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FLAME ATOMIC ABSORPTION DETERMINATION OF ZINC IN NATURAL WATERS USING THE METHANE - AIR FLAME

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ABSTRACT. The zinc content of some natural waters (river, well, sea, mineral water) and drinking water (tap) has been determined by flame atomic absorption spectrometry using the methane-air flame. The effect of hollow-cathode lamp current, the flame composition and the observation height in the flame on the absorption of zinc in the methane-air flame was studied at 213.9 nm. The best results were obtained with the lamp current of 3 mA, at the observation height of 7 mm, with the stoichiometric flame. The effect of Na, K, Ca, Mg, Al, ClO_4^-, SO_4^{2-}, and PO_4^{3-} on the absorption of zinc was studied too. The detection limit of 0.006 ± 0.004 $mg.l^{-1}$ was obtained at a significance level of 0.05, using the two-step Neyman-Pearson criterion. The zinc content of waters has been determined with the calibration curve and the standard addition method. In the case of low mineralization natural water the results of two methods agree.

INTRODUCTION

Zinc is a widespread element in litho-, hidro- and biosphere. Its mean concentration in Earth crust is of 45 $mg.kg^{-1}$, in sea and surface water of 10 $\mu g.l^{-1}$. Zinc is an essential element of all living organisms, taking part as the inorganic component of more than100 of vital enzyme [1]. Flame atomic absorption spectrometry (FAAS) is an adequate, sensitive method for the determination of zinc in low concentrations. Usually the high temperature C_2H_2-air, C_2H_2-O_2 and C_2H_2–N_2O flames are used as atomic source. The optimal conditions of the determination of zinc in these flames were established, the detection limits being of order of 10^{-2}-10^{-4} $mg.l^{-1}$ [2-16]. The low temperature (~ 2000 K) propane-butane-air (PB-A) flame was used in few cases for the determination of zinc, mostly in early stage of the flame atomic absorption spectrometry development [17-19]. The methane-air (M-A) flame has similar properties (temperature, burning velocity etc) with the PB-A flame [20]. To our best knowledge the behaviour of zinc in the M-A flame was not studied, and the detection limits are not known. The aim of this work is to study the behaviour of zinc in the M-A flame, to optimize the flame and instrumental parameters and the determination of zinc in natural waters, respectively.

EXPERIMENTAL

INSTRUMENTATION

The measurements were carried out at 213.9 nm with a single beam HEATH-701 (Heath Co., Benton Harbor, MI, USA) spectrophotometer using a zinc hollow-cathode lamp (NARVA, Germany), a HEATH EU-700 scanning monochromator, a HEATH EU-700-30 type photomultiplier module and a 1P28A (RCA, USA) photomultiplier (-700 V). The photomultiplier signal was recorded with a K-201 (Carl Zeiss Jena) strip chart recorder. The pneumatic nebulizer-spray chamber-burner system was used from an AAS-1 (Carl Zeiss Jena) atomic absorption spectrophotometer. The original slot type burner-head (for C_2H_2-air flame) was replaced with a similar, Mecker type, developed by us for atomic absorption measurements in the M-A flame [21]. In order to increase the nebulization efficiency the original 8 mm glass ball impactor was replaced with an 1 mm cylindrical one, placed at optimal distance of 5 mm from nebulizer head [22]. The air flow-rate was kept constant, 500 L/h, the flow rate of the methane being varied as a function of the gas mixture wanted. As CH_4 source the city gas of 99 % purity was used, from the pipe.

CHEMICALS

Stock standard solutions (1000 $mg.l^{-1}$) were prepared by dissolving the appropriate amounts of metals (Zn, Mg and Al (Specpure, Johson Matthey Chemicals Limited, England)) and compound ($CaCO_3$, Specpure, Johnson Matthey Chemicals Limited, England) in corresponding acid. KCl, NaCl (analytical grade, Reactivul, Bucuresti, Romania), HCl, H_2SO_4, $HClO_4$ and H_3PO_4 (analytical grade, Merck, Darmstadt, Germany)) were dissolved and diluted in double distilled water, respectively. For further dilutions double distilled water was used in all cases.

SAMPLING AND SAMPLE HANDLING

The river, sea and well waters were sampled and handled in accordance with the EPA-recommendations [23]. All determinations were carried out within 48 hours after sampling. The drinking water (tap water) from the laboratory was acidified and analysed just after sampling. The mineral waters (commercial available, “Anavie”, “Borsec”, “Perla”) were analyzed after the sealed bottles were opened, acidified and degassed by shaking. The samples were diluted 1:1 before measurements. The pH of all the measuring solutions was of 1.5 - 2, in accordance with the literature data [2, 23].

PROCEDURE

The behaviour of zinc in the M-A flame was observed in the flame up to h = 14 mm over the burner head (in 1mm steps), at three different flame compositions: 0.88; 1.00; 1.12 expressed in relative stoichiometric units (RSU). Four replicate measurements were made in each case. The mean, the standard deviation, the S/N was calculated for each h and flame composition investigated. The homogeneity of the means was tested by the F test at a significance level of 0.05. The slitwidth of the monochromator was of 0.050 mm, the sensitivity of the strip chart recorder was different in function of the absorption value measured. For a given set of determinations the sensitivity was kept constant.

RESULTS AND DISCUSSION

OPTIMIZATION OF THE FLAME AND INSTRUMENTAL PARAMETERS

First the effect of the hollow-cathode lamp current (i) on the zinc absorption was studied. The composition of the flame was kept constant, at 1.12 RSU. The concentration of the calibration solution was of 1 mg.l^{-1}. The absorption (A) was measured for different lamp current intensities, between 3 – 10 mA, in 1 mA steps. The variation of the absorption versus the lamp current is represented in Fig.1.

The absorption of zinc is maximal at i = 3 mA and decreases with the increase of the lamp current, due to the significant broadening of the lamp emission line with the increase of the current. The A – i relationship could be described best with an exponential decay curve of $A = 0.0464 + 0.02005 \exp(-(i - 3)/2.13)$. In conclusion, then optimal value of the lamp current for the determination of zinc is 3 mA. The low current is advantageous, because the thermal noise of the lamp is low, the reproducibility of the measurements is high and the lifetime of the lamp is also long.

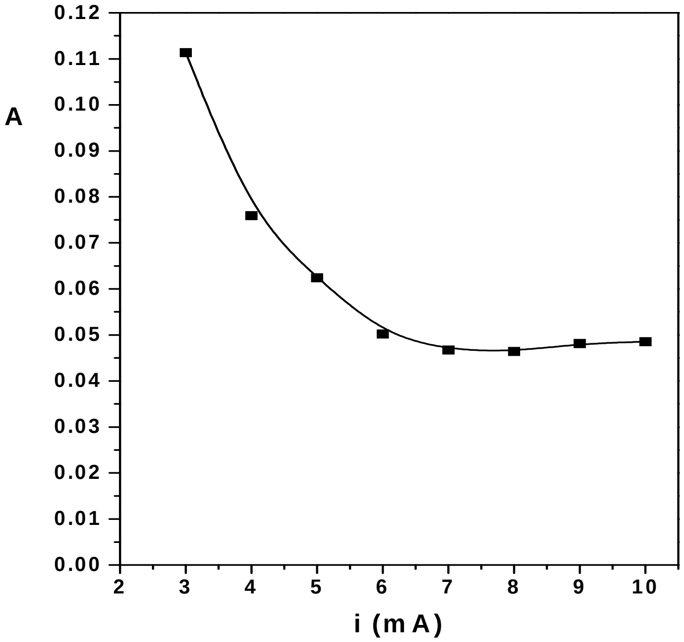

Figure 1. Variation of the absorption of 1 mg.l^{-1} zinc solution versus the hollow-cathode lamp current

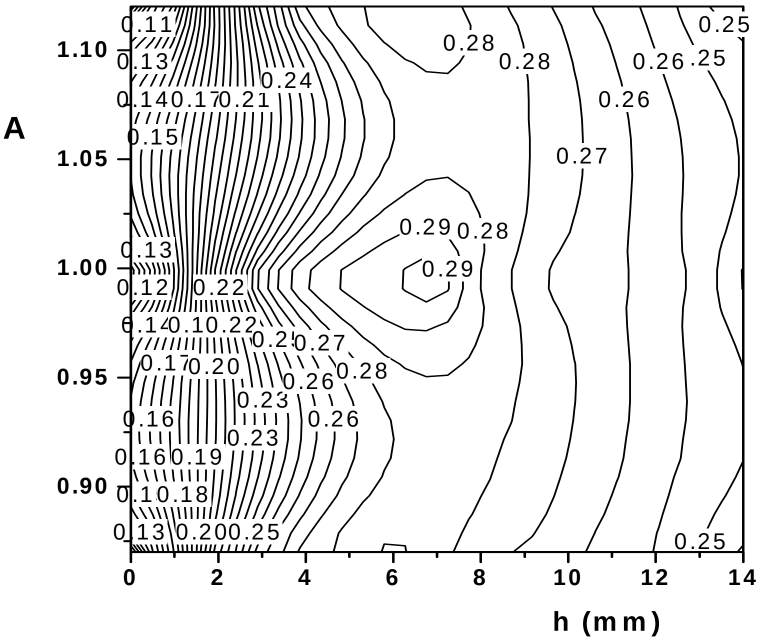

Figure 2. The 2D contour map of the absorption of the 1 mg.l^{-1} zinc vs. observation height and flame composition. The labels on the plot indicate the grid matrix values.

Further, the influence of the flame composition and that of the observation height on the absorption of zinc was investigated using three flame compositions (0.88, 1.00, 1.12 RSU) at the concentration level of 1 mg.l^{-1} of zinc. The lamp current was the optimal one. The data were processed using the MicroCal Origin™ Software package, version 5.0 (MicroCal Software Inc., MA, USA) and plotted as 2D contour map (Fig.2).

The analytical signal depends both on observation height and flame composition. The absorption increases slowly with the increase of the methane content of the flame, being the highest in stoichiometric conditions (1.00 RSU). The maximal absorption was observed at the same height of 7 mm over the burner head, regardless of flame composition. The standard deviation of all means was homogeneous, the magnitude of the S/N ratio being decided by the magnitude of the mean. In conclusion, the optimal conditions for the quantitative determination of zinc in the M-A flame are h = 7 mm and flame composition 1.00 RSU.

INTERFERENCES

The effect of Na, K, Ca, Mg, Al, SO_4^{2-} and PO_4^{3-} on the absorption signal of zinc of 1mg.l^{-1} was investigated up to a 500 fold excess, as possible inorganic interferents, present in natural waters. The effect of $HClO_4$ was tested too, as matrix modifier. The experimental conditions were the optimal ones, determined previously. The variation of the zinc absorption signal versus the concentration of the interferents is represented in Figure 3.

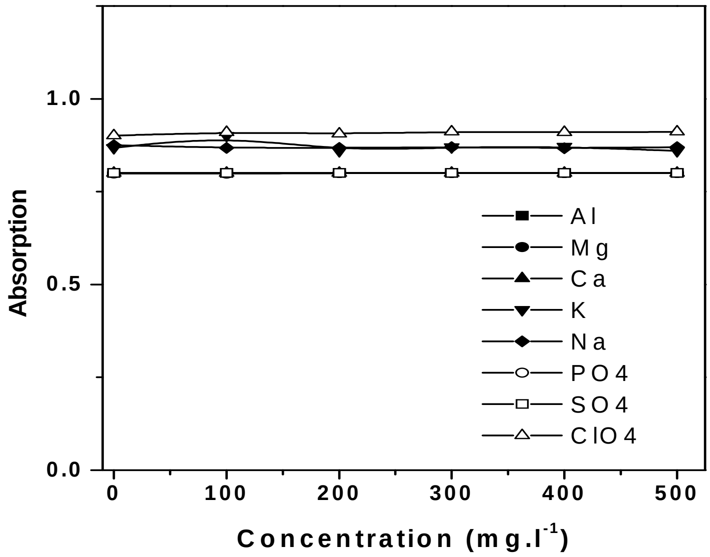

Figure 3. Influence of Na, K, Ca, Mg, Al, SO_4^{2-}, PO_4^{3-} and ClO_4^- on the absorption signal of zinc of 1 mg.l^{-1}

The results show that the studied inorganic ions do not influence the zinc absorption, even in high excess. We can consider that, like in the acetylene flames, zinc is free of interference of these inorganic ions in the methane-air flame. $HClO_4$ is inefficient, fact which suggests the free evaporation of the analyte from the condensed phase in the flame.

CALIBRATION, DETERMINATION OF THE DETECTION LIMIT

For the determination of the detection limit the variation of the analytical signal versus concentration was studied in the 0.01-10 mg.l^{-1} zinc concentration range. Four calibration curves were plotted, one curve covering one order of magnitude of concentration. Each calibration curve was established by using six standard solutions. Six replicate measurements were made at each concentration level. The homogeneity of the means and the linearity of the calibration curve were tested. The equation of the regression line, the confidence limits and the coefficient of correlation (R2) were calculated with the least squares method. The detection limit was calculated using the two step Neyman-Pearson model [24, 25], for the fixed values of (P10)0 = 0.025 and (P11)d = 0.975. The results are summarized in Table I.

Table I

Calibration data of zinc determination in the M-A flame

No. Eq	Concentration range (mg.l^{-1})	Equation of the calibration curve	Detection limit (mg.l^{-1})
1.	10 - 1	A = 0.1043 *C + 0.0944 R^2= 0.9701	Not determined
2.	6 - 1	A = 0.1362*C + 0.00569 R^2= 0.9990	0.36 ± 0.20
$3^{@}$	10 - 1	A = 0.034*C + 0.0009 R^2= 0.9994	0.30 ± 0.17
4.	1 – 0.1	A = 0.0908*C – 0.0008 R^2= 0.9995	0.031 ± 0.02
5.	0.1 – 0.01	A = 0.4089*C + 0.0024 R^2= 0.9974	0.006 ± 0.004

$^{@}$ burner held perpendicular to the optical axis, 8 mm optical path in the flame

In the 10 – 1 mg.l^{-1} concentration domain (eq.(1)) the A – C relationship is not linear in the whole concentration domain, but it can be approximated with a line. The close linearity exists in the 6 – 1 mg.l^{-1} concentration domain (eq.(2)) only. Holding the burner perpendicular to the optical axis of the spectrophotometer (8 mm optical path in the flame) the linearity can be extended up to 10 mg.l^{-1} of concentration level (eq.($3^{@}$)). The detection limits obtained for each concentration range are also summarized in Table I. The lowest detection limit of 0.006 ± 0.004 mg.l^{-1} is low, it is about one order of magnitude higher than that obtained with acetylene flames.

DETERMINATION OF ZINC IN WATER SAMPLES

The zinc content of the water samples was determined by the calibration and by the standard addition method. The later method was used in order to study the presence of interference and/or as reference method due to the absence of certified reference material. The determinations were carried out with optimized flame and instrumental parameters. Four parallel measurements were made in each case. The measuring sample solutions were prepared in 25 ml volumetric flasks, the samples were diluted 1:1. In the case of standard addition method 100 µl of concentrated zinc standard was added to the 25 ml of diluted sample. Three additions of standard were made, in 0.5 mg.l^{-1} concentration steps. It was calculated the regression line, the zinc content was determined from the intercept with the abscissa of the line. Using the data set, first it was tested the reproducibility of the standard addition method. The recoveries were within 97.7–122.8 % depending on the salt content of the water. The recovery values are close to 100 %, with most samples within the error of determination, so the standard addition method could be considered as the reference method. The results of the determination of zinc content of waters are summarized in Table II.

Table II

Results of analysis of water samples (n = 4)

Water sample		Concentration ($mg.l^{-1}$, by calibration)	Concentration ($mg.l^{-1}$, by standard addition)	Recovery (%)
Tap water		0.024 ± 0.011	0.022 ± 0.010	116.1
River water	Someş	Lower than detection limit	Lower than detection limit	-
Sea water	Black Sea	0.660 ± 0.012	0.575 ± 0.021	102.8
Mineral water	“Anavie”	0.039 ± 0.014	0.030 ± 0.015	91.9
	“Borsec”	0.085 ± 0.014	0.079 ± 0.011	119.7
	“Perla”	0.040 ± 0.014	0.044 ± 0.018	101.1
Well water	Nr. 1	0.048 ± 0.018	0.039 ± 0.020	97.7
	Nr. 2	2.993 ± 0.020	2.259 ± 0.030	122.1
	Nr. 3	0.025 ± 0.018	0.020 ± 0.011	91.9
	Nr. 4	0.295 ± 0.010	0.230 ± 0.015	104.2

The results of the two methods agree for the most of water samples, they are within the errors of the determinations (low salt content waters). Greater differences were obtained for sea water- and well water samples (Nr.2 and Nr.4), having a higher salt content. These differences could be attributed to the nonspecific absorption, due to incomplete evaporation of the sample in the low temperature M-A flame (light scatter) and the lack of the background correction (the spectrohotometer is not equipped with such a device). In these cases the standard addition method offers better results, closer to the real zinc content of waters For the low salt content waters the calibration method gives acceptable results, for the higher salt content waters the standard addition method is recommended. In conclusion zinc can be determined precisely in natural waters using the M-A flame.

CONCLUSIONS

In the M-A flame zinc exhibits a strong absorption of the resonance line, at the 213.9 nm. The absorption varies with the hollow-cathode lamp current, with the composition of the flame and observation height. The optimal lamp current is of 3 mA, that of observation height over the burner head is 7 mm, in stoichiometric flame (RSU = 1.00). The presence of K, Na, Ca, Mg, Al, SO_4^{2-}, and PO_4^{3-} do not effect the absorption of zinc. The absorption-concentration relationship is linear in the 0.01-6 $mg.l^{-1}$ range, the detection limit is of 0.006 ± 0.004 $mg.l^{-1}$ of zinc. The zinc content of natural waters can be determined precisely using the calibration or the standard addition method. In conclusion, M-A flame is a suitable for precise atomic absorption determination of zinc in natural waters.

REFERENCES

1. I. Pais, *A mikroelemek jelentösége a mezögazdasági termelésben. Kutatásuk helyzete a világban*, Kertészeti Egyetem, Budapest, 1984, p.11.
2. G.F. Kirkbright, M. Sargent, *Flame atomic absorption and fluorescence spectroscopy*, Academic Press, London, New York, San Francisco, 1974.
3. H. Armannson, *Anal.Chim.Acta*., 1979, **110**, 21.
4. S. Olsen, L.C.R. Pessenda, J. Ruzicka, E.H. Hansen, *Analyst* ,1983, **108**, 905.
5. A.S. Attiyat, G.D. Christian, *Talanta*, 1984, **31**, 463.
6. I. Gustavsson, L.. Hansson, *Int.J.Environ.Anal.Chem*., 1984, **17**, 57.
7. P. Koscielniak, *J.Anal.At.Spectrom*., 1987, **2**, 329.
8. T.V. Rodionova, V.M. Ivanov, *Zh.Anal.Khim*., 1986, **41**, 2181.
9. V.N. Savitskii,V.I. Peleshenko,V.I.Osadchii, ***Zh.Anal.Khim*., 1987,** 42**, 677.**
10. A.K. Singh, T.G.S. Kumar, *Microchem.J*., 1989, **40**, 197.
11. S. Hirata, K. Honda, T. Kumamaru, *Anal.Chim.Acta*, 1989, **221**, 65.
12. Z. Wang, S.Luo, Z. Gong, *Fenxi Huaxue*, 1990, **18**, 859.
13. H. Matusiewicz, R. Sturgeon, V.Luong, K.Moffatt, *Fresenius'J.Anal.Chem*., 1991, **340**, 35.
14. P. Bermejo-Barrera, R. Dominguez-Gonzalez, R. Soto-Ferreiro, A. Bermejo-Barrera, *Analusis*, 1995, **23**, 135.
15. F. Garcia-Sanchez, A. Navas-Diaz, Arbaizar, *Mikrochim.Acta*, 1995, **118**, 265.
16. G.I. Tsizin, E.M. Sedykh, L.N. Bannykh, N.M. Sorokina, Yu.A. Zolotov, *Zh.Anal.Khim*., 1995, **50**, 76.
17. J. Mohay, Z. Végh, *Fresenius' Z.Anal.Chem.*, 1988, **329**, 856.
18. J.A.F. Gidley, D.T Jones, *Analyst*, 1960, **85**, 249.
19. J.A.F. Gidley, D.T Jones, *Analyst*, 1961, **86**, 271.
20. A.G. Gaydon, H.G. Wolfhardt, *Flames, their Structure, Radiation and Temperature*, Chapman and Hill, New York, 1970.
21. E. Cordoş, L.N. Kékedy, R. Hui, *Patent RSR*, nr. 67867 / 1977.
22. L. Kékedy-Nagy, *Talanta*, 1997, **44**, 1919.
23. L.S. Clesceri, A.E. Greenberg, R.R. Trussel, *Standard Methods for examination of water and wastewater*, 17th Edition, Ed. 1-30, 1989 APHA – AWWA – WPCF.
24. C. Liteanu, I. Rîcă, *Statistical Theory and Methodology of Trace Analysis*, John Wiley, New York, 1980.
25. D.L. Massart, B.G.M. Vandeginste, S.N. Deming, Y. Michotte, L. Kaufman, *Chemometrics: a textbook*, Elsevier, New York, 1988.