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DETERMINATION OF PB(II), CD(II) IONS AFTER WASTEWATER TREATMENT PROCESS AT HOVSAN AERATION STATION

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ABSTRACT: *Hovsan aeration station is the largest wastewater cleaning center in south Caucasus region. Approximately, 60% of household sewage of Baku is discharged to Caspian Sea after treatment process. It is so necessary to analysis some toxic heavy metals in cleanded water such as cadmium and lead due to providing security of biodiversity of Caspian Sea and determining of cleaning effectiveness. Standard methods were used for determining of chemical characteristics of the household waste water. Pb, Cd contents samples were determined by inductively coupled plasma mass spectrometry (ICP-MS). The concentrations of metals in waste water samples after treatment process as follows: Pb (sample 1) 7.078 ppb, Pb (sample) 2 -5.522 ppb, Cd (sample 1) 4.766 pb, Cd(sample 2) 3.751 ppb. The concentrations heavy metals in the cleaned waste water samples from Hovsan Aeration Station were with the permissible limits of the European Union Directive and World Health Organization water quality guidelines.*

KEYWORDS: Heavy Metal Ions, Cadmium, Lead,Waste Water, ICP-MS

INTRODUCTION

Environment is an essential element of human existence. It is a result of interference of natural elements – earth, air, water, climate, biosphere – with elements created by human activity. All these interact with/and influence the existential conditions and the possibilities for future development of society. To protect the environment, mainly affected areas must be identified, assessed the degree of damage and determined the causes that have produced these imbalances.It is necessary to preserve the quality of the environment mainly throughout reducing negative effects of human activities. Potentially toxic metals resulting from anthropogenic activities cause severe disturbance of ecosystems [1, 2]. Water pollution is any chemical, physical or biological change in the quality of water that has a harmful effect on any living thing that drinks or uses or lives (in) it. Pollution of water occurs when substances that will modify the water in negative fashion are discharged in it. This discharge of pollutants can be direct as well as indirect. Water pollution is an appalling problem, powerful enough to lead the world on a path of destruction. Water is an easy solvent, enabling most pollutants to dissolve in it easily and contaminate it. The most basic effect of water pollution is directly suffered by the organisms and vegetation that survive in water, including amphibians.

On a human level, several people die each day due to consumption of polluted and infected water. All heavy metals are effected to human and environment by different ways. Lead does, in general, not bioaccumulate and there is no increase in concentration of the metal in food chains. Lead is not essential for plant or animal life. Of particular concern for the general population is the effect of lead on the central nervous system. Lead has been shown to have effects on hemoglobin synthesis and anaemia has been observed in children at lead blood levels above 40 µg/dl. Lead is known to cause kidney damage. Cadmium and cadmium compounds

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are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tends to bioaccumulate. Cadmium is not essential for plant or animal life. Cadmium is readily accumulated by many organisms, particularly by microorganisms and molluscs where the bioconcentration factors are in the order of thousands. In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd (II). The acute toxicity of cadmium to aquatic organisms is variable, even between closely related species, and is related to the free ionic concentration of the metal. Cadmium interacts with the calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water. Effects of long-term exposure can include larval mortality and temporary reduction in growth.

The natural water analysis for physical, chemical properties including trace element contents are very important for public health studies. These studies are also a main part of pollution studies in the environment [1-5]. Also, investigations of the quality of waste water samples have been continuously performed by researchers around the world. The determinations in household sewage have been performed using classical analytical techniques including titrimetric, gravimetric and modern instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), UV-Vis spectrophotometry, etc. Because of the low cost and easiness in usage, inductively coupled plasma-mass spectrometry is the main instrument for the determinations of the trace heavy metal ions in waste waters in the analytical chemistry laboratories [6-7]. The ICP-MS technique has a multi-element character and a high sample throughput, like ICP-OES, but it allows one to perform more sensitive measurements. Now ICP metod is sensitive and convenient method for the determination of metals in water and wastewater samples.

Experimental

Apparatus

Inductively coupled plasma mass spectrometer includes a mass spectrometer, detector, an ICP source, mass flow controllers for regulating ICP gas flows, a peristaltic pump for introducing samples and a computerized data acquisition and instrument control system.Mass-spectrometerpart consists of An interface (in particular a “sampler cone” and a skimmer cone), in which a small amount of the free ions generated by the plasma are transmitted. During this process the ions migrate from an environment with extremely high temperature and atmospheric pressure to a compartment at room temperature an high vacuum (< 0,001 Pa), Electrostatic lenses that focus (positive) ions onto the entry to the true mass-spectrometer, The true mass-spectrometer in the GI device has a quadrupole, composed of 4 metal rods which separate the ions on account of their mass by a kind of resonance principle and An electro-multiplier (a specific type of detector) containing active surfaces, which enhances the signal from one colliding ion so that a measurable pulse is generated.The sample aerosol is injected directly into the ICP, Subjecting the constituent atoms to temperatures of about 6000 to 8000°K.

General Discussion

In this method, analysts introduce sample material to an argon-based, high-temperature radio frequency plasma, usually via pneumatic nebulization. As energy transfers from the plasma to the sample stream the target elements dissolves, atomizes and ionizes. The resulting ions are

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extracted from the plasma through a differential vacuum interface and separated based on their mass-to-charge (m/z) ratio by a mass spectrometer.

Table 1. Recommended Analyte Masses and İnternal Standards

Materials and reagents

This study proposes to investigate the quality of clean waters influenced on biodiversity of Capiansea, specially for fishes. Samples were taken from Hovsan Aeration Station effluent pipeline that discharge to Capian Sea.Water samples were collected in high density polyethylene containerspreviously Water samples were stabilized with ultrapure nitric acid (0.5%)

Reagents and standards

Reagents may contain elemental impurities that might affect the integrity of analytical data data.Owing to the high sensitivity ICP-MS, high-purity reagents should be used whenever possible.All acids used for this method must of ultra high-purity grade.

a. Acids:

1. Nitric acid HNO_3,

2. Nitric acid HNO_3, 1+1: Add 500 ml HNO_3, 500 ml deionized water

3. Nitric acid (v/v) 2%: 20 ml HNO_3 100 ml deionized water and dilute to 1L

4. Nitric acid (v/v) 1%: 20 ml HNO_3 100 ml deionized water and dilute to 1L

b. Reagent water

c. Stock, standard and other required solutions

1. Internal standard stock solution: germanium,indium, lithium, scandium and thorium are suggested as internal standards add enough internal standards to all samples, Standards and quality control (QS) samples.

2. Instrument optimization/tuning solution:containing Beryllium, Cadmium, Cobalt, Copper, Germanium, Indium, Rhodium, Scandium, Terbium, Thallium, Barium, Cerium, Magnesium and Lead. Prepare this solution in 2% nitric acid. This mix includes all common elements used to optimize and tune various ICP_MS operating parameters. It may be possible to use fewer elements in this solution, depending on the instrument manufacturer's recommendations.

3. Calibration standards: a five standard calibration is recommended from 0 to 100 µg/l

e. Argon: Use a prepurified grade of argon unless it can be demonstrated that other grades can be used successfully. Prepurified argon is usually necessary because technical argon often contains significant levels of impurities.

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RESULTS AND DISCUSSION

Calibration Curve

A five standard calibration is recommended from 0 to 100 µg/l. Other calibration regimens are acceptable if the full suite of quality assurance samples and standards is run to validate any method changes. Fewer standards may be used and a two-point blank/mid-range calibration technique commonly used in ICP optical methods should also produce acceptable results. Calibrate all analytes using the selected concentrations. Prepare all calibration standards and blanks in a matrix of 2% nitric acid. Add internal standard mix to all calibration standards to provide appropriate count rates for interference correction.

Table 2 presents the concentrations of metals that were determined in water samples taken from the Hovsan Aeration Station effluent water pipeline.

The waste water samples after treatment process were analyzed by inductively coupled mass spectrometry. The concentrations of metals ions give in Table 1.

Cadmium, is widely distributed in the environment and anthropogenic source [8]. Concentrations in the waste water samples were in the range 3-4 µg/l.

Lead is one of the most abundant heavy metals in nature. It is an essential nutrient but could be also toxic for humans [12]. Most importantanthropogenic source of lead in the environment is combustion of gasoline with lead. Lead is discharged by vehicles into air them adsorbed from the air by environmental samples such as soil and plants [9-10,13]. In environmental lead suffers lead changes and find that the Pb^{2+} ion or as insoluble lead compounds.

The levels of lead in the samples were in range of 5-7µg/l. The highest concentrations were in first sample. Comparison the concentrations of metals in the samples have been shown in Figure 1. The highest concentration of cadmium and lead were obtained in first sample.

Figure 1.Comparison the concentrations of metals

The concentrations of lead and cadmium ions in the waste water samples from Hovsan Aeration Station were within the permissible limits for the biodiversity of Caspian Sea. The permissible limits of metals ions were given in Table 3.

Table 3. The permissible limits of metals ions in the water (for 98/83/EC and WHO)

CONCLUSIONS

ICP-MS method is available and adequate to identify and quantify metals present in natural and cleaned waste waters at trace levels, which are of particular relevance for toxicity control regions, may have been contaminated by toxic metals.

Comparison the concentrations of metals in the waste water samples with permissible limits of international unions show that concentrations Pb, Cd, in the both example under permissible limits.

It is evidenced that such amount of cadmium and lead is not hazardous for fishes and it is permissible for using this water in the agriculture.

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APPENDIX

Table 1. Recommended Analyte Masses and İnternal Standards

Element	Analytical Mass	Recommended İnternal Standards	İnterference Calculation
Cadmium	111	In	C111-1.073-C108-0.712*C106
Lead	208	Th	C208+C206+C207

Table 2 presents the concentrations of metals that were determined in water samples taken from the Hovsan Aeration Station effluent pipeline.

Table 2. Concentrations of metals

Sample	**Metal concentrations µg/l**	
	Cd	Pb
Sample 1	4.025	7.078
Sample 2	3.751	5.522

Figure 1.Comparison the concentrations of metals

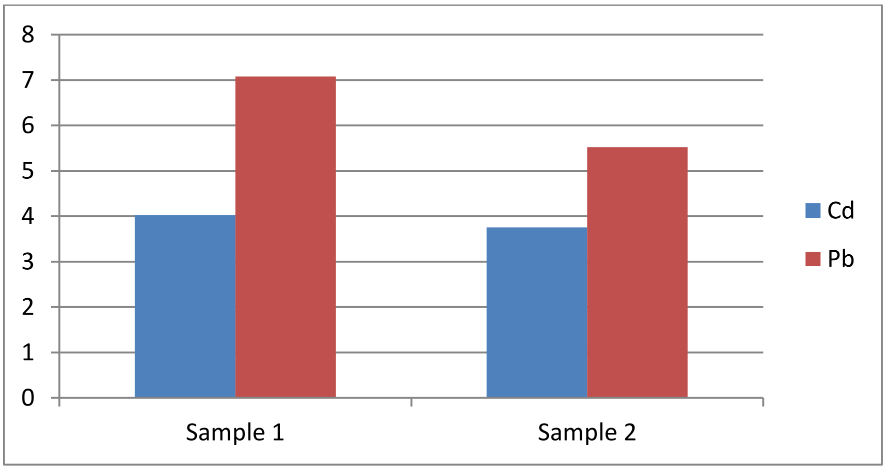

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Table 3. The permissible limits of metals ions in the water

	WHO 2011	EPA 2012	EU 2007	NHMRC 2011	Canadian committee 2012
Lead (Pb) µg/l	10	15	10	10	10
Cadmium(Cd) µg/l	3	5	5	2	5

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