0.0000	0.0016 ± 0.0001	0.0004 ± 0.0000	0.0005 ± 0.0000
Ag	0.0023 ± 0.0002	0.0023 ± 0.0001	ND	ND	ND
Si	6.559 ± 0.007	6.5923 ± 0.09	4.6513 ± 0.1	2.13 ± 0.12	7.6311 ± 0.45

Table 4B: Concentration (ppm) of the TEs in different factories.

Element	Concentration (ppm)	
	WHO standard	SASO standard
P	NL	NL
Cr	0.05	0.05
Cu	2	2
Mn	0.5	0.5
Mo	NL	0.07
Ti	NL	NL
V	NL	NLL
Ni	0.02	0.02
Si	NL	NL
Ba	0.3	0.7
Ag	NL	0.1

NL = No Limit Listed

**Table 5:** WHO and SASO Guide line for TEs maximum concentrations.

Element	Concentration (ppm)					
	Wells samples					
	1	2	3	4	5	6
Ba	0.0301 ± 0.003	0.02204 ± 0.002	0.04299 ± 0.003	0.05304 ± 0.004	0.0542 ± 0.004	0.04672 ± 0.003
P	0.08623 ± 0.005	0.02239 ± 0.001	0.04534 ± 0.001	0.04955 ± 0.002	0.05603 ± 0.002	0.0427 ± 0.003
Cu	0.00523 ± 0.0004	0.00222 ± 0.0001	0.00203 ± 0.000	0.00157 ± 0.000	0.00158 ± 0.000	0.00243 ± 0.0002
Mo	0.02827 ± 0.002	0.02003 ± 0.002	0.02998 ± 0.002	0.15031 ± 0.01	0.05024 ± 0.003	0.346 ± 0.03
Cr	0.00184 ± 0.0001	0.0026 ± 0.000	0.0017 ± 0.000	0.00404 ± 0.0002	0.00167 ± 0.000	0.00219 ± 0.0001

a: a mean value ± standard deviation (n=3)

**Table 6A:** Concentration (ppm) of the TEs in wells.

Element	Concentration (ppm)					
	Wells samples					
	1	2	3	4	5	6
Ti	0.00251 ± 0.0001	0.00347 ± 0.0003	0.00123 ± 0.0001	0.00042 ± 0.000	0.00156 ± 0.0001	0.00189 ± 0.0001
V	0.00962 ± 0.0006	0.00623 ± 0.0003	0.014279 ± 0.001	0.018072 ± 0.001	0.00983 ± 0.0003	0.047067 ± 0.002
Ag	ND	ND	ND	0.00578 ± 0.0004	0.00306 ± 0.0003	0.01837 ± 0.0009

a: a mean value ± standard deviation (n=3), ND= not detected

**Table 6B:** Concentration (ppm) of the TEs in wells.

Element	Concentration (ppm)					
	Wells samples					
	1	2	3	4	5	6
Mn	1.9037 ± 0.04	1.9623 ± 0.03	2.2877 ± 0.11	30.6023 ± 2.6	1.2577 ± 0.02	2.3393 ± 0.1
Si	11.15128 ± 0.8	14.48773 ± 1.1	15.60073 ± 1.3	27.32475 ± 1.8	20.05182 ± 1.8	35.82612 ± 2.1

a: a mean value ± standard deviation (n=3)

**Table 6C:** Concentration (ppm) of the TEs in wells.

Ministry of Petroleum, Khartoum, Sudan, for samples processing.

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