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Fe, Ni, Zn, Se and Hg Determination by Spectrometry Methods in Some Samples of Potable Water in Zawia City Libya

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Abstract: In Libya, ground water is the main source supply of drinking water. Analytical study has been done on some water samples in Zawia city. Twelve sites were chosen to represent wells of ground water owned by authority in Zawia city and two samples are commercial mineral water for comparing the result of study. This study aimed to investigate the quality of drinking water of Zawia city i.e. with respect to its contents of trace elements that may be present and its quality compared with the international specifications. In fourteen drinking water samples collected from different zones from Zawia city, Inductively coupled plasma optical emission spectrometry (ICP/OES) and graphite furnace atomic absorption spectrometry (GFAA) techniques were applied for determination of Fe, Ni, Zn, Se and Hg. Hg was also determined by atomic mercury analyze (AMA).

Key words: Determination · Heavy metals · (ICP/OES) · (GFAA) · Potable Water · Zawia City Libya

INTRODUCTION

Throughout history, the quality of drinking water has been a factor in determining human welfare. Currently, waterborne toxic chemicals pose the greatest threat to the safety of water supplies in indu-strialized nations. The quality of groundwater is subjected to a number of chemical influences. There are many possible sources of chemical contamination bgof water: these include wastes from industrial chemical production, metal plating operations and pesticide runoff from agri-cultural lands. Some specific pollutants include industrial chemicals such as chlorinated hydrocarbons, heavy metals including cadmium. Lead and mercury, saline water, bacteria and general municipal and industrial wastes. Many of the chemicals used or manufactured by industry have contaminated water supplies. Water pollution should be a concern of every citizen. Understanding the sources, interactions and effects of water pollutants is essential for controlling pollutants in an environmentally safe and econo- mically acceptable manner [1].

Heavy metals is a term means those metallic elements (like lead and mercury) that have a density equal to or greater than 6.0 g/cm3 [2]. Trace metals is another term used to refer to those metals that occur at very low levels of a few parts per million (ppm) or less in a given system [3]. Heavy metals are natural components of the environment, but there are very concern because they are being added to environment in increasing amounts. Some heavy metals (like lead)are not known to be essential nutrients and considered to be toxic, while others (like zinc) are essential in small amounts for human, plants and animal life, but they can be harmful if they are taken up in large amounts [4, 5]. Heavy metals may be the most harmful pollutants. Among those heavy metals are metals such as Cd and Pb which are generally toxic even at very low levels and potentially toxic metals such as Cu and Zn [6].

In all types of natural water, the toxic heavy metal levels remain in the trace or even ultra-trace range. The typical range remain in several hundred $\mu g l^{-1}$ in highly pollutant rivers. The toxic and pathological effects of some heavy metal as water pollutants have been tabulated in Table (1) [7].

Aim of the Present Work: In Libya, ground water is the main sources supply of drinking water. Zawia city depends on two water sources ground water, which considered the main source and rain water.

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Table 1: The toxic and pathological effects of some heavy metal as water pollutants (21)

Metal	Pathological effects on man
Zinc	Vomiting, renal damage, cramps.
Nickel	Carcinoma, myocarditis, nausea and vomiting
Selenium	Damage of liver, kidney and spleen, fever, nervousness, vomiting, low blood pressure, blindness and even death.
Hexavalechromium	Nephritis, gastro-intestinal ulceration, diseases in central nervous system, cancer.
Mercury	Abdominal pain, headache, diarrhoea, hemolysis, chest pain.

Heavy metals may be the most harmful pollutant. It is well known that excessive amount of heavy metals in drinking water leads to several health hazards. Generally, the common by known essential metals such as Na, Mg, K and Ca are usually determined in the drinking water but trace metals (toxic or non toxic) often were not taken in to consideration, since the trace metals may be present in drinking water in minute amounts, which need more sophisticated instruments and sensitive methods togather with the speciation analysis.

Inductivity Coupled Plasma technique (I.C.P) and Graphite furnace Atomic Abs- orption Spectrometer technique (GFAAS) are sensitive and selective to be used in the determination of many trace and ultra trace elements may be found in water samples.

The aim of the present work is to investigate the quality of drinking water of Zawia city i.e. with respect to its contents of trace elements (iron, nickel, zinc, selenium and mercury) that may be present and its quality compared with the international specifications such as (WHO).

MATERIALS AND METHODS

In this work water samples were collected from Zawia city, twelve samples were taken from Zawia city (by standard methods) [8]. from different sites after 15 min. from the opening of the taps. Samples from 1-12 are ground water collected with wall head taps, summarized in Fig. 1 and Table 2, all samples can be considered as tap water. Samples No.13 and 14 are commercial mineral water from the market. The water samples were collected in previously cleaned polyethylene bottles of 1.5L, They acidified to about pH= 2 by adding suitable amount of nitric acid and stored in polyethylene bottles then kept in a refrigerator at 4.0°C until required [9]. (this step has been carried when it only required).

Table 2: Sources of the Samples

Samples Number	The well
1	Salah Addin well
2	Trafic light well
3	Behind hospital well
4	Hai Alwahda well
5	Public square well
6	Sport college well
7	Sahib ainah mosque well
8	Sedi Abdalwahed well
9	Alfasi sch308ool well
10	Alfasi Grave yard well
11	Alfragaat mosque well
12	Addman well
13	Compared sample 1
14	Compared sample 2

Fig. 1: Map of Zawia City showing location of drinking water samples

Statistical parameters were done by Mintab 14 program such as STDEV, confidence interval extermination and one sample T test as tabled in Table (3 and 4). A test was done about following hypo-thesizes: 1- The relative concentration of Fe, Ni, Zn, Hg and Se in all samples is higher than or equals the permissible value as given by WHO (300, 50, 5000, 1 and 10 μgl^{-1} respectively). 2- The relative concentration of Fe, Ni, Zn, Hg and Se in all samples are less than or equal the permissible value as given by WHO (300, 50, 5000, 1 and10 μgl^{-1} respectively).

Table 3: Some Statistical parameters for elements under investigation by ICP-AES

Element	N	Average+ St Dev (μgl^{-1})	T test	Confidence interval 95%	P- value
Fe	14	26.4±1.86	-54.996	26.14-32.21	0.000
Ni	14	32.8±1.1	-12.828	31.5-35.02	0.000
Zn	14	34.1±4.55	-38.247	7.77-93.99	0.000
Se	14	61.3±2.12	6.823	58.72-107.56	0.000

Table 4: Some Statistical parameters for elements under investigation

Element	N	Average+ St Dev (μgl^{-1})	T test	Confidence interval 95%	P- value
Fe	14	25.37±19.42	-52.93	14.16; 36.58	0.000
Ni	14	12.5±6.84	-31.44	8.54; 16.45	0.000
Zn	14	60.2±14.92	-123.88	26.0; 146.3	0.000
Hg	14	0.304±0.08	-32.20	0.26- 0.35	0.000

RESULTS AND DISCUSSIONS

Since contamination of drinking water and the natural environment by toxic metals is a serious problem, so there are many studies have been carrying out for determination of heavy metal in water such as [10, 11, 12, 13, 14, 15]. Determination of heavy metals in different kinds of water is one of the important works in water analysis. There are many studies conducted in Libya for drinking water analysis for the determination of heavy metals such as showed in references [16, 17, 18, 19]. Table (5) Result of drinking water samples μgl^{-1} by ICP-AES.

Concentration of iron (Fe) in all samples are ranged from (>5.0–75 μg.l^{-1}) by ICP-AES as shown in Table (5) and Fig. (2) and ranged from (2.23-64.20 μg.l^{-1}) by GFAA Table (6) and Fig. (3). The higher concen-tration in samples No. (5 and 12). In all samples, Fe concentration was below the permissible value (300 μg.l^{-1}) according to the WHO. It's clear from the Table No. (3) that P value less than (300) i.e. that hypothesis No. (2) is accepted and hypothesis No. (1) is rejected. So we can say that relative concentration for Fe ranged from (26.14-32.21) at level confidence 95%, so the concentration of Fe is less than (32.21 μg.l^{-1}).

Concentration of Ni in all samples are ranged from (>10–40 μg.l^{-1}) by ICP-AES Table (5) and Fig. (4) and ranged from (2.38-20.97 μg.l^{-1}) by GFAA Table (6) and Fig. (5). The higher concentration in samples No. (3, 4, 9, 10,11and 12). Levels as high as 1 mg/liter have been reported in surface-waters, [20] although the levels are generally much lower, e.g., 5-20 μg/liter [21]. In all samples, Ni concentration was below the permissible value (50 μg.l^{-1}) according to the WHO. It's clear from the table No. (3) that P value less than (50) i.e that hypothesis No. (2) is ace-pted and hypothesis No. (1) is rejected. So we can say that relative concentration for Ni ranged from (31.5-35.02) at level confidence 95%, so the concentration of Ni is less than (35.02 μg.l^{-1}).

Table 5: Result of drinking water samples μgl^{-1} by ICP-AES

	Concentration (μg.l^{-1})				
Samples Number	Fe	Ni	Zn	Hg	Se
1	15	30	10	<10	46
2	11	30	02	<10	<40
3	26	40	10	<10	<40
4	23	40	30	<10	57
5	46	30	40	<10	60
6	15	30	30	<10	<40
7	21	40	40	<10	<40
8	14	40	40	<10	65
9	21	40	10	<10	<40
10	19	40	20	<10	70
11	30	40	60	<10	70
12	75	40	180	<10	<40
13	<05	<10	03	<10	<40
14	<05	<10	03	<10	<40

Table (6) Result of drinking water samples μgl^{-1} by GFAA

	Concentration (μg.l^{-1})		
Samples Number	Fe	Ni	Zn
1	15.22	18.07	7.82
2	12.54	20.97	12.35
3	32.18	16.22	19.88
4	43.08	13.95	19.12
5	64.20	6.73	34.47
6	21.15	8.98	26.27
7	21.22	20.40	23.57
8	11.84	9.20	29.32
9	21.31	17.75	21.07
10	20.23	18.07	12.75
11	21.61	16.76	55.88
12	64.16	1.97	576.26
13	4.16	2.38	2.65
14	2.23	3.49	0.99

Concentration of Zn in all samples are ranged from (2 –180 μg.l^{-1}) by ICP-AES Table (5) and Fig (6) and ranged from (0.99-576.26 μg.l^{-1}) by GFAA and Table (6) and Fig. (7). The large difference in zinc content is may

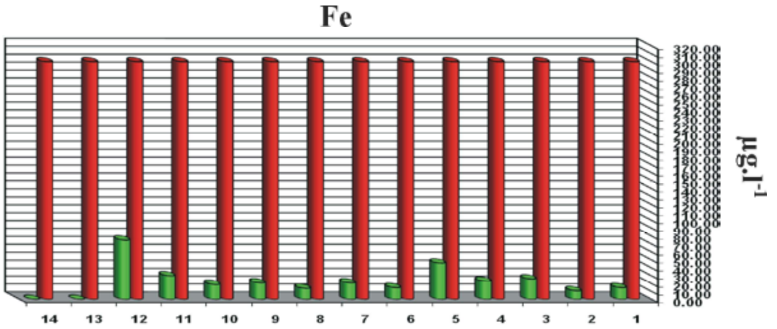

Fig. 2: The concentration of Fe in water samples by ICP-AES

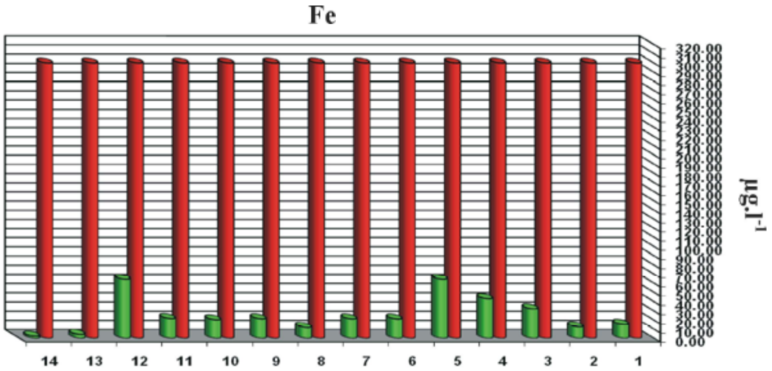

Fig. 3: The concentration of Fe in water samples by GFAA

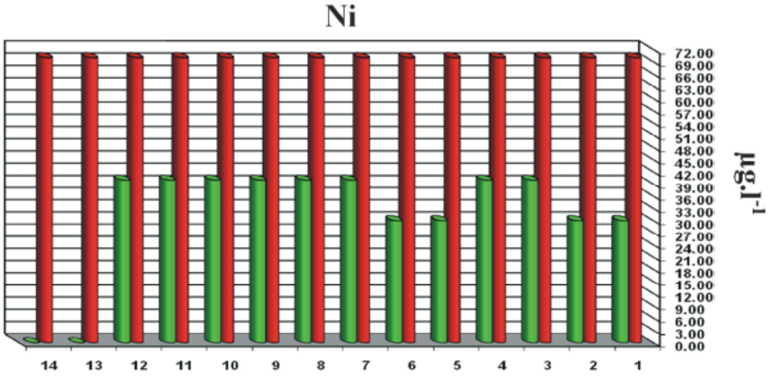

Fig. 4: The concentration of Ni in our samples by ICP-AES

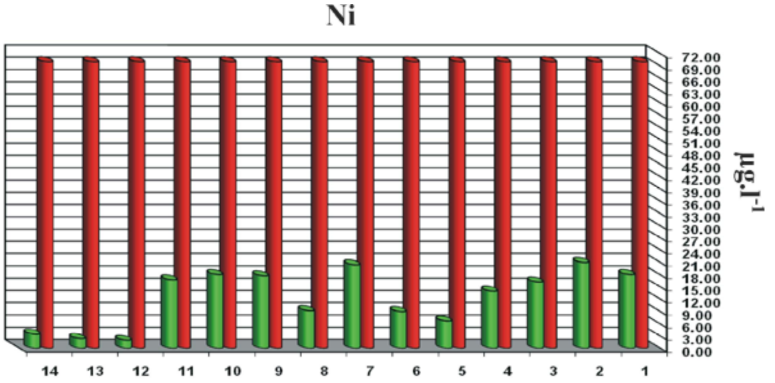

Fig. 5: The concentration of Ni in water samples by GFAA

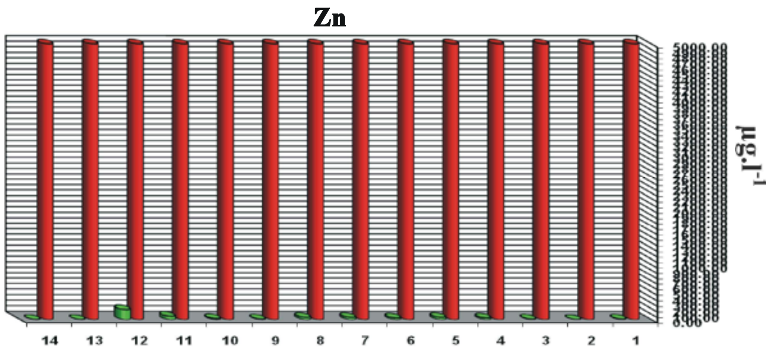

Fig. 6: The concentration of Zn in water samples by ICP-AES

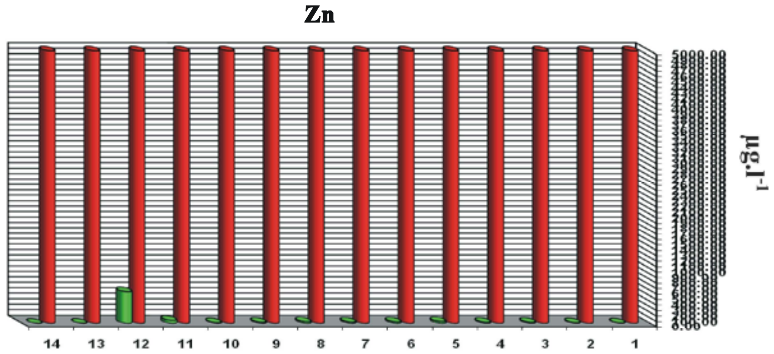

Fig. 7: The concentration of Zn in water samples by GFAA

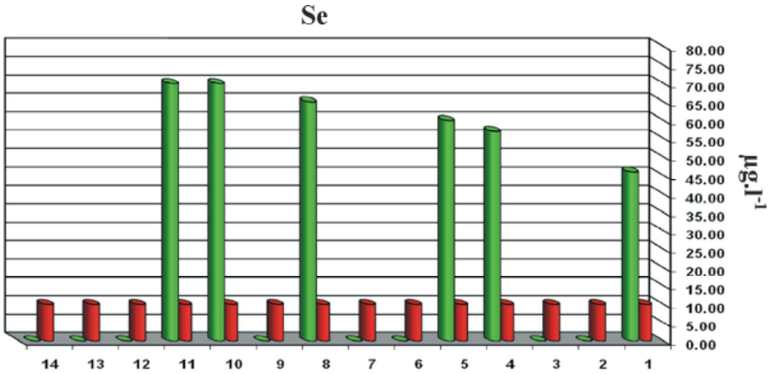

Fig. 8: The concentration of Se in water samples by GFAA

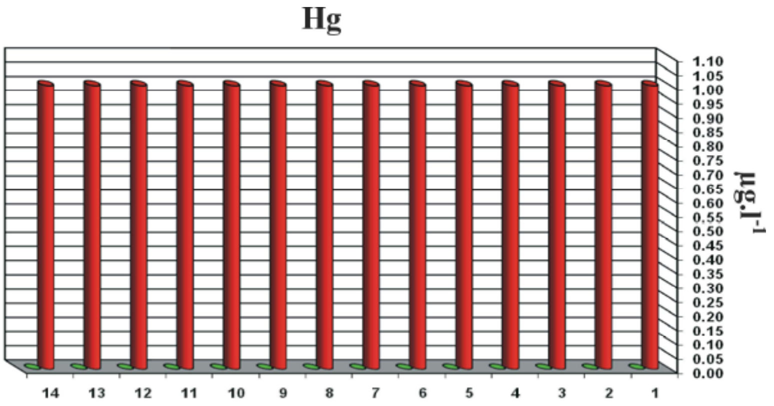

Fig. 9: The concentration of Hg in water samples by ICP-AES

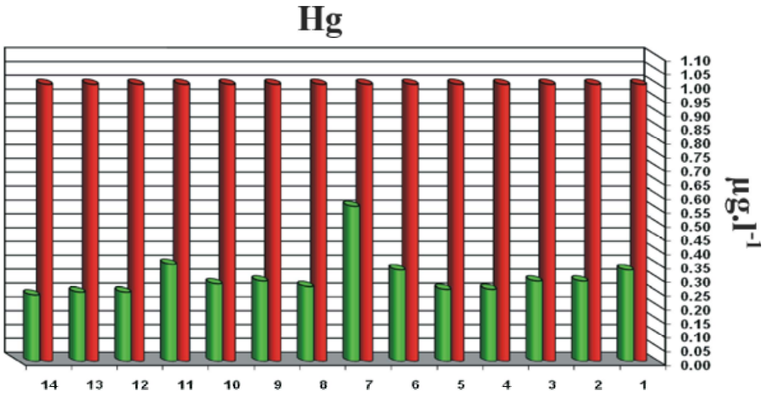

Fig. 10: The concentration of Hg in water samples by AMA

Table 7: Result of drinking water samples. µg.l^{-1} (AMA)

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Hg(ppb)	0.33	0.29	0.29	0.26	0.26	0.33	0.56	0.27	0.29	0.28	0.35	0.25	0.25	0.24

Table 8: Permissible values as given by WHO

No.	Element	Unit	WHO
1	Iron (Fe)	µgl^{-1}	300
2	Nickel(Ni)	µgl^{-1}	50
3	Zinc(Zn)	µgl^{-1}	5000
4	Selenium(Se)	µgl^{-1}	10
5	Mercury(Hg)	µgl^{-1}	1

due to kind of pipes however, the concentration of zinc in tap-water can be considerably higher than that in surface-water owing to the leaching of zinc from galvanized pipes, brass and zinc-containing fittings. Zinc conc-entrations in tap-water generally vary between 0.01 and 1 mgl^{-1} [24]. The higher concentration in samples No. (11 and 12). In all samples, Zn concentration was below the permissible value (5000 µg.l^{-1}) according to the WHO. It's clear from the table No. (3) that P value less than (5000) i.e that hypothesis No. (2) is accepted and hypothesis No. (1) is rejected, So we can say that relative concentration for Zn ranged from (7.77- 93.99) at level confidence 95%, so the conc-entration of Zn is less than (93.99 µg.l^{-1}).

Selenium occurs in natural waters in trace amounts as a result of geochemical processes, such as weathering of rocks and erosion of soils and is usually present in water as selenate or selenite; however, the elemental form may be carried in suspension [25, 26]. Concentr-ation of Se in all samples are ranged from(>40 –70 µg.l^{-1}) by ICP-AES Table (5), Fig. (8). The higher concentration in samples No. (10 and 11). In the samples No. (1,4,5,8,10 and 11) Se conc-entration was higher than the permissible value (10 µg.l^{-1}) according to the WHO. So it is may be possible that Se has infiltrated to these walls and contributed in elevating Se concentration in these walls. Whereas another samples are below the detection limit of the instrument by ICP-AES. It's clear from the table No. (3) that P value higher than (10) i.e that hypothesis No. (1) is accepted and hypothesis No. (2) is rejected, So we can say that relative concentration for Se ranged from (58.72-107.56) at level confidence 95%, so the concentration of Se is more than (58.72 µg.l^{-1}).

Mercury is toxic element and serves no beneficial physio-logical function in man. A maximum acceptable concen-tration of mercury (1µg/l) in drinking water has therefore been established. The presence of mercury in water has become a source of concern because of the finding that organic mercury is bio concentrated by fish. Concentration of Hg in all samples are below the detection limit of the instrument by ICP-AES table(5) and Fig. (9) and ranged from (0.24-0.56 µg.l^{-1}) by AMA Table (7), Fig. (10). The higher concentration in sample No. (7). In all samples, Hg concentration was below the permissible value (1 µg.l^{-1}) according to the WHO. It's clear from the table No. (4) that P value less than (1) i.e that hypothesis No. (2) is accepted and hypothesis No. (1) is rejected. So we can say that relative concentration for Hg ranged from (0.2569; 0.3503) at level confidence 95%, so the concentration of Hg is less than (0.3503).

CONCLUSION

The high concentration of heavy metals in all samples is shown for Fe, 75 µg.l^{-1} by ICP-AES and 64.20 µg.l^{-1} by GFAA. Ni, 40 µg.l^{-1} by ICP-AES and 20.97 µg.l^{-1} by GFAA. Zn, 180 µg.l^{-1} by ICP-AES and 576.26 µg.l^{-1} by GFAA. Se, 70 µg.l^{-1} by ICP-AES. Hg, in all samples was below the detection limit of the instrument by ICP-AES and 0.56 µg.l^{-1} by AMA, these were given in Tables (5) and (7). In sample No. (11) higher conc-entrations were Ni and Zn, while sample No. 12 higher conc-entrations were Fe and Zn, such high concentrations may be attributed to that water samples No (11 and 12) were obtained from locations near Azzawiya refining. The results indicated that the concentrations of Fe, Ni, Zn and Hg in all the water samples are less than the permissible values with regard to WHO.

While the higher conce-ntration of Se in all samples is shown for 70 µg.l^{-1} by ICP-AES, these are given in Tables (5). The higher concentration of selenium was found in samples No. (1,4,5,8,10 and 11) and another samples are below the detection limit. The concentration of Se in some samples was higher than the WHO permissible values. Results indicated possibly of infiltration which contributed to elevating Se concentration in these walls.

Comparison of used analytical methods: However, there is a close agreement between two techniques in most samples under investigation. In the other hand, there is a difference between the two techniques, The concentrations of the metal ions obtained (AAS) and (ICPES) gave the total metal i.e. total Fe, Ni, Zn, Se and Hg The differences between the two techniques used are mainly due to the manipulation of the AAS or ICPES. It seems that the technician who performed the analysis is not aware about the standard methods of analysis [27] There are some complications arising from the following: Interferences: including chemi-cal interferences, Sensitivity, detection limits and optimum concentration ranges.

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