Measurements of natural uranium concentration in Caspian Sea and Persian Gulf water by laser flourimetric method

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Background: Natural uranium exists in earth crust and seawater. The concentration of uranium might increase by human manipulation or geological changes. The aim of this study was to verify susceptibility of laser flourimetry method to determine the uranium concentration in Caspian Sea and Persian Gulf water. Materials and Methods: Laser flourimetric method was used to determine the uranium concentration in several samples prepared from Caspian Sea and Persian Gulf water. Biological and chemical substances were eliminated in samples for better evaluation of the method. Results: As the concentration of natural uranium in samples increases, the response of instrument (uranium analyzer) increases accordingly. The standard deviation also increased slightly and gradually. Conclusion: Results indicate that the laser flourimetry method show a reliable and accurate response with uranium concentration up to 100 µg/L in samples after removal of biological and organic substances. Iran. J. Radiat. Res., 2005; 3 (3): 123-127

Keywords: Uranium, laser flourimetry, Caspian sea, Pearsian Gulf water.

INTRODUCTION

Natural uranium exists in earth crust and in seawater with a higher concentration in seawater. Uranium is a naturally occurring element with an average abundance in the earth crust of about 2 mg per kg (range 0.1 to 20 mg per kg). It is more abundant than silver or gold. It has adverse effects on the human health. The major health effect of uranium is its chemical toxicity, rather than its radiological hazard(1-4). The chemical toxicity was thought to be similar to lead. The maximum contaminant level (MCL) of uranium was determined to be about 30 μg/L by U.S Environmental Protection Agency (EPA)(5). Natural uranium is a mixture of three isotopes. They have long half-lives that allow them to be transported to water supplies. Uranium 238 with a half life (t1/2) of 4.5×10^9 vears (99.285% natural abundance), uranium 235 with a half life of 7.04×10^8 years (0.71%) natural abundance), and uranium 234 with a half life of 2.24×10⁵ years (0.0053% natural abundance) are naturally occurring isotopes emitting alpha (α) radiation⁽⁶⁾. Thus, natural abundances of isotopes and the half-lives give 0.33, 0.015 and 0.33 pCi/µg (12.2, 0.6, and 12.2 mBq/µg) of natural uranium for U-238, U-235, and U-234, respectively, or 0.68 pCi/µg (25mBq/µg) totals⁽⁷⁾. The groups of uranium isotopes are found in the earth's crust with an abundance of 4×10^{-4} %⁽⁸⁾ and are found in rocks and minerals such as granite. metamorphic rocks monazite sand, and phosphate deposits as well as in uranium minerals such as uraninite, carnotite and pitchblende⁽⁹⁾. All these sources can come in contact with water that may change the uranium concentration in the sea water. It is also a trace element in coal, peat, and asphalt and is present in some phosphate fertilizers at a level of about 100 µg/g or 67pCi/g (2.5Bq/g)⁽⁷⁾. Despite its widespread abundance, uranium has not been shown to be an essential element for human⁽⁸⁾. There has been reported that the activity of natural water from U-234 is higher than U-238. The U-234/U-238 activity ratio usually ranges between 1 and 3 (10, 11). According to the most recent reports fixed mass ratio and fixed activity ratio are still used natural uranium. Isotopic composition of natural uranium activities are 48.9%, 2.2%, and 48.9% (6, 12). The best-known use of uranium is as a fuel in nuclear power

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reactors. It is also used in inertial guidance devices, gyro compasses, as a counter weight for missile reentry vehicles, as shielding material, and as X-ray targets(13). Uranium may be found chemically in valence states +2, +3, +4, +5, +6, the most common being the hexavalent and tetravalent states. The hexavalent state is the most important of all in water; because, almost all tetravalent compounds are practically insoluble⁽¹⁴⁾. Many large rivers in the Northern part of Iran end up to the Caspian Sea, thus it may changes to natural concentration.

In this study, the concentration of natural uranium in Caspian Sea and Persian Gulf water was determined by laser flourimetry instrument (uranium analyzer) provided by IAEA with addition of certain amount of uranium standard to the samples. Chemical treatment of the samples could reduce interference of organic substances.

MATERIALS AND METHODS

Sampling locations

Water samples were collected from six locations of 10 to 12 meter depth, within 15 km from west to east coast of Caspian Sea. The mean concentration of natural uranium in Caspian Sea water of Iran, measured in a previous study was $7.2 \pm 0.5~\mu g/L~(ppb)^{(15)}$. Three samples from Persian Gulf, near Bandar Abbas, were selected to have an average concentration measurement. One sample from the coast near Ramsar city (Caspian Sea) and one from Persian Gulf were chosen for the experiments. The pH of samples was brought to 1 for preservation.

Sample preparation and analysis

The organic substances existing both in Caspian Sea and Persian Gulf can affect the response of the laser flourimetry instrument. The measured amount of salt in Caspian Sea and Persian Gulf water were about 10 and 40 gram per liter, respectively. Direct method for natural uranium measurement (without Chemical treatment) was impossible without dilution for Persian Gulf water and 40 times dilution may be needed to make the

measurement possible. The result showed lower laser flourimetry instrument response up to 20%.

Several sample sets of Caspian Sea and Persian Gulf water (7×3) were prepared and their concentrations were increased by 0, 2, 5, 10, 20, 50, and 100 μg/L of uranium standard. Simple chemical treatments of the samples for removal of organic substances and fluorescence measurement of natural uranium in final solutions, by standard addition method were carried out according to procedure recommended by the instrument manufacturer and were analyzed for natural uranium contents by laser-induced flourimetry technique, using Scintrex UA-3 uranium analyzer⁽¹⁶⁾. Using laser flourimetry instrument and with chemical treatments, the concentration of uranium from 0.05 µg/L up to 100 µg/L (ppb) can be measured without any dilution. To do so, the measurements were done for each set of samples and the mean of the results was calculated. The chemical samples treatment, that is removal of organic substances, was carried out by addition of natural uranium standard manually to 36 Caspian Sea and Persian Gulf water samples with a volume of 5 milliliters. The uranium concentrations of these samples were determined by uranium analyzer and the means of the results were calculated.

RESULTS AND DISCUSSION

The measured concentration of natural uranium in Caspian Sea water was $6.12\pm0.18~\mu\text{g/L}$ in comparison with the average concentration measured previously as $7.2\pm0.5~\mu\text{g/L}$ from six different locations⁽¹⁵⁾. Treatment and analysis of seven samples showed the concentration of natural uranium in distilled water range from 0.02 to $0.03~\mu\text{g/L}$.

The results of measurements of natural uranium concentration in Caspian Sea water after addition of natural uranium standard is summarized in table 1 and shown in figure 1. Figure 2 shows mean natural uranium concentration in Caspian Sea water (6.12 \pm 0.18 µg/L) and the concentrations of uranium in Caspian Sea water with addition of natural uranium standard versus standard deviation. As seen, the response of laser

Caspian Seawater	Result of measurements (µg/L)			Mean (μg/L)	Std. D (µg/L)	Actual Concentration
	1	2	3		\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	(µg/L)
0 ppb Added	6.27	5.93	6.16	6.12	0.178	6.12
2 ppb Added	7.87	7.34	7.17	7.46	0.365	8.12
5 ppb Added	10.34	10.68	11.60	10.87	0.652	11.12
10 ppb Added	14.28	13.91	15.21	14.47	0.673	16.12
15 ppb Added	20.22	19.92	18.24	19.46	1.067	21.12
20 ppb Added	28.99	26.92	26.47	27.46	1.344	26.12

53.71

107.60

51.29

103.52

2.711

6.307

56.12

106.12

51.79

106.70

48.36

96.26

Table 1. The results of measurements of natural uranium concentration in Caspian Seawater after addition of natural uranium standard with their standard deviation.

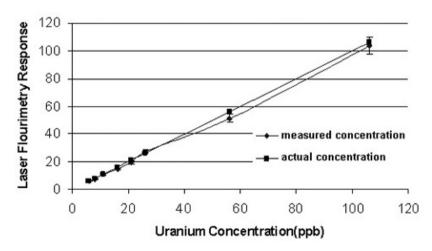
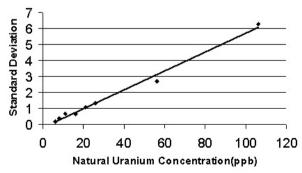


Figure 1. Mean natural uranium concentration in Caspian Seawater versus instrument response.



50 ppb Added

100 ppb Added

Figure 2. Natural uranium concentration in Caspian Seawater versus standard deviation.

flourimetry increases with the mean natural ranium concentration in Caspian Sea water.

Average concentration of the Persian Gulf water is measured to be $3.53 \pm 0.1 \mu g/L$ using

three samples. Previously reported concentration of natural uranium in coastal sea water was 3 $\mu g/L^{(17)}.$ The results of measurements of natural uranium concentration in Persian Gulf water after addition of natural uranium standard is summarized in table 2 and shown in figure 3.

Figure 4 shows the mean natural uranium concentration in Persian Gulf water and the concentration of uranium standard in Persian Gulf water as uranium manually increased versus standard deviation.

The concentration of natural uranium measured are as low as 0.02-0.03 $\mu g/L$ in distilled water that is higher than only two approved methods by EPA. Thus, the

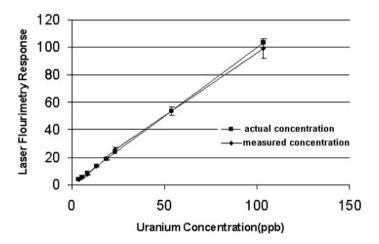


Figure 3. Mean natural uranium concentration in Persian Gulf water versus instrument response.

Table 2. The results for measurements of natural uranium concentration in Persian Gulf water with addition of natural uranium standard and their standard deviation.

Persian Gulf Seawater	Result of measurements $(\mu g/L)$			Mean (μg/L)	Std. D (µg/L)	Actual Concentration
	1	2	3	, o 1	(μβ/11/	(µg/L)
0 ppb Added	3.62	3.57	3.41	3.53	0.11	3.53
2 ppb Added	5.21	5.26	5.44	5.30	0.13	5.53
5 ppb Added	7.26	6.84	7.74	7.28	0.45	8.53
10 ppb Added	12.67	13.50	13.68	13.46	0.54	13.29
15 ppb Added	19.61	17.65	20.7	19.11	1.28	18.53
20 ppb Added	25.42	27.27	24.71	25.80	1.32	23.53
50 ppb Added	52.14	57.35	51.47	53.65	3.22	53.53
100 ppb Added	92.31	99.25	105.97	99.18	6.83	103.53

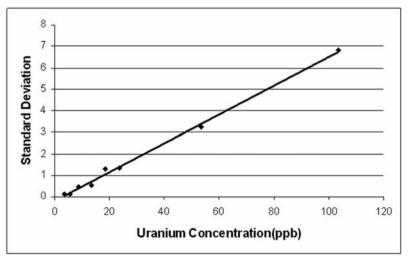


Figure 4. Standard deviation versus natural uranium concentration in Persian Gulf Sea water.

concentration in distilled water is very low and can be negligible for all measured samples^(5, 16). Measured natural uranium concentrations in Caspian Sea water can be compared to the actual values. As seen, the mean concentration of all samples; where natural uranium standard was manually added before the chemical treatment, is close to the actual values. In figure 1, the measured values, can be compared to the actual values. Also in figure 2, it can be seen the standard deviation increases gradually and its increase at 100 µg/L (ppb) is not very large (6.31) and is acceptable. Similar results were obtained for Persian Gulf water (figures 3 and 4).

It is verified that increases of natural uranium in Caspian Sea and Persian Gulf water samples cannot cause lower response of laser flourimetry instrument using the method of removal of biological and organic substances. The results show a linear increase as concentration increases versus instrument response (figures 1 and 3). Also, results indicate that as the concentration of natural uranium in water samples increases, the efficiency of procedure and instrument dose not decrease and remains constant. The response of laser flourimetry instrument increased properly and the existence of biological and organic materials in the samples, while chemically treated, did not affect response of the instrument. In conclusion, the results indicate that the laser flourimetry response is reliable and accurate for uranium concentrations up to 100 µg/L in water samples obtained from Caspian Sea and Persian Gulf. More research should be carried out to verify the accuracy of laser flourimetry method for samples obtained from other locations of Caspian Sea and Persian Gulf water with different and higher concentrations of biological and organic substances.

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