

## Determination of trace elements (Cr, Al, Pb) by atomic absorption in natural water of Kyiv

**Maksym Polumbryk, Vira Ischenko, Oleg Polumbryk**

*National University of Food Technology, Kyiv, Ukraine*

---

### Abstract

#### Keywords:

Water  
Nature  
Drinking  
Etaas  
Microelement

---

#### Article history:

Received 12.06.2014  
Received in revised form  
13.05.2014  
Accepted 30.06.2014

---

#### Corresponding author:

Maksym Polumbryk  
E-mail:  
mx\_pol@yahoo.com

**Introduction.** The control of microelements in water is a one of the most important factor of the humans health in urbanized cities. ETAAS method with chemical modifiers has been used in drinking water analysis.

**Materials and methods.** All measurements of Al, Cr and Pb concentration in superficial and ground water samples were performed with atomic absorption spectrophotometer (model Saturn-3MP, Ukraine), equipped with graphite electrothermal atomizer (model Graphite 2).

**Results and discussion.** The significant differences between concentrations of lead in the two lakes can be explained by near location to highway of lake in Holosievo region and its contamination by some above mentioned gasoline additives. Unfortunately, the Al content in river Lybid is higher than acceptable level, which associated with continuous using of metal pipes, made from alloy with high aluminium content and uncontrolled emission of detergents and dyes as well. The presence of high content of chromium may be associated with both natural and anthropogenic sources. This may associated with lixiviation of industrial solid wastes, which responsible for water contamination during intensive building. The high river water contamination by chromium also was observed

**Conclusion.** Health hazards related to the lead in drinking water are negligible. Most attention should be focused on Al and especially Cr content in natural water of Kyiv city because their high concentration in sources of drinking water. It is interesting, that consumption of water rich in chromium may have potential health benefit for some individuals such as diabetics, which is known have low chromium content in blood plasma.

---

## Introduction

Chromium is an essential trace element for human health (Kabata-Pendias A. and Mukherjee A.B., 2007; Vincent J.B., 2010). This micronutrient is a cofactor for insulin function, it is reported to affect some of enzymes that control cholesterol level and beneficially impact on lipoproteides ratio (Evans G.V., 1989; Broadhurst C.L. and Domenico P., 2006; Sharma S. et. al., 2011). Chromium deficiency resulted in increased cholesterol and blood sugar level, coronary dysfunction, lipid abnormalities and an increased risk of atherosclerotic disease (Newman et al., 1978). However, excessive concentration of Cr compounds, especially when they are inhaled, may lead to a lung cancer among workers in certain industries (IARC Society, 1990), nasal and small intestine cancer in some species of test animals (Stout M.D. et.al., 2009). The sources of Cr in human diet are vegetables, beer and brewer's yeasts, whole grains, nuts as well as cheese, liver and marine food (Kabata-Pendias A. and Mukherjee A.B., 2007). The Cr picolinate has been used as the main source of Cr both in medical practice and food fortification (Evans G.V., 1989; Broadhurst C.L. and Domenico P., 2006).

However, the role of aluminium and lead is doubtful. Both of these microelements are present in tissues of animal and human body, but there is no positive effect has been found so far. Aluminium is known to be a neurotoxicant effect which can cause motor neuron disease and brain cells damage due to the excess of this element (Meizi M. et. al., 1993). Industrial Al dust can play a role in aetiology and pathogenesis of Alzheimer disease (Polizzi et.al., 2002). It is known that Al can bind phosphate anions, decreasing availability of P compounds (Kabata-Pendias A. and Mukherjee A.B., 2007). Lead (Pb) is the one of the most dangerous contaminant. Human organism cannot distinguish Ca from Pb, which resulted in the accumulation of the last in the bones and teeth (Kabata-Pendias A. and Mukherjee A.B., 2007). The excessive exposure of Pb may cause several disorders of human health, such as damage of kidney and nervous system, hypertension, cardiovascular and cerebrovascular disease, cancer development, inhibition of heme formation, which further may lead to anemia and porphyria, may associated with erectile dysfunction and depression (Anis T.H. et. al., 2007). The children are the main group of risk because they retain more Pb than adults due to physiological and metabolical differences. If the diet is low in Fe, Ca and proteins, the absorption of Pb would be increased.

The main sources of Pb, Al, Cr and other microelements are the soil, air and ground water. Further they appear in tap water and finally in food. Canned bottles, which made from aluminium, may also play a role of contaminant of food and additional source of this microelement for humans. Aluminium compounds have been utilized as a coagulant on the most water supply plants, which resulted in the increased concentration of Al in drinking water. Lead compounds were used as an anti-knock additive in gasoline in the last century and still illegally used in several counties of Eastern Europe despite the strong restriction.

According to WHO acceptable levels of Pb, Cr, Al are 0.03, 0.05 and 0.2 mg/l respectively (WHO, 1995). These levels are equal to those of Ukrainian regulations of maximum permissible concentration in ground water.

Atomic absorption analysis with electrothermal atomization (ETAAS) is a most commonly used technique for determination of chemical elements at low concentration owing to its low time of analysis, availability, high sensitivity and specificity in different species, in particular in ground water (Acar O. et. al. 2000; Acar O., 2001; Correia P.R.M. et. al., 2003). However, the direct elements determination by ETAAS method is complicated due to the interference effects of salts in sample matrix. To overcome interferences in sample matrix during measurements, preconcentration and temperature

program correction (Gai R.A. et.al., 2006), chemical modification (Acar O., 2001; Acar O. et.al., 2000), coacervative extraction of trace elements prior to determination (Hagarova I. et. al., 2013) and other technique have been used. One of the most often employed approach is the addition of chemical modifiers to the sample. The main purposes of chemical modification are to reduce interference effects and stabilize volatile elements. Method of the direct determination of Pb, Al and Cr in natural water samples by atomic absorption with application of chemical modification technique was used in this work.

## Materials and methods

All measurements of Al, Cr and Pb concentration in superficial and ground water samples were performed with atomic absorption spectrophotometer (model Saturn-3MP, Ukraine), equipped with graphite electrothermal atomizer (model Graphite 2). The analytical lamps with wavelengths 283.3 nm for Pb, 357.9 nm for Cr and 309.3 nm for Al have been used in this work. Hollow-cathode lamps of Cr and Al both were operated at 10 mA, whereas Pb lamp – at 5 mA. The slit width used 0,2 nm for Cr and Al measurements and 0,15 nm for Pb. The ramp time was within the range 0,2-0,5 s. Argon used as a carrier gas, the flow of which was equal to 0,25 l·min<sup>-1</sup>. The measurements were repeated twice. The optimized temperature program for Cr, Al and Pb determination is given in Table 1.

**Table 1**

**Temperature program for the determination by ETAAC**

Step	Temperature, °C	Hold time, s	Ar, flow rate (ml·min <sup>-1</sup> )
Dry-1	90	20	250
Dry-2	110	5	250
Pyrolysis	400 (Pb)	5	250
	600 (Cr)	10	
	1200 (Al)	10	
Atomization	1400 (Pb)	5	0
	2500 (Cr)	4	
	2400 (Al)	3	
Cleaning	2700	3	250

All the chemicals used were on analytical grade. Sulfuric, nitric and hydrochloric acids, Fe(III), Mg, Ca chloride, as well as potassium (chloride, sulfate, nitrate) and sodium (chloride, hydrocarbonate, hydrophosphate) salts and also chemical modifiers, including citric, sulfosalicylic, ascorbic, tartaric and oxalic acids, triethanolamine, complexon III were obtained from Sigma-Aldrich Chemical Co. Initial solutions of Pb, Cr and Al were prepared by solubilization of high purity metals in nitric (Pb), hydrochloric (Cr and Al) acids. The Certified Reference Materials (Ukrainian State Standard Samples of Metal Solutions) were used in order to obtain calibration solution of Pb, Cr and Al. Solutions with concentration lesser than 1 µg/ml were prepared in the day of measurements by dilution of the initial solutions.

The natural water samples were preliminary treated by nitric acid just at place of the probe selection. All the samples were exposed to ultrasonic cleaning in order to remove some natural ligands, including fulvic and humic acids before microelements determination. The aqueous solutions were acidified to pH 2±0,1 by nitric acid. Statistical analysis was performed with Student's t-test method (95% confidence level).

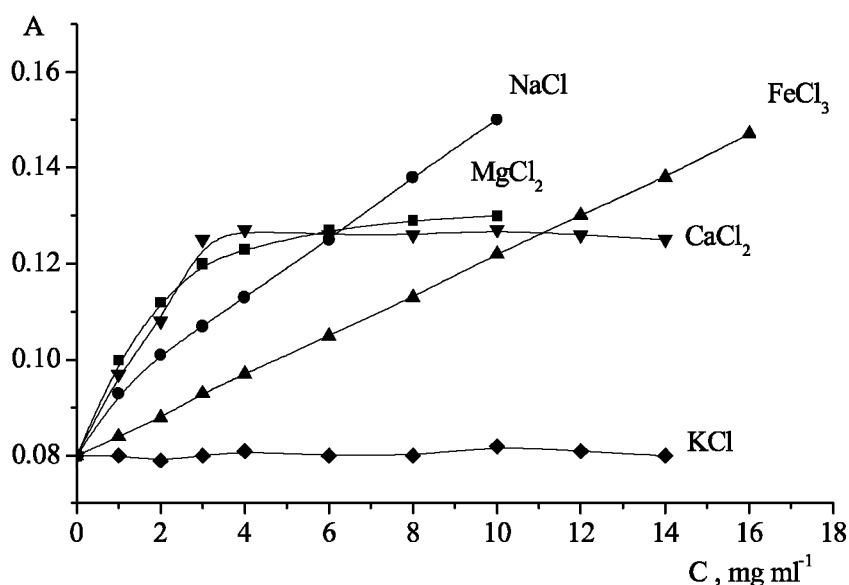
## Results and discussion

The direct atomic absorption analysis of Pb, Cr and Al in natural waters is complicated due to interfering action of water macro components even at low salinity level. Utilization of the chemical modifiers (CM) is a method which allows direct measurements of these elements in the water samples. The chemical modifiers in ETAAC assays are the additives, which can transform certain element or matrix component into the suitable for atomization form. CM application has offered the opportunity for element analysis to increase the detection limit, which is  $10\text{-}10^3$  times higher than for a conventional method. It has been reported that utilization of organic chelating agents favoring relieve negative impact of matrix components, and therefore improve analytical signal. Several chemical modifiers including citric, sulfosalicylic, ascorbic, tartaric and oxalic acids, triethanolamine, complexon III were used for direct determination of Cr, Al and Pb in natural waters at the presence of macro components. These compounds are well known modifiers which able to form stable complexes with metal cations and resulted in the reducing of atomization temperature.

### Chromium

It is well known that natural waters contain mainly ions of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{HPO}_4^{2-}$ . These ions have been used in analytical procedure, particularly in sea and ground water analysis in water samples preparation, which mimic natural samples so-called synthetic water. Influence of above mentioned ions on analyte signal received much attention, since they may cause an undesirable action. The impact of the most important cations on chromium atomization was studied by preparing water samples with ions concentration similar to those of natural ground water of total low salinity up to 3 mg/ml with Cr concentration 0,08 mg/ml.

The investigations of influence of natural waters macro components on Cr analytical signal showed that either chlorides of Ca and Mg initially caused drastic rise of analytical signal, which further was stabilized (fig. 1).



**Figure 1. Chromium atomization in chloride aqueous solutions in presence of  $\text{Cr}^{3+}$  ( $C = 0,08 \mu\text{g/ml}$ )**

The rise of potassium content has almost no impact on Cr atomization process, which has offered the opportunity to use potassium salts as the components of the water samples matrix, which mimic natural waters. According to experimental data, the value of chromium analytical signal is constant in all the cases. Thus, it makes it possible to reduce undesirable effect of macro components of water samples at chromium determination by ETAAS. However, rise of sodium and ferric chloride (III) content in aqueous solution cause an increase of chromium signal absorbance. Therefore these cations can be used in synthetic solution only in presence of chemical modifiers. Subsequent experiments have shown that it is possible to determine Cr in natural waters using surrogate solutions, which imitates natural with potassium chloride addition.

#### *Lead and Aluminium*

The most effective chemical modifier was found by the follow procedure. All the solutions were acidified by nitric acid (1:1) in order to reach pH  $2,0 \pm 0,1$ . The CM concentration being changed during measurements, the total salinity in one set of water samples was 0 g/l, in a second 10  $\mu\text{g/l}$  with analyte concentration in all the samples 0,2  $\mu\text{g/ml}$ .

It was found that the increase of natural water salinity in presence of triethanolamine and citric acid resulted in the little rise of Pb analytical signal in a beginning, whereas further increase of salinity lead to the signal drop. The negligible decrease of analytical signal in the presence of sulfosalicylic acid and complexon III has been observed. Application of tartaric acid was caused an increase of analytical signal with rise of macrocomponents concentration. Only in presence of ascorbic and oxalic acids the analytical signal has been stabilized with improving of the method sensitivity. It has been determined that the optimal concentration of these modifiers is 1  $\mu\text{mol}\cdot\text{ml}^{-1}$ . Organic modifiers are favor to improve the method sensitivity and atomization conditions and minimize the disturbances, which caused by natural waters salinity. At the high level of salinity of natural waters, the presence of ascorbic acid favoring Pb determination, improve sensitivity and accuracy of measurements and give more linearity to the calibrating chart.

The better chemical modifiers for the Al determination in natural water are ascorbic acid and triethanolamine at different total level of salinity of water samples, that had changed up to 10 g/l. Further, ascorbic acid was used as a modifier owing to its high availability. The analytical signal of aluminium linearly related to its concentration at different salinity level. The data spread of the mean value of analytical signal not exceeded 20 %.

Kyiv is the one of the most populated city in Eastern Europe, which accounted more than 3 million people so that the quality of food and drinking water have received great attention due to their impact on health. The main sources of tap water in Kyiv are Dnipro river and underground Lybid river as well as lakes. However, consumption of tap water continuously decreased because of awareness of its strong pollution by hazardous metals. Therefore, the minor sources of drinking water, especially water from artesian well become more popular, so that quality control of these kinds of water is very important.

It is known, that Cr, Al and Pb are able to contaminate drinking water due to their presence in materials of water-pipes and contamination of soil as well. Therefore, we have determined concentrations of these microelements in several sources of natural water in the presence of 1  $\mu\text{mol}\cdot\text{ml}^{-1}$  ascorbic acid, which was used as a chemical modifier. The results are given in table 2.

**Table 2**

**Results of Cr, Al and Pb determination in natural waters of Kyiv city**

Analyte	Sample	Determined using calibration curve, $\mu\text{g}\cdot\text{ml}^{-1}$	Added, $\mu\text{g}\cdot\text{l}^{-1}$	Found, $\mu\text{g}\cdot\text{l}^{-1}$	Recovery, %	
Pb	Lybid river	< 5	0	—	—	
			20	18,8±1,2	94	
			50	45,4±2,5	91	
Cr		290±20	0	283±11	—	
			20	301±12	91	
			50	342±26	114	
Al		291± 9	0	294±8	—	
			20	303±11	93	
			50	341±21	101	
Pb	Lake water (Holosievo region)	27,6±1,6	0	28,1±0,8	—	
			20	49,4±1,1	103	
			50	76,2±1,8	98	
Cr		83±2	0	82±11	—	
			20	101±13	92	
			50	134±16	104	
Al		135±7	0	133±8	—	
			20	150±11	92	
			50	185±16	89	
Pb		Lake water (Sovky)	5,1±4	0	6±3,1	—
				20	24±3,3	91
				50	53,5±3,2	97
Cr			110±20	0	112±18	—
				20	125±19	93
				50	161±23	91
Al			3,5±0,3	0	3,8±0,1	—
				20	22±1,2	88
				50	50,5±2,3	94
Pb	Artesian deep water		Less than detection limit	0	—	—
				20	16,8±1,2	94
				50	46,4±2,6	91
Cr			63±5	0	61±5	—
				20	83±6	95
				50	112±9	98
Al			78±7	0	74±6	—
				20	98±6	91
				50	126±11	94

The insight into Table 2 revealed that Pb content in all choosen sources of drinking water is lesser than maximum permissible level. The significant differences between concentrations of lead in the two lakes can be explained by near location to highway of lake in Holosievo region and its contamination by some above mentioned gasoline additives. We have suggested that the high amount of Pb collected in unsoluble forms in the bed slits of lakes and rivers. Unfortunately, the Al content in river Lybid is higher than acceptable level, which associated with continuous using of metal pipes, made from alloy with high aluminium content and uncontrolled emission of detergents and dyes as well. The presence of high content of chromium may be associated with both natural and anthropogenic sources. This may associated with lixivation of industrial solid wastes, which responsible for water contamination during intensive building. The high river water contamination by chromium also was observed (Nduka J.K.S. and Orisakwe O.E., 2007). Consumption of this kind of water over a long period of time may cause a nasal cancer. High content of chromium in river and lakes is a result of soil pollution by this metal in Kyiv, whereas relatively high Cr concentration in artesian water may be associated with some elements of water supply system, rich in chromium.

Calibration graphs for the direct determination of Pb, Al and Cr in drinking water sources were obtained by addition of microelements standard samples with 1  $\mu\text{mol}\cdot\text{ml}^{-1}$  ascorbic acid. In all cases calibration graphs were linear up to 1 mg/l of each of these microelements. The precision of the Al, Cr and Pb determination calculated on 6 replicate analysis of each sample was expressed as a rate of recovery of added standard solutions of these elements, that was not exceeded 90 %.

## Conclusions

The approach of Al, Cr and Pb determination in natural water samples by ETAAS has been evaluated and demonstrated to be an effective for routine measurements of these trace elements. The methodology has shown adequate accuracy and selectivity. Surprisingly, in all water samples lead content was below WHO recommended limit of 0,03 mg/l and changed from 5,1  $\mu\text{g/l}$  to 27,6  $\mu\text{g/l}$ . Thus, health hazards related to the lead in drinking water are negligible. Most attention should be focused on Al and especially Cr content in natural water of Kyiv city because their high concentration in sources of drinking water. It is interesting, that consumption of water rich in chromium may have potential health benefit for some individuals such as diabetics, which is known have low chromium content in blood plasma.

## References

1. Acar O. (2001), Determination of cadmium and lead in biological samples by Zeeman ETAAS using various chemical modifiers, *Talanta*, 55, pp. 613-622. doi: 10.1016/S0039-9140(01)00468-4; PMID: 18968407.
2. Acar O., Turker A.R. and Kilic Z. (2000), Determination of bismuth, indium and lead in spiked sea water by electrothermal atomic absorption spectrometry using tungsten containing chemical modifiers, *Spectrochim. Acta A.*, 55, pp. 1635-1641. doi:10.1016/S0584-8547(00)00258-5.
3. Anis T.H., Karaksy E.I., Mostafa A., Gadalla T., Imam A., Hamdy H., and Abuel-Alla O. (2007), Chronic lead exposure may be associated with erectile dysfunction, *J.Sex. Med.*, 4, pp. 1428-1436, doi:10.1111/j.1743-6109.2007.00587.x; PMID: 17727353

4. Broadhurst C.L., and Domenico P. (2006), Clinical studies on chromium picolinate supplementation in diabetes mellitus – a review, *Diabetes Technol. Therap.*, 8, pp. 677-687. doi:10.1089/dia.2006.8.677; PMID: 17109600;
5. Correia P.R.M., Nomura C.S. and Oliveira P.V., (2003), Multielement determination of cadmium and lead in urine by simultaneous electrothermal atomic absorption spectrometry with an end-capped graphite tube, *Anal. Sci.*, 19, pp. 1519-1523. PMID: 14640451
6. Evans G.W. (1989), The effect of chromium picolinate on insulin controlled parameters in humans, *Internat. J. Biosocial. Med. Res.*, 11, pp. 163-180.
7. Gai R.A., Cerutti, S., Gasquez J.A. et.al. (2006), Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination, *Talanta*, 68, pp. 1065-1070. doi:10.1016/j.talanta.2005.06.069; PMID: 18970432
8. Hagarova I., Bujdos M., and Kubova J. (2013), Coacervative extraction of trace lead from natural waters prior to its determination electrothermal atomic absorption spectrometry, *Spectrochim. Acta*, B. doi:10.1016/j.sab.2013.03.010
9. IARC Society (1990), Chromium and chromium compounds, In Chromium, nickel and welding, *IARC Monographs on the evaluation of carcinogenic risks to humans*. 49, pp. 49-256.
10. Kabata-Pendias A., and Mukherjee A.B. (2007), *Trace elements from soil to humans*, Springer, Berlin,. ISBN 3-540-32713-4.
11. Meizi M., Banin E., Roll M. and Rousseau A. (1993), Toxic effects of aluminium on nerve cells and synaptic transmission, *Progr. Neurobiol.*, 40, pp. 89-121. doi:10.1016/0301-0082(93)90049-X; PMID: 8380935.
12. Nduka J.K.C. and Orisakwe O.E. (2007), Heavy metal levels and physico-chemical quality of potable water supply in Warri, *Nigeria. Ann. Chim.*, 97, pp. 1505-1512. doi: 10.1002/adic.200790071; PMID: 17970302.
13. Newman H.A., Leighton R.F., Lanese R.R. and N.A. Freedland (1978), Serum chromium and angiographically determined coronary artery disease, *Clin. Chem.*, 24, pp. 541-544. PMID: 646861.
14. Polizzi S., Piza E., Ferrara M., Buglani M., Papaleo A., Albrea R. and Palmi S. (2002), Neurotoxic effects of Aluminium among foundry workers and Alzheimer's disease, *Neurotoxicol*, 23, pp. 761-774. doi:10.1016/S0161-813X(02)00097-9; PMID: 12520766.
15. Sharma S., Agrawal R.P., Choudhary M., Jain S., Goyal S and Agrwal V.(2011), Beneficial effect of chromium supplementation on glucose, HbA<sub>1c</sub> and lipid variables in individuals with newly onset type-2 diabetes., *J. Trace Elem. Med. Biol.*, 25, pp. 149-153. doi: 10.1016/j.jtemb.2011.03.003; PMID: 21570271.
16. Stout M.D., Herbert R.A., Kissling G.E., Collins B.J., Travlos G.S., Witt K.L. and Hoth M.J. (2009), Hexavalent chromium is carcinogenic to E344/N rats and B6C3F1 mice after chronic oral exposure, *Environ. Health Perspect.*, 117, pp. 716-722. doi:10.1289/ehp.0800208; PMID: 19479012.
17. Nadiya Yamborko, Ievheniia Ostrova (2013), Component structure of pollutants and functional state of microbial cenosis of soil, isolated from organochlorine waste burial, *Ukrainian Food Journal*, 2(1), pp. 42-45.
18. Slavov Al. K., Denkova Z. R., Hadjikinova M. V. (2013), Morphological, physiological and biochemical characteristics of seven bacterial strains for wastewater treatment, *Journal of Food and Packaging Science Technique and Technologies*, 2(1), pp.9-15.
19. Vincent J.B., (2010), Chromium celebrating 50 years as an essential element?, *Dalton Trans.*, 39, pp. 3787-3794. doi:10.1039/b920480f; PMID: 20372701.
20. WHO (1995), *Guidelines for drinking water quality*, World Health Organization, Geneva, Switzerland, pp. 121.