# Identification of Heavy Metals from Ten Watering Campuses (Ground Waters) of Ilam-Iran

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Thirteen elements As, Ba, Cd, Co, Cr, Cu, Hg, Fe, Ni, Pb, Se, Sn and Zn in 10 watering campuses of ground waters in Ilam state, Iran were detected by inductively coupled plasma (ICP) in aqueous samples. The results show that all the 13 elements have concentration in the range of standard based on WHO, Iran, USA and European standards of drinking water.

**Key Words:** Heavy metals, Ground waters, Iran.

## INTRODUCTION

The potential sources of heavy metals pollution are various effluents emanating out of industries, domestic activities and erosion of natural deposits. However, if these metals are continuously released into the biosphere, they may inevitably affect the terrestrial and aquatic organisms. Thirteen heavy metals As, Ba, Cd, Co, Cr, Cu, Hg, Fe, Ni, Pb, Se, Sn and Zn are essential trace elements, having an important role in many body functions. These elements are required in small amounts and are toxic in large amounts[1]. Chronic ingestion of them in daily diet can cause some toxicological effects[2-4]. As, Ba, Cd, Hg and Pb are well recognized to be highly toxic and hazardous elements to human health[5-7]. In view of the above toxicological effects, the quantification of heavy metal ions in human body fluids at trace levels is important, especially in the assessment of occupational and environmental exposure to toxic metals[5]. Hence, the development of sensitive, precise and reproducible method for the determination of these 13 hevay metals elements in biological samples is of paramount importance. Various detection techniques including inductively coupled plasma mass spectrometry (ICP-MS)[1,8], flame atomic absorption spectrometry (FAAS)[9,10] electrothermal atomic absorption spectrometry (ETAAS)[11,12] and inductively coupled plasma optical emission spectrometry (ICP-OES)[13] have been reported for the determination of heavy metals. Of all theses detection techniques, ICP-OES has gained strong recognition in trace heavy metals analysis due to the following advantages: multi-elemental analysis capability, large dynamic linear range, low

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detection limits and high productivity[14]. Despite the aforementioned advantages, direct determination of heavy metals ions in biological fluids is limited due to their low level of concentration and matrix interferences. Thus, preconcentration is required in order to bring the concentration of the analytes into the range of the detector, while separation is called to eliminate potentially interfering matrix constituents.

## EXPERIMENTAL

A spectroflame atomic emission spectrometer, ICP Model M (Spectro Analytical Instruments, Germany) was used for the determination of As, Ba, Cd, Co, Cr, Cu, Hg, Fe, Ni, Pb, Se, Sn and Zn. Sequential spectrometer was used with following parameters: frequency, 27.12 MHz; power, 1.1kW; demountable quartz torch, Ar/Ar/Ar; coolant gas Ar, 14.0 L min$^{-1}$; auxiliary gas Ar, 0.5 L min$^{-1}$; nebulizer gas Ar, 1.0 L min$^{-1}$, nebulizer pressure, 2.4 bar; glass spray chamber according to Scott, sample flow rate, 1.0 mL min$^{-1}$; observation height 11 mm; holographic grating, 2400 groovesmm.1; dispersion of grating in the first reciprocal order, 0.55 nm mm$^{-1}$; wavelength range of monochromator 165-460 nm. The wavelengths (integration time) for As: 189.64 nm (5 s), Ba: 455.40 nm (5 s), Cd: 214.44 nm (3 s), Co: 228.62 nm (4 s), Cr: 205.55 nm(3 s), Cu: 324.78 nm (3 s), Fe: 259.94 nm(3 s), Hg: 194.23 nm (4 s), Ni: 221.65 nm (5 s), Pb: 220.35 nm (5 s), Se: 196.09 nm (3 s), Sn: 147.52 (5 s) and Zn: 206.19 (4 s).

Stock standard solutions of As, Ba, Cd, Co, Cr, Cu, Hg, Fe, Ni, Pb, Se, Sn and Zn at a concentration of 1000 mg L$^{-1}$ were obtained from Merck. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. The solution of 2,2′-bipyridyl at a concentration 0.01 mol L$^{-1}$ was prepared by dissolving 0.7810 g of the reagent (from POCh, Poland) in 500 mL of water. The solution of erythrosine (disodium salt tetraiodofluoresceine) at a concentration 0.01 mol L$^{-1}$ was prepared by dissolving 7.24 g of the reagent (from Chemapol-Praha) in 1000 mL of water. The solution of lanthanum at a concentration 1 mg La mL$^{-1}$ was prepared by dissolving 1.5584 g La(NO$_3$)$_3$·6H$_2$O (from Loba Feinchemie) in 500 mL of water. Buffer solution of pH 4.5 was prepared by mixing of a 55 mL acetic acid at a concentration of 0.2 mol L$^{-1}$ and 45 mL sodium acetate solution at a concentration of 0.2 mol L$^{-1}$. All the chemicals were of analytical grade quality. Water was purified with an Elix 3 system (Millipore, USA). The accuracy of the method was assessed by analyzing the following certified reference material (CRM): NCS ZC85006 Tomato (China National Analysis Center for Iron & Steel 2000).

**Co-precipitation of the elements studied in a model solution:** Lanthanum (0.2 mg) and 1 mL of 10.2 mol L$^{-1}$ solutions of 2,2′-bipyridyl and erythrosine were added to the mixture of assayed metals which contained 2 g of Cd and Co, 10 g of Pb and Ni and also 20 g of Cu and Zn in 100 mL. Then, pH of the precipitate (4.5) was fixed using an acetate buffer. The obtained samples were heated on the water bath for 20 min in the temperature of 60 ºC. Deposits formed in these conditions were centrifuged and the solution was decanted. Precipitate were digested in 1 mL

of sodium hydroxide with concentration of 0.2 mol $L^{-1}$ for ICP-OES method or in 1 mL of ammonia solution (1 + 1) for F-AAS method. The solutions were diluted to 10 mL with water (final volume). The metals content of the final solution was determined by ICP-OES. Calibration was carried using different standard solutions of Cd, Co, Cu, Ni, Pb and Zn submitted to the same preconcentration and determination procedures.

## RESULTS AND DISCUSSION

Ten watering campuses and the results are presented in Table-1.

Elements As (< 0.0012 ppm), Cd (< 0.0010 ppm), Co (< 0.0050 ppm), Cr (< 0.0040 ppm), Hg (< 0.0008 ppm), Ni (< 0.0012 ppm), Pb (< 0.0014 ppm), Se (< 0.0037 ppm) and Sn (< 0.0015 ppm) in 10 watering campuses have lower concentration than upper limit of concentration and are in the lowest concentration in drinking water of these campuses.

Elements Cu, Fe and Zn in these watering campuses have concentration in the region of international standards[15,16] and campus numbers 5 and 7 from a zinc amount point of view they are among the best drinking water of state (Table-1).

TABLE-1
OBTAINED RESULTS FROM ANALYSIS OF
10 WATERING CAMPUSES IN ILAM, IRAN

| Elements | Watering campuses | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Ba | 0.0220 | 0.0200 | 0.0450 | 0.0210 | 0.0530 | 0.0210 | 0.0290 | 0.0170 | 0.0300 | 0.0280 |
| Cu | 0.0023 | 0.0018 | 0.0046 | 0.0064 | 0.0051 | 0.0036 | 0.0031 | 0.0029 | 0.0064 | 0.0046 |
| Fe | 0.0098 | 0.0111 | 0.0151 | 0.0071 | 0.0112 | 0.0199 | 0.0093 | 0.0096 | 0.0141 | 0.0069 |
| Zn | 0.0068 | 0.0049 | 0.0046 | 0.0084 | 0.0569 | 0.0327 | 0.0555 | 0.0315 | 0.0123 | 0.0199 |

1 = Bijnawand; 2 = Shabab; 3 = Pelekabood; 4 = Mirzabeygi; 5 = Janjan; 6 = Sarabkalan;
7 = Naboowat; 8 = Kharabanan; 9 = Teranchehelzari; 10 = Chalab.

Barium has a concentration in region 0.017 to 0.053 ppm and from an international standard point of view such as WHO and USA, it is much lower than standard limit but from an Iranian standard point of view with No. 1053 it is upper than allowable limit in all drinking water campuses. In order to reduce the amount of barium in used drinking water, it is recommended to set up separation units of undesired barium ion in watering campuses specially No. 5 and 3, although from an international standard point of view (Table-2). All of these watering campuses are among the best sources of drinking water.

Based on the results obtained in the present work (Table-1), it can be concluded that the proposed technique is suitable for the determination of heavy metals concentration in water samples. The simplicity and versatility of the procedure makes it attractive for its use in the quality control of water samples. This study also showed that the concentration of heavy metals in the water samples should not drastically affect human health. However, risk assessment paradigms might underestimate the

TABLE-2
INTERNATIONAL STANDARDS OF DRINKING WATER

| Element | Iran standard | U.S. standard Ref. (15) | Euro. standard | WHO standard (Ref. 16) |
|---|---|---|---|---|
| As | 0.050 | 0.010 | 0.0500 | 0.010 |
| Ba | 0.010 | 2.000 | Not mentioned | 0.700 |
| Cd | 0.010 | 0.005 | 0.0100 | 0.003 |
| Co | Not mentioned | Not mentioned | Not mentioned | Not mentioned |
| Cr | 0.050 | 0.100 | 0.0500 | 0.050 |
| Cu | 1.500 | 1.000 | 0.0500 | 2.000 |
| Fe | 1.000 | 3.000 | 0.1000 | 5.000 |
| Hg | 0.001 | 0.002 | 0.0002 | 0.001 |
| Ni | Not mentioned | Not mentioned | 0.0200 | 0.020 |
| Pb | 0.100 | 0.015 | 0.1000 | 0.010 |
| Se | 0.010 | 0.050 | 0.0100 | 0.010 |
| Sn | Not mentioned | 1.000 | 0.1000 | 1.000 |
| Zn | 15.000 | 5.000 | 5.0000 | 3.000 |

effects on children and elderly people who may be more susceptible to adverse effects of ingested low doses of heavy metals.

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