



STUDY ON THE APPLICATION OF ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROMETRY FOR THE DETERMINATION OF METALLIC Cu, Pb, Zn, Cd TRACES IN SEA WATER SAMPLES

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ABSTRACT: The trace amount of some heavy metallic elements (Cu, Zn, Pb, Cd) in sea water samples were determined directly (without separation) and quantitatively by using Electro-Thermal Atomization Atomic Absorption Spectrometry (ETA-AAS). The effect of mainly major constituents such as Na, Mg, Ca, K, and the mutual effect of the trace elements, which were present in the matrix on the absorption intensity of each analyzed element was studied. The adding of a certain chemical modification for each trace element was also investigated in order to eliminate the overall effect of the background during the pyrolysis and atomization. The sea water sample after filtering through a membrane with 0.45 μ m-hole size was injected in to the graphite tube via an autosampler (MPE50). The absorption intensity of each element was then measured on the VARIO-6 under the optimum parameters for spectrometer such as: maximum wavelength, current of hollow cathode lamp, and that for graphite furnace such as dry temperature, pyrolysis temperature, atomization temperature, ect.

The analytical procedures were set-up and applied for the determination of these above mentioned elements in the synthesized sea water sample and in the real sea water samples with high precision and accuracy.

I. INTRODUCTION

The Earth is covered more than 70 percent of area by Oceans and Seas. Sea water is the precious resource for the human due to the role of climate regulation and that of the ensurance of mankind life. Oceans and seas contain a huge volume of water, and they thus became the human's ideal places for waste deposition from long time ago[1]. As the risk of environmental pollution caused by the human activities has been increased, the research on hydrometeorology (including marine hydrometeorology) over the world has been concentrated for finding out the causes and the rule of pollution [2,3]. The estimation of chemical compositions of sea water and the content of soluble heavy metal ions such as Cu, Pb, Zn, Cd... in sea-water area where the monitoring was taken place by the seasons and time and their changes have been the important tasks on the research of marine environment, that were carried out systematically via the monitoring stations setting up along the coastal north-east sea's region of our country by Center for Marine Hydrometeorology.

The quantitative determination of these mentioned above elements is rather difficult due to their low contents in high salinity. Nowadays, the popular methods for analysis of these trace amounts are often the advanced techniques such as ICP-AES, ICP-MS, TXRF, NAA...in conjunction with the chemical pre-treatment[4,5,6,7,8]. For serving the demands from the research of marine environment, and to introduce the sufficient analytical procedures in the routine works, and from the fact that the advantageous technique, which has been employed for recent years in the world is AAS with the support of electrothermal atomization in a graphite furnace, the atomic absorption spectrometry (AAS) is selected. With the use of this technique, the trace

elements in high salinity matrix can be determined directly (without any chemical pre-treatment) and quantitatively.

II. EXPERIMENTAL

II.1 Chemicals and Apparatus

All chemicals are of the analytical grade. The standard stock solutions (Cu, Pb, Zn, Cd) 1000 µg/ml for AAS (made of Merck company) were used for the study. High purity deionized distilled water (with the resistance ~18MΩ) was used for further dilution.

Argon Gas with high purity (99,999%).

Atomic Absorption Spectrometer VARIO-6 (Analytik Jena AG, equipped with the auto-optimization of selected parameters) with graphite furnace function (the atomization took place in a graphite wall-type tube) in connection to an Auto-sampler MPE50.

Vacuum pump (GAST DOA-P725-BN, made in USA) was used for the filtration of the sample solutions (through the filtrate membrane with 0.45 µm hole-size).

II.2 Procedures

The experiments were carried out at room temperature. The test solutions were prepared by mixing the standard solutions at a certain concentration.

The sea water samples in accordance with specifications[5] after receiving from the sender were filtered through a membrane with 0.45 µm hole-size and it would be ready for the determination of the trace elements using AAS or for further chemical treatment before the measurement if it was required.

A portion of sample was added a certain volume of dilute HNO₃ for getting 0.5% HNO₃ in the final solution. This solution with or without a certain amount of a modifier was filled up in a 2 ml-measuring cup on a tray of Autosampler MEP-50, then the measurement of the absorption intensity of each element was taken place on ETA-AAS under the optimum parameters such as the max. wavelength, hollow-cathode current for spectrometer, measured mode (Peak Height or Peak Area), dry temperature, pyrolysis temperature, atomization temperature, clean temperature, and the ramp of each step for graphite furnace.

III. RESULTS AND DISCUSSION

III.1 The Effect of some mainly major components in sea water on the Absorption Intensity of Cu, Pb, Zn, Cd

Due to the high salinity, the sea water gave a rather thick matrix with the high content of Na, Mg, Ca, and K. The effect of these major elements on the absorption intensity (Abs.) of each analyzed element was studied. Figure 1 showed an example of the interference caused by sodium. The adding of Na ion influenced with the absorption of whole studied elements. It enhanced very much the Abs. of Zn, a little value of Pb but impaired the Abs. of Cu and Cd when Na concentration is about 11 mg/ml, which is similar to that in sea water. The presence of Mg and Ca in sea water also caused the severe influence with these element traces while K ion seemed not interfere with the Abs. of all analyzed elements.

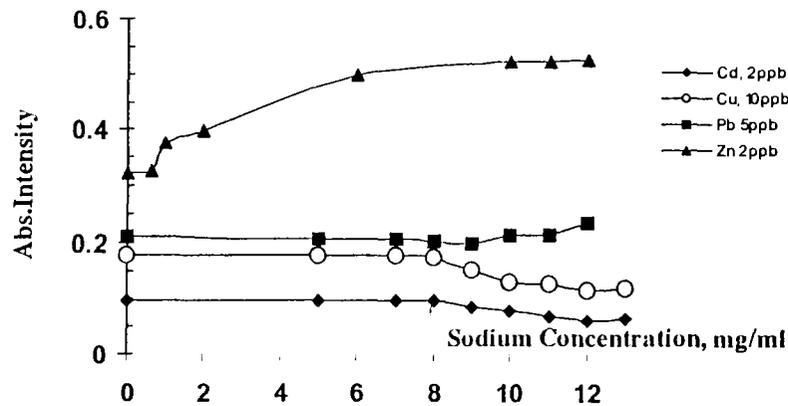


Fig.1 Effect of Sodium Ion on the Absorption Intensity of Cu, Pb, Zn, Cd

III.2 The Effect of some trace elements, and mutual effect of the analyzed elements on the Absorption Intensity of Cu, Pb, Zn, Cd

At the same level of concentration in sea water, only few trace elements showed the interference with each other on its determination due to the advantages of the selectivity, which was supplied by the hollow cathode lamps. Figure 2 showed an example of the mutual effect of some trace elements being present at the background on Abs. of lead trace. Ni trace seemed influence with the Abs. of Pb seriously even its content was equal to that of Pb. Overall effect caused by the trace elements accompanied with Pb in sea water lowered the Abs. of Pb about 35%. It was thus required to eliminate this interference for the quantitative determination of Pb.

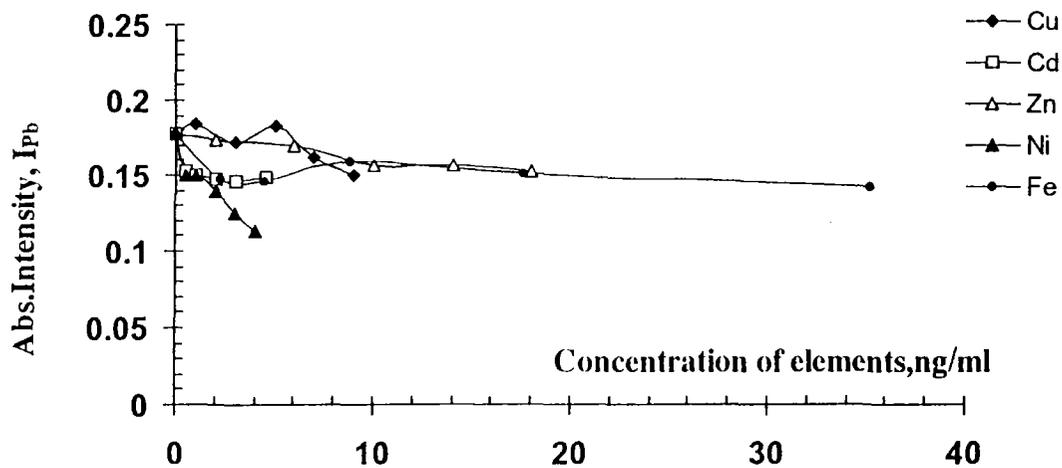


Figure 2: Effect of some trace elements in sea water on the Lead Absorption Intensity

III.3 Adding the chemical modifications for eliminating the background interference

Due to the advantages when using graphite furnace, the adding a certain modifier to the sample solution was simply and effectively for reducing the background interference during the pyrolysis[9,10,11,12]. The addition of 20mg/ml NH_4NO_3 or a mixture of 20 $\mu\text{g}/\text{ml}$ $\text{Pd}(\text{NO}_3)_2$ and 10 $\mu\text{g}/\text{ml}$ Ascorbic acid could overcome the severe influence of the matrix with the Abs. of Cu or Pb. Similarly, the interference of the matrix on the determination of Cd and Zn was eliminated when the mixture of 20 $\mu\text{g}/\text{ml}$ $\text{Pd}(\text{NO}_3)_2$ and 10 $\mu\text{g}/\text{ml}$ Ascorbic acid or only 20 $\mu\text{g}/\text{ml}$ $\text{Pd}(\text{NO}_3)_2$ was added into the sample solution.

III.4 Linearity and the Calibration of Cu, Pb, Zn, Cd

The linearity was received for all analyzed trace elements within the studied range of concentration. The dependency of the absorption intensity of each element on its concentration was studied in the presence of an artificial sea water background [5] and the calibrations were then plotted for each element trace. Figure 3 showed the results.

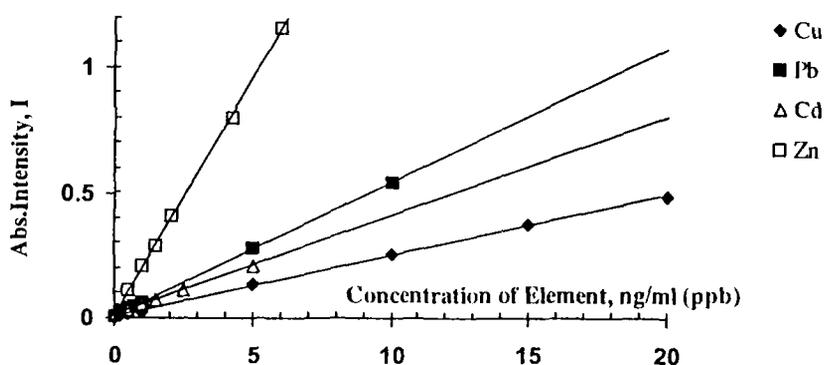


Figure 3: The Calibration for the determination of Cu, Pb, Zn, Cd in Sea Water

III.5 Analysis of sea water samples

Table 1: Analysis of an Artificial Sea Water Sample (SSTD)

Trace Element	Certified Value ($\mu\text{g}/\text{l}$)	Found Value ($\mu\text{g}/\text{l}$) by ETA-AAS	Error (%)	Found Value ($\mu\text{g}/\text{l}$) By ICP-AES
Cu	5.010	5.114 \pm 0.025	+ 2.10	4.948 \pm 0.153
Pb	2.498	2.314 \pm 0.003	- 7.40	2.420 \pm 0.012
Zn	10.000	10.056 \pm 0.021	+ 0.56	9.886 \pm 0.012
Cd	2.513	2.717 \pm 0.003	+ 8.12	2.425 \pm 0.012

Table 2: Analysis of the Sea Water Samples

Sample Code	Cu ($\mu\text{g/l}$)		Pb ($\mu\text{g/l}$)		Zn ($\mu\text{g/l}$)		Cd ($\mu\text{g/l}$)	
	by AAS	by E.C.	by AAS	by E.C.	by AAS	by E.C.	by AAS	by E.C.
03-01	3.965 \pm 0.103	4.085 \pm 0.032	0.725 \pm 0.060	0.676 \pm 0.076	6.674 \pm 0.015	6.551 \pm 0.072	0.665 \pm 0.035	0.771 \pm 0.026
03-02	7.005 \pm 0.070	7.136 \pm 0.021	0.823 \pm 0.017	0.767 \pm 0.035	12.350 \pm 0.005	12.690 \pm 0.033	0.534 \pm 0.033	0.541 \pm 0.019
03-03	4.346 \pm 0.063	4.253 \pm 0.083	0.793 \pm 0.022	0.727 \pm 0.052	10.360 \pm 0.024	9.166 \pm 0.056	0.475 \pm 0.026	0.433 \pm 0.044
03-04	3.123 \pm 0.032	3.175 \pm 0.019	0.837 \pm 0.019	0.780 \pm 0.039	13.210 \pm 0.011	13.422 \pm 0.054	0.541 \pm 0.052	0.507 \pm 0.061
03-05	2.440 \pm 0.001	2.413 \pm 0.046	0.824 \pm 0.034	0.767 \pm 0.041	8.651 \pm 0.016	8.413 \pm 0.029	0.428 \pm 0.056	0.397 \pm 0.048

E.C. = Electrochemical method

An artificial sea water sample and five sea water samples were analyzed according to the studied procedure. The metal ion concentration was then calculated on the base of calibration, and the result was given in Tables 1 and 2. Due to the lack of the Certified Reference Materials, the artificial sea water sample, which was prepared [5] and the contents of trace elements was analyzed by using a standard procedure on ICP-AES [8] was used for the statistic evaluation and for the comparison of the accuracy obtained from the studied analytical technique. The results agreed well with that received from a common electrochemical method and the data showed reasonable deviation and high reproducibility.

IV. CONCLUSION

The work has been fully achieved the aiming goals as the following.

- The necessary physical parameters for the determination of Cu, Pb, Zn, Cd on the AAS VARIO 6 with ETA-AAS mode were selected and optimized using an automatic controller supplied by a special WINAAS software computer program.
- The effect of some mainly major components such as Na, Mg, Ca, K and that of several metallic trace elements in matrix of sea water sample solution on the determination of Cu, Pb, Zn, Cd was studied, and the optimum conditions for determining these elements were established, the analytical procedures were then set up for the quantitative analysis of trace heavy metal ions in sea water samples.
- The application of the studied results in the analysis of sea water samples was thus carried out in the laboratory of Center for Analytical Chemistry &

Environment, ITRRE. The statistic data showed the reliable reproducibility and high precision and accuracy.

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