

Trace Metals in Water Samples Taken from Azerbaijan Sector of Caspian Sea

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Abstract: The present study was conducted to investigate the heavy metal contents (As, Ba, Cd, Co, Cr, Cu, Ga, Mo, Mn, Rb, Pb, Cu, Ni, V, U and Zn) in seawater samples, which were collected at two c (5 and 100 m), from 9 different sites of Azerbaijan sector of the Caspian Sea. The Agilent 7700x Series ICP-MS (inductively coupled plasma mass spectrometry) with HMI (high matrix introduction) system applied to analysis seawater. It was shown, the average concentrations of elements as Cr, Co, Cu, Mn, Pb and Zn in surface water slightly higher than their concentrations in depth water at 100 m. Practically it is not deference of the Mo, Rb and U average concentrations of As, Ga and Ba in samples taken from 100 m, were significantly higher than the concentration in surface samples. Dependence concentration of elements from water columns depth can be explained in accordance with the geochemical system of classification of dissolved forms of elements in the sea water.

Key words: Heavy metals, Caspian Sea, ICP-MS, polution.

1. Introduction

The Caspian Sea is the largest lake on our planet. It is bigger than the Great American lakes and Lake Victoria in Africa by surface area. However, it is unique not only because of its size. As distinct from other lakes, the water of the Caspian Sea is not fresh, but brackish. Each liter of Caspian water contains 10-13 g of salt making this water unsuitable for drinking or irrigation. However, the comparison of the Caspian water to oceanic water shows that it contains three times less salt than that of the World Ocean. Physically, the Caspian Sea is one of extremes. Its salinity varies greatly. Morphologically, the Sea is divided into three parts, the northern shallow part (average depth 6 m), the middle section with an average depth of 190 m (maximum depth 788 m), and the southern Caspian with a maximum depth of 1,025 m. The Caspian Sea occupies a deep depression on the boundary between Asia and Europe with a water level at present 27 m below sea level. It is approximately 1,200 km long with a maximum breadth of 466 km, contains 79,000 km³ of water, and has a total coastline of more than 7,000 km. The Caspian is fed by five major rivers or river groups: in the north the Volga (80% of total inflow) and the Ural (5%); in the west the Terek, Sulak, Samur (4-5%) and the Kura (7-8%); and, in the south, the short mountain rivers from the Iranian Alborz range (4-5%). Azerbaijan has more than 800 km of coastline along the Caspian Sea and almost the entire country is part of the Sea's catchment area. The littoral states of the Caspian Sea are the Republic of Azerbaijan, the Islamic Republic of Iran, the Republic of Kazakhstan, the Russian Federation and Turkmenistan [1-3].

Environmental problems of the Caspian Sea are multiple and various in their origin. On one hand, they are caused by the commercial use of the sea; on the other hand, human activity impacts coastal areas, including input from rivers in the Caspian. As the Caspian is an inland water body, anthropogenic (man-caused) impacts on catchment area (about 3.5 million km²) accumulate here. Anthropogenic impact on the Caspian ecosystem occurs concurrently with

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various natural endogenous and exogenous processes. It is primarily sea level changes, periodical seismic activity, surges and retreats, mud volcanoes and neo-tectonics. Special features of the Caspian include constant alterations of its area, volume, and configuration of the coastline and water column structure. Anthropogenic activity, as well as a natural impact, can have a chronic (long term) or acute (short term) effect. The sources of pollution are industrial, agricultural and accidental discharges and sewage. The main sources of pollution to the Caspian Sea have generally been considered to be offshore oil production and land-based sources, notably the Volga River. The presence of oil in the Caspian Sea region has been known since ancient times and the oil reserves were amongst the first to be exploited in the world. Baku was a centre for oil production at the turn the 20th century and developed further of development during the era of the Soviet Union. Exploration and exploitation, especially of offshore reserves, have blossomed since the break-up of the Soviet Union. Public opinion polls in the region have highlighted concerns about the oil and gas industry as a source of pollution to the environment of the Caspian Sea. Oil production areas cover vast areas of the coastal zone, particularly along the south coast of the Apsheron peninsula in Azerbaijan. Population growth and industrial development in the Caspian region have generated an immense pollution problem. Ten million people live adjacent to the Caspian Sea and 60 million more live in the Volga River watershed. The World Bank estimates that one million cubic meters of untreated industrial wastewater is discharged into the Caspian annually. Soviet oil extraction left behind polluted soil and water, rusty

equipment, and well fires that burned for years. Meanwhile, the five countries surrounding the sea are rushing to exploit still untapped oil deposits.

Since the Caspian is an enclosed body of water, it has limited carrying capacity compared to larger and more open bodies of water. Pollution entering to the Caspian is either biogeochemically altered, or remains in the Sea for years; none escapes and dilution is limited from external buffering waters. In the former Soviet Union. water and sediment quality measurements were taken on a regular basis and with good coverage. In Azerbaijan, the situation reported to be changing, and the number of monitoring surveys has increased. Within the current situation, over the same period the flux of pollutants into the Caspian has changed, with a drastic reduction in industrial and agricultural activity in Turkmenistan, Kazakhstan, the Russian Federation and Azerbaijan [4-6].

The present study was conducted to investigate the heavy metal contents (As, Ba, Cd, Co, Cr, Cu, Ga, Mo, Mn, Rb, Pb, Cu, Ni, V, U and Zn) of seawater the Caspian sea were collected from 9 different sites in Azerbaijan region as shown in Table 1.

It is known the analysis of ultra trace elements in sea water samples is one of the most difficult analytical tasks in the field of environmental monitoring, as extremely low detection limits for elements buried in a highly saline matrix is required. The use of ICP-MS (inductively coupled plasma mass spectrometry) for direct sea water analysis is currently limited by spectral and non-spectral interferences caused by the sea water matrix. Although the technique of ICP-MS is very powerful by virtue of its sensitivity and selectivity, one of the operational limitations is that of the total amount of dissolved

 Table 1
 The geographical coordinates of sampling stations.

Station No.	Easting	Northing	Station No.	Easting	Northing	
St.1	411,348	4,378,000	St.6	520,428	4,438,465	
St.2	506,110	4,456,694	St.7	524,875	4,440,258	
St.3	506,927	4,443,481	St.8	529,128	4,433,186	
St.4	515,426	4,443,978	St.9	538,557	4,431,453	
St.5	519,131	4,434,107				

Isotope	Cl	Ca	Na	Κ	Ar
V ⁵¹	ClO				
Cr ⁵²	ClOH				ArC
Cr ⁵³	Cl ³⁷ O				
Mn ⁵⁵			Na ₂ O	K ³⁹ O	ArNH
Fe ⁵⁶		CaO		КОН	ArO
Fe ⁵⁷		СаОН			ArOH
Ni ⁵⁸		Ca ⁴² O			
Co ⁵⁹		Ca ⁴³ O, Ca ⁴² OH			
Ni ⁶⁰		Ca ⁴⁴ O, Ca ⁴³ OH			
Cu ⁶³			NaAr		
Zn ⁶⁴		Ca ⁴⁵ O			
Cu ⁶⁵		Ca ⁴⁵ OH			
Zn ⁶⁷	ClO ₂				
As ⁷⁵	ArCl				

 Table 2
 Major interferences of alkali and alkaline earth adduct ions on transition metal isotopes in a typical seawater matrix.

solids which may be introduced into the system. This limitation comes about in part because samples may deposit condensate on the sampler cones over a prolonged analytical run causing signal changes and hence degrading the signal stability. The effect of such higher levels of dissolved salts may also be to cause polyatomic interferences on key target analyte elements. Table 2 indicates the extent of these interfering ion species.

One particular example of this effect is in the determination of trace elements in heavier environmental samples such as seawater and borehole waters. In particular, the effects of oxide/hydroxide adduct ions of alkali and alkaline earth elements, common constituents in such natural samples, can effectively mask the determinations of most transition elements [7-11]. Pre-concentration techniques such as solvent extraction, ion exchange and carrier precipitation have been extensively studied with reference to sea water analysis [12, 13].

To avoid this problems the Agilent 7700x Series ICP-MS applied to analysis seawater. The Agilent 7700x ICP-MS combines the simplicity of a single collision cell mode (helium mode) for polyatomic interference removal with the superior matrix tolerance of its unique HMI (high matrix introduction) system. In order to reduce salt deposition in the

nebulizer the humidifier is used. The humidifier humidifies the carrier gas and reduces salt deposition in the nebulizer. Third generation ORS3 (octopole reaction system) cell technology provides higher sensitivity and more effective interference removal than ever before in complex, high matrix samples, eliminating the need for reactive cell gases in routine analysis. Helium mode on the ORS3 is so effective that interference correction equations can also be eliminated. These two factors redefine ease of use in ICP-MS, removing two of the most common causes of errors in multi-element analysis of complex samples.

2. Materials and Methods

Water samples, collected from surface and bottom seawater layer with a 12-liter PVC Niskin sampler equipped with a Teflon-coated spring, suspended from stainless steel hydro wire and allowed to flush for 5 min before closing, in acid cleaned polythene containers, packed and transported in ice-box for analysis. Surface samples were collected from all sites a depth not exceeding 5 m, whereas bottom samples were collected from 9 sites a depth 100 m.

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 used. Milli-Q ultra pure water (resistivity 18.2 MQ/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.

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).Agilent's new HMI accessory for the 7700x and 7700s ICP-MS systems permits the direct analysis of samples containing percent level dissolved solids including neat seawater without prior dilution. The HMI accessory uses a combination of highly optimized robust plasma conditions and a technique termed "aerosol dilution". The net effect is a reduction in the amount of sample and solvent reaching the plasma and MS (mass spectrometer) interface of up to 30 times compared to a standard system. This reduction leads to higher plasma temperature, reduced suppression, improved stability and significantly lowers oxides.

The samples were analyzed for As, Ba, Cd, Co, Cr, Cu, Ga, Mo, Mn, Rb, Pb, Cu, Ni, V, U and Zn using an Agilent model 7700x ICP-MS. Multi-element calibration working standards solutions were prepared dilution of from 10 appropriate mg/L bv multi-element stock standard solutions - (Part# 8500-6940 in 5% HNO₃) in 1% HNO₃ 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. Instrument drift and matrix effects during measurement were corrected by using the internal standards include Sc, Ge, Rh, In, Tb 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 were analyzed. 7700x ICP-MS

operating condition used for He mode, which is shown in Table 3.

3. Results and Discussion

Certified Reference Seawater Probe CASS-5 of the Institute for Environmental Chemistry, Canada, were included to analysis directly after a simple 1+2 dilution with 1% nitric acid, as quality control samples to ensure the accuracy of the results. The percentage recovery of Vanadium 107.1%, Chromium was 107.5%, Manganese was 100.3%, Cobalt was 94.3%, Nickel was 97.6%, Copper was 95.7%, Zinc was 101.9%, Arsenic was 109.1%, Molybdenum was 104.5% and Uranium was 96.9%. The result of analysis indicated good recoveries of all determined metals with exception only Lead. After three time dilution, the observed concentration for lead was less than MDL (method detection limit), therefore it was not possible to measure exact concentration for this element.

The values and ranges of element concentrations in the water samples taken from the surface 5 m depth are presented in Table 4. The concentrations of the analyzed elements in Caspian Sea surface water were as following: As: ranged between 1.431-1.607 ug/L, average concentration-1.511 ug/L, Ba: ranged between 8.980-13.211 ug/L, average concentration-11.036 ug/L, Co: ranged between 0.032-0.060 ug/L, average concentration-0.042 ug/L, Cr: ranged between 0.139-0.502 ug/L, average concentration—0.277 ug/L, Cu: ranged between 0.696-1.0190 ug/L, average concentration-0.811 ug/L,

 Table 3 Operating condition used for He mode.

Operating condition	Mode
RF power	1,600 W
Plasma gas flow	15 L/min
Carrier gas flow	0.6 L/min
Nebulizer pump	0.1 rps
Smp. depth	8 mm
Dilution gas flow	0.4 L/min
S/C temp	2 degC
Pulse HV	1,045 V
Analog HV	1,682 V
He gas flow	5 mL/min

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	V	Cr	Mn	Co	Ni	Cu	Zn	As	Pb	Мо	U	
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	
Results of analyses	1.41	0.11	2.63	0.09	0.32	0.36	0.73	1.35	< 0.01	10.86	3.08	
Refence value	1.32	0.11	2.62	0.10	0.33	0.38	0.72	1.24	0.011	9.82	3.18	
Recovery (%)	107.14	107.55	100.27	94.33	97.61	95.73	101.85	109.08		110.59	96.86	

 Table 4
 Analytical performance based on reference seawater (ug/L).

Table 5 The concentrations of the analyzed elements in surface water (from 5 m depth).

	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	As	Rb	Мо	Ва	Pb	U
5 m	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L								
St1	0.788	0.139	0.482	0.035	1.013	0.852	1.832	0.996	1.475	8.17	16.87	10.06	0.057	6.32
St2	0.723	0.182	0.279	0.038	0.850	0.773	0.668	0.673	1.494	8.27	17.45	11.15	0.168	6.13
St3	0.857	0.164	0.295	0.032	0.883	0.696	0.714	0.843	1.431	8.33	16.94	8.98	0.138	6.69
St4	0.761	0.170	0.385	0.060	0.827	0.771	1.223	0.896	1.567	8.40	16.88	10.77	0.186	6.04
St5	0.780	0.247	0.547	0.052	0.964	1.090	1.959	1.210	1.474	8.57	16.75	13.21	0.212	6.52
St6	0.769	0.221	0.349	0.042	0.916	0.767	0.932	1.147	1.607	8.11	16.92	12.32	0.361	6.18
St7	0.706	0.394	0.284	0.034	0.930	0.750	0.762	0.933	1.454	8.30	16.97	11.08	0.139	6.08
St8	0.799	0.474	0.483	0.034	0.941	0.814	2.052	1.111	1.561	8.52	16.91	11.60	0.323	6.25
St9	0.770	0.502	0.286	0.046	0.870	0.784	2.361	0.902	1.532	8.42	17.46	10.15	0.589	6.27
Mean	0.773	0.277	0.377	0.042	0.911	0.811	1.389	0.968	1.511	8.34	17.02	11.04	0.242	6.27
Min	0.706	0.139	0.279	0.032	0.827	0.696	0.668	0.673	1.431	8.11	16.75	8.98	0.057	6.04
Max	0.857	0.502	0.547	0.060	1.013	1.090	2.361	1.210	1.607	8.57	17.46	13.21	0.589	6.69
Stdev	0.044	0.141	0.103	0.010	0.059	0.113	0.662	0.168	0.059	0.15	0.26	1.26	0.160	0.21

Mn: ranged between 0.279-0.547 ug/L, average concentration-0.377 ug/L, Mo: ranged between 16.754-17.460 ug/L, average concentration-17.018, Ni: ranged between 0.827-1.013 ug/L, average concentration-0.911 ug/L, Ga: ranged between 0.673-1.210 ug/L, average concentration-0.968 ug/L, Pb: ranged between 0.057-0.589 ug/L, average concentration -0.242 ug/L, U: ranged between 6.038-6.686 ug/L, average concentration - 6.275 ug/L, V: ranged between 0.706-0.857. average concentration-0.773 ug/L and Zn: ranged between 0.668-2.361 ug/L, average concentration-1.389 ug/L respectively (Table 5).

The concentrations of the analyzed elements in Caspian seawater column depth 100 m were as following: As: ranged between 2.509-3.078 ug/L, average concentration 2.721 ug/L, Ba: ranged between 25.294-32.388 ug/L, average concentration—28.459 ug/L, Co: ranged between 0.030-0.051 ug/L, average concentration—0.036 ug/L, Cr: ranged between

0.147-0.525 ug/L, average concentration—0.260 ug/L, Cu: ranged between 0.638-0.842 ug/L, average concentration-0.745 ug/L, Mn: ranged between 0.0242-0.666 ug/L, average concentration-0.0.360 ug/L, Mo: ranged between 16.68417.361 ug/L, average concentration-16.991 ug/L, Ni: ranged between 0.874-0.970 ug/L, average concentration-0.929 ug/L, Ga: ranged between 2.575–3.029 ug/L, average concentration—2.753, Pb: ranged between 0.068-0.589 ug/L, average concentration-0.198 ug/L, U: ranged between 6.080-6.714 ug/L, average concentration—6.333 ug/L, V: ranged between 0.862-1.007 ug/L, average concentration-0.951 ug/L and Zn: ranged between 0.782-1.985 ug/L, average concentration—1.246 ug/L respectively (Table 6).

The average concentrations of elements as Co, Cr, Cu, Mn, Zn and Pb in surface water slightly higher than their concentrations in depth water at 100 m. There was little variation in Nickel concentrations, with average concentration of 0.911 ug/L in surface water and 0.929 ug/L at 100 m. Comparatively higher vanadium average concentration was found in the samples taken at 100 m with than those concentration surface samples. In contrast the concentrations of As, Ga and Ba in samples taken from 100 m, were significantly higher than the concentration in surface samples. Practically it is not deference of the Mo, Rb and U average concentrations in surface and 100 m depth column water.

In Table 7, are compared the mean concentraions of microelements in Caspian Sea (in 100 m depth) with they mean concentration in the World Ocean.

As can be seen from Table 7 the difference of mean concentrations of As, Ba, Cr,Cu and Mn in Caspian Sea water from those concentrations in World Ocean are insignificantly. The level concentrations of Ga, Mo, Pb and U in Caspian Sea water higher than those levels in World Ocean Sea water. In contrast the concentrations of Ni, V, Co and Rb water are lower in Caspian Sea relative to those in the oceanic water. In the view that are still not possible to explain the differences the distribution of element concentrations observed in the waters of the Caspian Sea and the World Ocean precious. For this, it is necessary to conduct large-scale surveys doubt in the littoral states of the Caspian Sea.

The aurhors understand that the comparison of concentration determined metals, reported for Caspian Sea by different papers are difficult because of different methods for sampling, sample preparation and determination were used.

In accordance with the geochemical system of classification of dissolved forms of elements in the sea water [14, 15], the microelements in Tables 5 and 6 are subdivded into conservative (Mo, Rb and U), biogenic (V, Cr, Ni, Zn, Ga, As and Ba) and lithogenic (Mn, Co, Cu and Pb).

Table 6 The concentrations of the analyzed elements in Caspian seawater column depth 100 m.

	V	Cr	Mn	Со	Ni	Cu	Zn	Ga	As	Rb	Мо	Ва	Pb	U
100 m	ug/L													
St1	0.944	0.163	0.500	0.031	0.939	0.723	1.122	2.789	2.726	8.85	16.94	26.69	0.068	6.28
St2	0.959	0.195	0.666	0.051	0.970	0.825	0.930	2.803	2.908	8.08	17.01	29.86	0.211	6.12
St3	1.007	0.147	0.248	0.033	0.933	0.638	0.782	2.575	2.509	8.40	17.12	25.29	0.078	6.71
St4	0.979	0.383	0.287	0.030	0.932	0.842	1.293	3.029	3.078	8.41	16.68	32.39	0.147	6.10
St5	0.990	0.321	0.309	0.033	0.910	0.785	1.985	2.752	2.589	8.15	16.99	27.77	0.147	6.66
St6	0.928	0.263	0.324	0.032	0.960	0.675	0.806	2.856	2.703	8.00	16.68	31.89	0.348	6.08
St7	0.862	0.525	0.242	0.044	0.896	0.747	0.851	2.669	2.772	8.40	17.36	28.20	0.146	6.24
St8	0.928	0.168	0.371	0.032	0.874	0.753	1.553	2.656	2.629	8.68	16.82	26.81	0.119	6.51
St9	0.963	0.171	0.294	0.039	0.948	0.720	1.895	2.653	2.578	8.17	17.31	27.24	0.513	6.29
Average	0.951	0.260	0.360	0.036	0.929	0.745	1.246	2.753	2.721	8.35	16.99	28.46	0.198	6.33
Min	0.862	0.147	0.242	0.030	0.874	0.638	0.782	2.575	2.509	8.00	16.68	25.29	0.068	6.08
Max	1.007	0.525	0.666	0.051	0.970	0.842	1.985	3.029	3.078	8.85	17.36	32.39	0.513	6.71
Stdev	0.043	0.128	0.139	0.007	0.031	0.066	0.467	0.136	0.179	0.284	0.245	2.426	0.145	0.239

 Table 7 Comparision of the mean concentraions of microelements in Caspian Sea (in 100 m depth) with they mean concentration in the World Ocean.

	As	Ba	Cr	Со	Cu	Ga	Мо	Mn	Ni	Rb	Pb	U	V	Zn
	ug/L	ug/L	ug/L	ug/L										
World Ocean (mean)	2.60	21.0	0.20	0.39	0.90	0.03	10.0	0.40	6.60	120	0.03	3.30	1.90	5.00
Caspian Sea (100 m depth)	2.72	28.5	0.26	0.04	0.75	2.75	17.0	0.36	0.93	8.35	0.198	6.33	0.95	1.25

Conservative-type trace metals interact only weakly with particles, and have concentrations that maintain a relatively constant (in space and time) ratio to salinity. Trace metals with conservative-type distributions in seawater such as Molybdenum, Rubidium and Uranium are involved in the major biogeochemical cycles of particle formation and destruction, but this is negligible relative to their concentration in seawater.

Trace metals with biogenic-type distributions are significantly involved with the internal cycles of biologically derived particulate material. Their distributions are dominated by the internal cycle of assimilation by plankton in surface waters and the export production or transport of part of this material out of the surface layer followed by oxidation and remineralization of the bulk of this material in deeper waters. Consequently, their concentrations are lowest in surface waters where they are assimilated by phytoplankton and/or adsorbed by biogenic particles, and increase in the subsurface waters as sinking particles undergo decomposition or dissolution.

Trace metals with lithogenic-type distributions have strong interactions with particles. Their concentrations tend to be maximal near major sources such as rivers, atmospheric dust, bottom sediments, and hydrothermal vents. Concentrations decrease with distance from the sources and, in general, the concentrations of the scavenged metals tend to decrease along the flow path of deep water due to continual particle scavenging [16, 17].

4. Conclusions

This research study was attempt, which covered near Baku Gulf surveyed areas of Caspian Sea. The Agilent 7700x ICP-MS combines the simplicity of a single collision cell mode (helium mode) for polyatomic interference removal with the superior matrix tolerance of its unique HMI system. Third generation ORS3 cell technology provides higher sensitivity and more effective interference removal than ever before in complex, high matrix samples, eliminating the need for reactive cell gases in routine analysis. These two factors redefine ease of use in ICP-MS direct determination of those trace metals in sea water samples. Certified Reference Seawater Probe CASS-5 of the Institute for Environmental Chemistry, Canada, were included in analysis directly after a simple 1+2 dilution with 1% nitric acid, as quality control samples to ensure the accuracy of the results.

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