DETERMINING FLOTATION CONDITIONS
OF ZINC WITH COPPER α-BENZOIN-OXIME

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ABSTRACT

Precipitation flotation conditions of zinc which is an essential element for living organisms are determined by using copper-α-benzoin-oxime as a new type of carrier. The effects of pH change, amounts of α-benzoin-oxime and copper and formation period of related complexes as well as the effect of various other metals are reported. With this method, concentration of zinc was increased 20 times together with 95% recovery. The detection limit for zinc was found to be 1.375 µg/L by use of flame atomic absorption spectrometry.

KEYWORDS:
Zinc, drinking water, flotation, copper alpha-benzoin-oxime, AAS.

1. INTRODUCTION

Zinc is present in several foodstuffs and the environment allowing plenty of samples for its analysis [1]. Zinc has an important role in terms of health and well-being, and it is a mineral that needs to be present in almost all living cells [2] as it is used as enzyme activator for several enzymatic reactions in the human body. Toxicity level of zinc and many zinc compounds is usually low. In very high doses of zinc have negative impact on all creatures as well as on the environment. Pre-concentration or separation must be applied for analytic determination when very low levels of zinc are to be determined since natural abundance is usually low. Voltammetry, flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) or induced plasma atomic emission spectrometry (ICP-AES) are frequently used methods to determine zinc levels. With reported zinc determination, limits are 8.0 ng/ml Zn for FAAS, 1 ng/ml Zn for GFAAS or 0.05-1.3 ng/ml Zn for ICP-AES, respectively [3]. Flotation method is proven to be simple when compared to other pre-concentration methods, such as liquid–liquid extraction, ion change and co-precipitation. Therefore, it is especially advantageous in saving time and resources when working with large volumes of samples [4]. Flotation techniques were originally developed for enriching low concentration of heavy metals in natural waters. It is also possible to separate and pre-concentrate metals by using ion flotation method, as phenyl benzoquinone monophenyl thiosemicarbazone and zinc are enriched and separated from human bio-liquid and pharmaceutical samples by means of this method [5]. Precipitation flotation method found applications from determining fluoride levels from wastewaters to producing semi-conductors containing fluoride [6]. There are a number of studies reported in literature separating zinc by means of colloidal precipitation flotation with collectors, such as iron (III) oxide and aluminum (III) oxide, or ion flotation with dithiocarbamate derivatives. Cundeva and Staříkov [7] studied pre-concentration of zinc by using colloidal precipitation flotation and determined its level by flame atomic absorption spectrometry. Both iron (III) oxide and iron (III) tetra-methylene-dithiocarbamate are used as colloidal collector reagents. Iron (III) oxide is used as the first collector reactive during co-precipitation at the time of induction, whereas iron (III) tetra-methylene-dithiocarbamate is used as the second collector reactive for improving pre-concentration. As being robust, fast and cost-effective, colloidal precipitation flotation ensures easy separation and concentration of heavy metals from sample matrix. For example, the readings on AAS, Cd, Cu, Fe, Ni, Pb, Zn and Tl, are separated and concentrated by the use of this method prior to determining their levels by using cobalt hexa-methylene-dithiocarbamate as collector reactive during pre-concentration [8]. Likewise, it is proven that cobalt (III) hexa-methylene-dithiocarbamate can be used in flotation method as collector reactive during pre-concentration for nickel, iron and lead ions in waters before determination on AAS [9]. In this study, copper α-benzoinsxime is used as a carrier to enrich zinc concentration and improve flotation conditions. High levels of recovery, short process durations, low quantities of chemicals used, and cost-effective equipment can be listed as advantages of the proposed method. Although, the chelating agent has been used with different methods to determine other metals, this is the first time, it has been used to determine Zn concentration.

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2. MATERIALS AND METHODS

2.1. Reagents

Zinc standards were prepared from 1000-ppm zinc stock solution. Copper solution was prepared from Cu(NO₃)₂·2.5H₂O (Merck) solid. 0.05% α-benzoin-oxime (Merck) was prepared by dissolving it in 0.25 M NaOH (Merck) solution, and pH value of the environment was adjusted with NaOH and HNO₃ solutions. The ionic intensity of the environment was ensured with saturated KNO₃ (Merck). 0.5% of sodium dodecyl sulphate (NaDDS) used as surface active substance was prepared in ethanol solvent of 96%. 0.1 M NH₄NO₃ (Merck) solution was used for elution and 4 M HNO₃ (Merck) and concentrated HNO₃ for dissolving the precipitate formed. Ethanol and concentrated HNO₃ solution were used for cleaning the colon at the end of flotation. All solid chemicals were of analytical purity and de-ionized water was used during all experimental stages. A simple procedure was applied for analyzing zinc in drinking waters. Drinking water samples were collected from Anatolian Side of Istanbul and Izmit Umuttepe. For this purpose, polyethylene tanks were pre-processed with concentrated HNO₃ and washed with de-ionized water. Water samples were filtered to eliminate possible impurities. 1 ml of concentrated HNO₃ (68%) was added to water samples in order to prevent possible hydrolytic precipitation of some mineral salts, and it was ensured that water samples are kept within the pH range of 2-3 providing protection for the samples.

2.2. Apparatus

A colon having a length of 70 cm and a diameter of 4 cm was used for flotation. Filtering funnel number 4 was attached to the end of the colon. This system was placed on a desiccator with a grinding cover and side outlet. A pH-meter (Hanna pH 211) with combined glass electrode was used for pH measurements. Kika model magnetic mixer and an Ulvac brand vacuum pump were also used. Zinc quantity analysis was conducted with a Perkin Elmer model Flame A Analyst 800 Atomic Absorption Spectrometer (see Table 1).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyte</td>
<td>Zn</td>
</tr>
<tr>
<td>Wavelength (nm)</td>
<td>213.9</td>
</tr>
<tr>
<td>Lamp current (mA)</td>
<td>15</td>
</tr>
<tr>
<td>Spectral width slit (nm)</td>
<td>0.7H</td>
</tr>
<tr>
<td>Flame</td>
<td>Air / acetylene</td>
</tr>
<tr>
<td>Acetylene flow rate (L/min)</td>
<td>2.0</td>
</tr>
<tr>
<td>Background correction</td>
<td>Cu</td>
</tr>
<tr>
<td>Time of measurement (sec)</td>
<td>3</td>
</tr>
</tbody>
</table>

2.3. Flotation Procedure

When calibration of pH-meter was performed, 500 ml of de-ionized water was added to a 600-ml beaker, and pH electrode was submerged into the solution. 3 ml saturated KNO₃ was added to the beaker on the magnetic mixer for the purpose of adjusting the intensity. 0.5 ml of 0.05% α-benzoin-oxime was added, and then pH was brought to 10.25 with 0.25 M NaOH, and 2500 µg Cu²⁺ were added. This was followed by the addition of 1 ml 25 ppm Zn²⁺ to standard solution. The whole solution was mixed for 15 min during which blue-green precipitation was observed. Changes of pH which occurred during precipitation formation were adjusted with diluted NaOH and HNO₃ solutions. At the end of this duration, 1 ml of 0.5% NaDDS was added, and it was mixed for one more min but then the magnetic mixer was turned off. Beaker, magnet and surface of the electrode were washed with 0.1 M NH₄NO₃ solution in order to clean remaining complexes. Elution solution was also transferred to the colon. After transferring the solution and elution solution to the flotation colon, ventilation was carried out for 1-2 min by means of pendant switch at the bottom of the colon through which air bubbles were provided. Once it was observed that the complex was formed (air bubbles in the upper part of colon resembling foam), the solution was restored until it becomes clear. Subsequently, vacuum pump was connected to the side outlet of the desiccator and the solution was taken from the bottom part of the colon and collected entirely in the desiccator apart from the complexes, as they remained in sintered parts and walls of the colon. Waste solution in the desiccator located at the bottom of the flotation mechanism was discharged, and a graduated cylinder of 100 ml was placed in the desiccator in a manner that its opening will be to the funnel at the end of the colon. For the purpose of removing the complex remaining on the colon walls and dissolving the complex, the colon was dissolved with concentrated HNO₃ that was heated up to a certain level in order to generate 2.5 ml of vapor. Acid solution collected at the bottom of the colon was drawn by means of a capillary connected to the end of pendant switch and colon walls were cleaned once again. Later on, the colon was cleaned 3 more times with 5 ml of HNO₃ which was heated up to a certain level in order to generate 4.0 M of vapor. All the complexes on the walls were thus cleaned. By making use of the vacuum pump, highly acidic solution was collected in the graduated cylinder placed in the desiccator. The solution in the graduated cylinder was transferred to a 25-ml volumetric flask, and it was topped up to this level by adding 4.0 M HNO₃ solution to prepare for FAAS measurement. After each flotation process, the colon was filled with distilled water twice to clean it. At the end of an experiment, the colon was cleaned twice more with distilled water, and this time followed by ethanol.

3. RESULTS AND DISCUSSION

3.1. Change of pH and Its Effect on Flotation

The most important step of this method is the improved step of determining the pH during the co-precipitation step, and pH value indicates the degree and marking of the load on the surface of collector particles. Hence, pH has a direct impact on complex formation with analyte...
as well as on all types of formation systems and their
terminated by collectors. Furthermore, it
has an impact on the stability of the foam during pH flota-
tion step and successful separation of solids from liquid phase
[8]. pH values lower than 8.0 are not used in this study, since
it was reported that it does not form an α-benzoin-oxime
complex with copper. Therefore, pH is adjusted to 8, 9,
10, 10.25, 10.50 and 11 by using 0.25 M NaOH, and with
diluted HNO₃ for the purpose of determining optimum pH
of the flotation process conducted. The amounts of 2.5 mg
copper, 0.5 ml 0.5% α-benzoin-oxime and 1 ppm zinc
appeared to be measures for stability. With lower pH values,
formation of precipitation is not observed. It is specified that
flotation can not be realized due to partial protonation of
surface active substance if pH is between 3–5 in the envi-
ronment where alcohol solution of sodium dodecyl sulfate
is present, and that metal recovery is increased when pH
is more than 6 [10]. Graph in Fig. 1 (pH vs. recoveries cal-
culated from the data obtained from FAAS) shows that the
optimum pH value is 10.25. pH values are adjusted with
appropriate concentrations of NaOH and HNO₃. As a
result of the flotation, it is observed that zinc does not
cause white precipitants in the form of zinc-oxide and
zinc-hydroxide even if it is exposed to high levels of pH.
Precipitant color is blue-green at pH 10.25, and the high-
est recovery is achieved with this value. Zinc ions were
not discovered in the filtrate by using FAAS.

![Graph](image1)

**FIGURE 1** - Optimum pH values (flotation conditions; 2.5 mg
Cu(II), 0.25 mg α-benzoin-oxime, 1 ppm Zn(II)).

3.2. Examining impact of copper quantity

Impact of the amount of copper on the complex formed
with α-benzoin-oxime and on zinc recovery was determined
by adding different quantities of copper (Fig. 2). As a result
of the flotation formed by taking 500 ml from 5 mg/ml
copper solution, the rate of recovery was approximately
95%. Interference of high copper quantity during 20 times
concentration of zinc has an impact on flotation produc-
tivity. Copper acts as the carrier element as well as the ele-
ment forming collector reactives.

3.3. Determining the optimum of α-benzoin-oxime quantity

At this stage, α-benzoin-oxime quantity in the envi-
ronment is changed for flotation; a series of flotations
were performed on an environment where 2.5 mg copper

![Graph](image2)

**FIGURE 2** - Optimum copper quantity (flotation conditions; 0.5-5 mg
Cu(II), 0.25 mg α-benzoin-oxime, pH 10.25, 1 ppm Zn(II)).

![Graph](image3)

**FIGURE 3** - Optimum α-benzoin-oxime quantity (flotation condi-
tions; 0.05-0.5 mg α-benzoin-oxime, 2.5 mg Cu(II), pH 10.25, 1 ppm
Zn(II)).

at pH 10.25 is present, and the recoveries calculated by
using results obtained from FAAS of α-benzoin-oxime are
displayed in Fig. 3 where it is determined that the optimum
quantity is 0.25 mg. Plenty of agent-forming chelate should
be added in order to form metal complexes in quantitative
terms. As for the impact of collector reactive on the flota-
tion during co-precipitation, it is specified that recovery of
metal under examination is stable after α-benzoin-oxime
quantity increases to a certain level [11].

3.4. Selection of surfactant

Sodium dodecyl sulfate (NaDDS), an anionic surface
active substance, is used in this study. Adding surface ac-
tive substance provides a significant advantage for turning
hydrophilic parts on the surface of floating types into hy-
drophobic ones, and for separation of so formed metal che-
late from diluted phase on the foam layer [5]. Furthermore,
formation of excessive foam quantity makes it difficult to
take precipitants from the flotation colon, and also dissolu-
tion in concentrated nitric acid [12-13]. The same flotation
procedure is performed with linear alkyl benzene surface
active substance which is also an anionic surface-active sub-
stance. However, zinc recovery obtained is lower than that
of flotation process performed with NaDDS. Hence, lin-
ear alkyl benzene surface active substance is not used for
any other procedure.
3.5. Complex formation duration

A certain period of time is necessary for forming complexes on flotation process with co-precipitation. Complex formation periods of 5, 15 and 30 min were employed in this study, and it was found that the optimum zinc recovery is achieved with the period of 15 min. This period of time was also used on several flotation studies with co-precipitation reported in the literature [7-11].

3.6. Study of interference with other metals

Utilization of solutions prepared by starting from nitrate salts of cadmium (II) (Cd), lead (II) (Pb), calcium (II) (Ca) and cobalt (II) (Co) ions and interference of these metals to the process of zinc determination were investigated. Zinc recovery in the presence of these metals and their impact on the recovery turned out to be different from what was originally expected. As it can be seen from Table 2, zinc recovery is increased if concentrations of Cd(II), Pb(II) and Co(II) metal ions are increased. However, there is a decrease with Ca(II) metal ions. The reason for this might be that these metals have an impact on the complex formed by Zn(II) and copper-α-benzoinoxime during co-precipitation. Furthermore, this incident resembles the impact of salt on extraction techniques. But this requires a further study.

<table>
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<tr>
<th>Sample</th>
<th>Added (µg/l)</th>
<th>Estimated (µg/l)</th>
<th>Found (µg/l)</th>
<th>R (%)</th>
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<tbody>
<tr>
<td>Ičmit-Umâyîlêpê</td>
<td>4</td>
<td>36.00</td>
<td>35.10</td>
<td>97.5</td>
</tr>
<tr>
<td>Tap water</td>
<td>8</td>
<td>40.00</td>
<td>39.90</td>
<td>99.8</td>
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<table>
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<th>Sample</th>
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<th>Found (µg/l)</th>
<th>R (%)</th>
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</thead>
<tbody>
<tr>
<td>Içmit-Umâyîlêpê</td>
<td>-</td>
<td>-</td>
<td>1103</td>
<td>-</td>
</tr>
<tr>
<td>Anatolian Side</td>
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<td>1107</td>
<td>1062</td>
<td>95.9</td>
</tr>
<tr>
<td>Tap Water</td>
<td>8</td>
<td>1111</td>
<td>1072</td>
<td>96.5</td>
</tr>
</tbody>
</table>

4. CONCLUSION

Co-precipitation process is applied for pre-concentration of zinc with copper-α-benzoinoxime precipitant reactive. Flotation process is frequently used for pre-concentration of metal ions since it is a cost-effective, easy and sensitive method. Zinc is 20-fold concentrated from a diluted solution. The conditions required for flotation in order to pre-concentrate zinc 20 times were established as follows: 10.25 for the pH value of basic medium, 2.5 mg Cu (II) ion, 0.5% 0.05% α-benzoinoxime and NaDDS surface active substance. More than 95% zinc recovery is achieved with these optimum conditions. Furthermore, impact of interference of Pb (II), Ca (II), Cd (II) and Co (II) ions into flotation conditions are also reported, and it appears that apart from Ca, the rest have a positive influence with increased concentrations.

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