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DETERMINATION OF BASIC CATIONS AND TRACE METALLS IN SOME WATER SOURCES OF AZERBAIJAN

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The major and trace metal contents of water samples from some water sources of Azerbaijan assessed using an Agilent 7700x ICP-MS system. 45Sc, 72Ge, 103Rh, 115In, 159Tb and 209Bi were chosen as the internal elements and the effect of matrix, interface and fluctuation of instrument was overcome effectively. Collision/reaction technology was used to eliminate the interference of polyatomic ion. Comparison of the all elements contents in all the water sample exception sodium in well water from Calilabad region with EU and WHO limits showed that the mean levels of all the metals were below the maximum permissible levels for drinking water.

Keywords: *trace metal, cations, polyatomic ions concentration.*

INTRODUCTION

Interest in water analysis is due to the enormous importance of water to all categories of living things. It is necessary for the healthy development of man, animals and plants. Drinking water plays an important role in the bodily intake of true element by human. Drinking water from a tap, such as a private well or public water system, is a source of potential exposure to environmental contaminants. Natural contamination of heavy metals usually originates from weathering of minerals, rocks and aquatic environments which result in the entry of heavy metals into water bodies. Disposal of industrial effluents, wastes (domestic and industrial), such as sewage sludge and mining effluents, are other causes of contamination. Many of the metals are retained relatively strongly in the surface water and soil and do not readily leach out – causing accumulation that may ultimately pose a threat to humans, animals, plants and microbes. Concerning the chemical quality of drinking water and health issues, most emphasis has been placed on excessive amounts of various elements.

Furthermore, drinking water may not be available where the people live, and according to tradition women often have to walk for hours to get the daily water ration for a family. The environmental pollution caused by these heavy metals is a long-term and irreversible process. Such metals are not required for routine functioning of the human body and can be toxic even at low concentration. Their toxicity is made by forming complexes with proteins where they contain carboxylic acid (–COOH), amine (–NH) and thiol (–SH) groups. These modified biological molecules lose their proper functions and consequently lead to breakdown or cell death. As heavy metals combine with these groups, they inhibit vital enzymes or may disturb the formation of some proteins necessary for catalytic functions of enzymes. In addition to that some of these heavy metals can incite the production of harmful radicals and result in oxidation of biological molecules.

It should be noted, however, that water-related health problems can also occur due to element deficiencies. Even through some trace elements are essential to man, at elevated levels essential as well as non essential element can cause morphological abnormalities: reduce growth increase mortality and mutagenic effects [1-5]. The toxicity of metals is dependent on their solubility and this in turn depends on pH and on the presence of different types of anions and other cautions. Water pollution has been a subject of active investigation for a long time.

Interest in this has grown because of the perceived hazardous effects of trace element. The major aim of the study was to report on the assessment of the trace metals present in the water sources earmarked for this study.

MATERIALS AND METHODS

Water samples reported here were taken from a small rivers (Ax-ox chay, Girdiman chay), water reservoirs (Khanbulaqchay and Vileshchay), springs (Orand bulaq in Lerik region and Simkend bulaq in Astara region), and horizontal drainage in Yardimli region and drinking water well in the village of Calilabad region. The samples have collected by both the special equipment "DURA BULL” intended for these purposes and hand. After rinsing several times with river water, vessel of this equipment, the samples have collected on 15-20 cm a below from surface of water. A part of samples (approximately 200 ml), after a filtration through membranous the filter pore size 0.45 µm acidified by the concentrated pure nitric acid up to 0.2 % (v/v) of sample were stored at temperature 4^0C for measurement of the dissolved metals. The dissolved metals were defined from samples filtered through membranous the filter pore size 0.45 µm, without preliminary sample preparation. All plastic-ware (sample bottles, pipette tips, filtration unit and flasks were soaked in 10% v/v HNO3 for 24 h and rinsed with ultra pure water before being used. Milli-Q ultra pure water (resistivity 18.2 MΩ cm, pH (5.5–6.5) was used throughout, and all laboratory operations. In the laboratory by adding an appropriate volume of nitric acid the acid concentration of the samples are adjusted to approximate at 1% (v/v) nitric acid solution.

The samples were analyzed for Na, K, Ca, Mg, B, Al, As, Cr, Ni, Se, Sb, Cu, Cd and Pb using an Agilent model 7700x inductively coupled plasma -mass spectrometry. Hg was detected by cold vapor production using SnCl2 (Varian SpectrAA 220FS + VGA-77). Multi-element calibration working standards solutions were prepared by appropriate dilution of from 10 mg /L multi-element stock standard solutions (Part # 8500-6940 and Part # 8500-6948) in 5% HNO3 and 10%HCL/1%HNO_3 correspondingly. The blank and calibration solutions were measured under optimized conditions. The calibration curve was automatically plotted by the instrument. Linear correlation coefficient (r) in all calibration curves were better than 0.9995. Internal standards include Li6, Sc, Ge, Rh, Tb, Lu and Bi were prepared by appropriate dilution from stock ICP-MS Internal Standard Mix Part# 5188-6525 and added on-line at the time of analysis using a second channel of the peristaltic pump. For quality control purposes, duplicate samples, matrix-spike sample and reference material BCR-610 obtained from European Commission Community Bureau of Reference were analyzed.

An Agilent 7700x ICP-MS system was used to measure each sample in helium mode, using standard Agilent-recommended auto tuning for robust tuning conditions (around 1.0 % CeO/Ce). In general, an ICP-MS spectrum consists of a mass/intensity value for each isotope present in the sample. There are only about 240 naturally occurring isotopes of the 100 or so naturally occurring elements, so on average, each element has more than one isotope, but not that many more [6,7]. Complicating the situation somewhat is the fact that there are isobaric overlaps where more than one element can possess an isotope at the same nominal mass. This increases the possible number of isotopes an element can have and reduces the number of interference-free isotopes. A number of elements, including selenium, tin, xenon, barium, and others have as many as eight or more naturally occurring isotopes. And several elements including beryllium, sodium, aluminum, cobalt, arsenic, and about a dozen other less common ones, is mono isotopic, that is, they possess only one naturally occurring isotope. Quantification in ICP-MS is based upon the signal intensity of a unique mass (isotope) for each element. After considering the isobaric overlaps, every naturally occurring element except indium has at least one "unique" isotope — that is, one that is free from direct overlap from another element, and most have more than one. So, in a perfect world, quantification in ICP-MS should be as simple and unambiguous as the spectra themselves. This is, of course, not true, and the reason is that the simple elemental spectra are complicated by spectral interferences from numerous sources, mainly from polyatomic and doubly charged ions.

It is known the He mode is more effective method to remove multiple polyatomic interferences in complex matrices [7]. This mode is not only simpler and more consistent in operation, but it also generates more reliable data for multielement analysis of complex samples under a single set of operating conditions. Standard cell gas flow rates and kinetic energy discrimination (KED) bias voltages were used in this mode.

Instrument parameters

RF Power: 1550 W	S/C Temp: 2 degC
Plasma Gas flow: 15 L/min	Discriminator: 4.5 mV
Carrier Gas flow: 1.05 L/min	Pulse HV: 945 V
Nebulizer Pump: 0.1 rps	Analog HV: 1682 V
Smpl Depth: 8 mm	He Gas flow: 5 mL/min

RESULTS AND DISCUSSION

In the table 1 are given the data of elements concentration received at our measurements in comparison with the certificated data for reference material BCR-610 for ground waters and as it is visible from the table results of our measurement, well conformity with reference values. Recovery obtained from measurement of matrix-spike sample is better than 12%.

The samples were analyzed for Na, K, Ca, Mg, B, Al, As, Cr, Ni, Se, Hg, Sb, Cu, Cd and Pb. The levels of the elements in the water sample are given in table 2. As shown in table 2 observation concentration ranges cover between one and to orders of magnitude and of all elements content exception Na, Mg, As, Al, Cr and Se in water of Vileschay water reservoir greater than other water sources. Relatively high concentration for B, Na, Mg, Cd, Cr and Se has been found in well water sample taken from Calilabad region. High value for concentration arsenic is observed in springs Orandbulaq and in Xanbulaqchay water reservoir. For all water samples low levels for concentration are detected for elements as Cd, Cu, Ni, Sb and Pb. In general, Cd, Hg and Pb were below correspondingly detection limits in samples.

Table 1. Concentration of elements in reference material BCR-610

Element	Al	As	Cd	Cu	Ni	Pb	Na	Ca	Mg
Ref.value ug/L	159	10.8	2.94	45.7	23.3	7.78	51700	72500	32700
Found ug/L	159.1	11.47	3.12	47.2	21.94	7.85	51950	71200	31950
Recovery %	100.0	106.2	106.1	103.3	94.2	100.9	100.5	98.2	97.7

Table 2. Concentration of elements in measured water samples

	Sodium	Potassium	Calcium	Magnesium	Aluminium	Arsenic	Chromium	Nickel	Selenium	Mercury	Antimony	Copper	Cadmium	Lead	Boron
	mg/l	mg/l	mg/l	mg/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l
Baku2	21.3	2.23	76.4	28.9	1.01	0.348	0.612	0.043	1.142	<0.2	0.025	0.035	<0.01	0.012	_
Ax-oxchay	5.2	0.77	53.4	7.9	0.79	0.217	0.216	0.299	0.547	<0.2	0.021	0.151	<0.01	0.012	_
Girdimanchay	39.4	3.61	61.0	23.0	29.51	0.228	0.077	0.726	1.501	<0.2	0.199	0.422	<0.01	<0.01	261
Yar.hor.dren	39.8	2.37	107.0	21.8	0.46	0.914	0.326	0.377	1.55	<0.2	0.109	0.740	<0.01	<0.01	135.7
Lerik spring.	75.6	1.20	72.7	16.9	2.51	2.186	0.182	0.604	<0.5	<0.2	0.107	1.106	<0.01	0.016	263.7
Xanbulaq	11.0	1.20	22.2	5.1	15.6	2.263	0.054	0.499	0.544	<0.2	0.254	0.768	<0.01	0.014	27.18
Vileshchay	98.4	4.80	101.0	12.5	4.11	1.468	0.043	1.495	0.961	<0.2	0.349	1.528	<0.01	0.014	305
Ast.spring	15.5	0.25	17.3	2.1	20.93	1.755	0.366	0.061	<0.5	<0.2	0.142	0.253	<0.01	<0.01	19.01
Well	337.0	2.62	53.6	33.0	3.25	1.002	4.065	0.254	4.348	<0.2	0.039	0.468	0.012	0.015	453
Min	5.2	0.25	17.3	2.1	0.46	0.217	0.043	0.043	<0.5		0.021	0.151	<0.01	<0.01	19.01
Median	39.4	2.23	61.0	16.9	3.3	1.0	0.2	0.4	1.1		0.1	0.5			261.0
Max	337.0	4.80	107.0	33.0	29.51	2.263	4.065	1.495	4.348		0.349	1.528	0.012	0.016	453
Ord	2	1	1	1	2	1	2	2	1		1	1	0	1	1

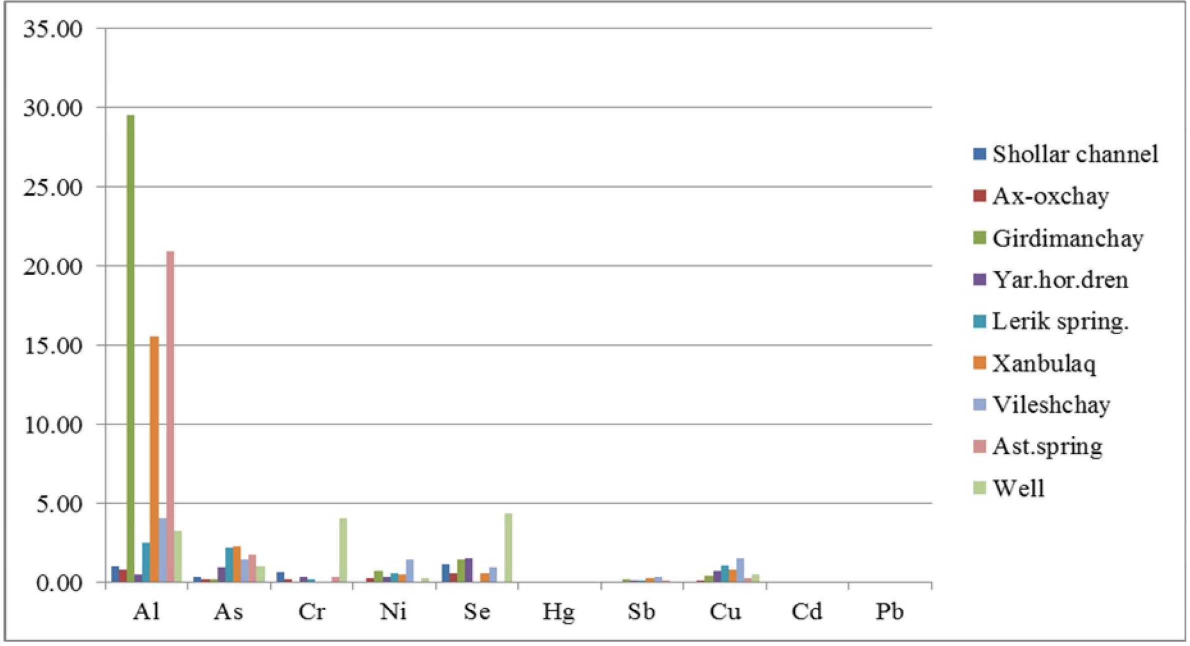
Min.-minimum, Max.-maximum and Ord., orders of magnitude covered by the data log (Max/Min)—a value of half of the detection limit is used for calculation of those elements for which the minimum concentration was below the detection limit (values in bold in the Ord. column).

The distribution diagram of each metal in dependence from water sources are shown in Fig 1. As may be seen from Fig.1 concentrations of elements as As, Cd, Cr, Cu, Hg, Sb, Se and Pb exception only Al, is below than 5μg/L.

A comparison of this study with maximum acceptable concentration for drinking water from other countries and both limits of EU directive (The European Union [8,9] and WHO (World Health Organization-WHO is the directing and coordinating authority for health within the United Nations system is shown in table 3. The directive defines 'surface water status' as the general expression of the status of a body of surface water, determined by the poorer of its ecological status and its chemical status. Thus, to achieve 'good surface water status' both the ecological status and the chemical status of a surface water body need to be at least 'good'. Ecological status refers to the quality of the structure and functioning of aquatic ecosystems of the surface waters.

Water is an important facet of all life and the water framework directive sets standards which ensure the safe access of this resource.) It is responsible for providing leadership on global health matters, shaping the health research agenda, setting norms and standards, articulating evidence-based policy options, providing technical support to countries and monitoring and assessing health trends.).

Fig.1 Distribution of elements in water samples



Maximum acceptable concentrations (MAC) have been established for certain substances that are known or suspected to cause adverse effects on health. Each MAC has been derived to safeguard health assuming lifelong consumption of drinking water containing the substance at that concentration.

Table 3. Comparison of measurement results with water standards

	Unit	Present study	MAC for Norwest	MAC for Canadian	MAC for Ireland	EU directive MAC	WHO MAC
Na	mg/l	5.2-337	200	<200	150	200	
K	mg/l	0.77-4.8			12		
Ca	mg/l	53.4-101			200		
Mg	mg/l	7.9-33			50		
Al	ug/l	0.46-29.5		100		200	
As	ug/l	0.22-1.47	25	25	10	10	10
Cr	ug/l	0.077-4.1	50	50	50	50	50
Ni	ug/l	0.043-1.5			50	20	20
Se	ug/l	0.547-4.35	10	10	10	10	10
Hg	ug/l	<0.2	1.0	1	1	1	1
Sb	ug/l	0.021-0.349		6.0	10	5	5
Cu	ug/l	0.035-1.528	1000		500	2000	2000
Cd	ug/l	<0.01	5.0	5.0	5.0	5.0	3
Pb	ug/l	<0.01-0.016	10	10	50	10	10
B	ug/l	19.01-453		5000	2000	1000	500

Drinking water that continually contains a substance at a level greater than its MAC will contribute significantly to consumers' exposure to the substance and may, in some instances, induce deleterious effects on health. As shown in table 3 in all samples, the mean level all elements exception Sodium in the well water from Calilabad region were below the EU and WHO limits for MAC in drinking water.

CONCLUSION

The research work revealed that the entire water sample meets the EU and WHO limits for both major and trace metals. The results of the present study clearly demonstrated that considered water sources not polluted with As, Cd, Cu, Cr, Hg, Ni, Sb, Se and Pb by human activity. It means that the investigated water sources are not polluted. This study also demonstrates the necessity of documenting natural element concentrations and variation in drinking water resources on a regional scale. However, regular monitoring should be ensured by the authorities concerned.

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AZƏRBAYCANIN BİR SIRA SU MƏNBƏLƏRİNDƏ ƏSAS KATİONLARIN VƏ METAL İZLƏRİNİN TƏYİNİ

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Azərbaycanın bir sıra su mənbələrində əsas kationlar və ağır metal izləri Agilent firmasının 7700x İCP-MS cihazında təyin edilmişdir. 45Sc, 72Ge, 103Rh, 115In, 159Tb və 209Bi daxili standartlar kimi seçilməklə matrisadan, interfeysdən və cihazın fluktasiyasından olan təsirlər effektiv dəf edilmişdir. Çoxatomlu ionlardan irəli gələn interferensiyalar Collision/reaction texnologiyasından istifadə edilməklə aradan götürülmüşdur. Təyin edilmiş bütün elementlərin miqdarının içməli su üçün Aİ və ÜST direktivlərindən irəli gələn maksimium yol verilə bilən hədlə müqayisəsi göstərir ki, Cəlilabad rayonundan götürülmüş quyu suyundakı natriumun miqdarı istisna olmaqla yerdə qalan bütün elementlərin konsentrasiyaları bu həddən kiçikdir.

Açar sözlər: *ağır metallar, kationlar, çoxatomlu ionlar, qatılıq.*

ОПРЕДЕЛЕНИЕ ОСНОВНЫХ КАТИОНОВ И СЛЕДОВ ЭЛЕМЕНТОВ В НЕКОТОРЫХ ВОДНЫХ ИСТОЧНИКАХ АЗЕРБАЙДЖАНА

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Следы тяжелых металлов и основных катионов определены на приборе ИСП-МС модель 7700 x фирмы Agilent. 45Sc, 72Ge, 103Rh, 115In, 159Tb и 209Bi изотопы были избраны как внутренние стандарты и эффекты, связанные с матрицей, интерфейсом и флуктуацией прибора были преодолены. С использованием Collision/reaction технологии была исключена интерференция от многоатомных ионов. Сравнение концентраций определяемых элементов с максимально допустимыми нормами, констатированными в директивах ЕС и ВОЗ для питьевых вод, показало, что в субартезианской воде Джалилабадского района за исключением натрия, содержание остальных элементов не превышает допустимые нормы.

Ключевые слова: *тяжелые металлы, катионы, многоатомные ионы, концентрация.*

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