Determination of zinc in corn plant by FAAS after sorption on amberlite resin XAD-16 impregnated with 1, 4-diaminoantraquinone

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Abstract

The present paper describes a procedure for separation, pre concentration and sequential determination of trace amounts of zinc in corn plant, by Flame Atomic Absorption Spectrometer (FAAS). It is based on acid digestion of samples with nitric and sulfuric acid and then passing the bufferized sample through the column containing impregnated resin for pre concentration of interest ion. After adsorption of metal ions on solid phase, adsorbed ions were eluted using HCl (2M) as eluent and subsequent determination was done with FAAS. For access to the highest recovery, various parameters such as PH, ionic strength, type of eluent, sample and eluent flow rate were optimized. In this manner, the recovery obtained, was quantitative (95%) and LOD (3Sb/m), RSD were obtained 1.2µg.ml⁻¹, 6.7% respectively.

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**Introduction**

Zinc is a micronutrient, meaning it is in very small amounts by the corn plant. Even though zinc is needed in small amount, it has a huge impact on how a corn plant grows and ultimately how much yield is produced (Johnson, 1999). Zinc plays a critical role in corn plant as follows:

- Aids to the synthesis of growth hormones and proteins
- It is needed in the production of chlorophyll and carbohydrate metabolism
- It is essential for the transportation of calcium throughout the corn plant
- Necessary for cell elongation, the increase in leaf and node size along with grain formation.

While zinc efficiency in corn result in poor root development, stunted growth, small leaves, shortened internodes, delayed silk, and chalky kernels (Rehm et al., 2002).

Determination of this heavy metal in corn plant in trace amount is a task for analytical chemist’s. However, in many cases the available analytical instrumentation does not show enough sensibility for the realization of the analysis in these natural samples (Christian, 1994).

There are several methods for the determination of metal ions. The two most frequently used methods are flame atomic absorption spectrometry and electro thermal atomic absorption spectrometry (Cai et al., 2002), (Cerutti et al., 2003), (Tobiasz et al., 2009).

Solid phase extraction technique is used in the wide range for pre concentration and separation of ultra trace metal ions. In conventional solid phase methods, a polymeric matrix used to bind the chelating reagents on it through chemical reactions. But its application was limited for not having economic treatment in wide range and need to long time for chemical binding of chelating agent to polymeric support (Jain et al., 2006), (Hennion, 1999), (Reis et al., 2000), (Teixeira et al., 2000), (Teixeira et al., 1998), (Juang and Su, 2004). Alternatively, solvent impregnated resins (SIRs) do not have the problems of conventional adsorbent resins and benefit from advantages of LLE and SPE. Furthermore, high capacity and metal binding strength are the other important characteristics of the SIRs (Prabhakaran and Subramanian, 2004), (Prabhakaran and Subramanian, 2003), (Hosseini and Hosseini-Bandegharari, 2011).

In this work we have used from amberlit resin XAD-16 impregnated with chelating agent 1, 4-diaminoantraquinone as adsorbent solid phase that packed in mini column. Adsorbent process was done after passing analytical sample through the column and then elution done via HCl as elution. Finally determination was done using atomic absorption spectrometer.

**Materials and methods**

All the materials used, were of analytical grade and supplied by E.Merk, Darmstadt, Germany. Stock solution of Zn (II) ion was prepared at concentration of $1.0 \times 10^{-3}$ M by dissolving the appropriate amounts of its nitrate salt in deionized water and diluting to the mark (100 mL) with distilled water.

The following buffer solutions with concentration of 1M were made and used to adjust the pH and strength of the working solutions: acetic acid/sodium acetate for pH 4-6; ammonium nitrate/ammonia for pH 6-9 and HCl/NaOH for PH over than 9. The working solutions were adjusted at the pH 9 and ionic strength of 0.05M using ammonium/ammonia buffer solution. These solutions were prepared daily by diluting the stock solution.

A corning 130 model pH-meter was used for pH measurement. A flame atomic absorption spectrometer with Variant AA240 model was used for all absorbance measurements. Finally, for indicating of morphology difference between XAD-16 resin before and after impregnation, the scanning electron microscopic (SEM) micrographs were obtained using a VEGA/TESCAN instrument at an accelerating voltage of 25 kv.
**Preparation of SIR**

1.5000g of chelating agent DAAQ (1, 4-diaminoantraquinine) was located into a 100ml stopper flask and mixed manually. Then 30ml 1, 2-dichloro ethane was added to it and mixture was mixed for a few minutes to disperse chelating agents into solvent. After that, exactly 1.5000g of the amberlit resin was added to the mixture and shaken for at least 24 h. After separation of impregnated resin beads with a porous filter, they were rinsed with aliquots of distilled water and HCl 6M until the filtrate solution didn’t show absorbance against distilled water. Figure 1 shows SEM micrographs of amberlit resin before and after impregnation with chelating agent 1,4-diaminoantraquinone.

**The determination procedure**

100ml sample solution containing Zn^{2+} with concentration exactly 10^{-6} M was passed through a mini column (10cm length and 5mm diameter) packed with 0.7 g impregnated resin at flow rate 1ml/min. After that, the column was eluted with 15ml deionized water for removing free pollutants. Then elution process was done by 5ml HCl 2M at flow rate 0.5ml/min. The effluent was subjected to the FAAS for the Zn (II) determination.

For access to the highest recovery, various parameters such as PH, ionic strength, type of eluent, sample flow rate and eluent flow rate were optimized.

**Results and discussion**

**Effect of PH on the extraction of the Zn (II)**

For investigation of this parameter, various buffer solutions of Zn (II) in the PH range of 2-11 was prepared. Then, these solutions were passed through the column at flow rate 1ml/min. Elution process was done using 5ml HCl 2M at flow rate 0.5ml/min. The results show that the best recovery is gained at PH=9. At PH upper this amount, absorbance is decreased that is probably related to precipitation or complex formation of Zn (II) with hydroxyl group (Fig.2.).

**Table 1. Determination of Zn (II) in corn plant.**

<table>
<thead>
<tr>
<th>added (µg.ml^{−1})</th>
<th>found (µg.ml^{−1})</th>
<th>recovery%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>36.2</td>
<td>105.55</td>
</tr>
<tr>
<td>40</td>
<td>56.7</td>
<td>101.25</td>
</tr>
<tr>
<td>60</td>
<td>75.8</td>
<td>99.73</td>
</tr>
<tr>
<td>80</td>
<td>99.1</td>
<td>103.23</td>
</tr>
</tbody>
</table>

**Effect of sample flow rate on extraction process**

A series buffer solutions Zn^{2+} at PH=9 were used for investigation of this factor. These solutions were passed through the column at different flow rates from 0.5 to 3ml/min while elution process was fixed at 0.5 ml/min. The results show that optimum sample flow rate is 1ml/min (Fig.3.).

**Effect of ionic strength on extraction of Zn (II)**

For study of ionic strength on extraction process, water samples were prepared at different concentration of ammonium nitrate in the range 0.01-0.5mol/L. Absorbance data show that with increasing of NH_{4}NO_{3} concentration to 0.05M, recovery increases. After that, decreasing in recovery factor is probably due to salting effect (Fig.4.).

**Breakthrough Volume**

The breakthrough volume is an important parameter in SPE because breakthrough volume represents the sample volume that can be pre concentrated without loss of analyte during elution process (Mester and Sturgeon, 2009).

To evaluate this parameter, various samples of Zn(II) that PH and ionic strength of them were adjusted at...
optimum amount, prepared while in all of them, mmol of Zn(II) was constant and volumes of the sample varied from 100 to 1000 ml. These solutions were analyzed according to recommended method in above. The results show that with addition of volume to 400ml, recovery is convenient (> 90%) but at volumes upper than this amount, decreasing in recovery is obvious.

Analytical application
In treatments with aliquots of 400 ml of the solutions, Zn (II) contents was extracted with the SIR with chelating agents (i.e. DAAQ) and then subjected to the determination procedure. The calibration curve was linear in the range of 0.01-0.6µg.ml⁻¹.

\[
\text{Zn (II): } A = 0.3745C + 0.0053 \quad R^2=0.9956.
\]

Where A is the absorbance, C is concentration of Zn (II) and R² is the correlation coefficient.

The limit of detection (LOD) that defined as three times of the standard deviation of blank (n=7) divided to the slop of calibration curve (3Sb/m), was found to be 1.2µg.ml⁻¹

Analysis of real sample
For investigation of reliability of method, the proposed method was applied to determine Zn (II) metal ion in different sections of corn plant including leg, leaf and seed collected from agricultural soils of Neyshabur, a city in Khorassan Razavi. Preparation of samples was as follows:

Exactly, 1 g of each powder sample was digested with 150 mL 12 M H₂SO₄ at 250 °C for 4 h followed by 100 mL 65% HNO₃ at 100 °C for 4 h again. After cooling, they were filtered through a membrane filter with a pore size of 0.45 mm. The filtrate solution was gently heated till to obtain a moisture residue. The residue was transferred into a 100-mL volumetric flask and re dissolved in 25 mL 1 M HCl. After adjusting its pH using the buffering solution, it was diluted to the mark and subjected to the extraction/ determination processes.

The accuracy of the measurements was investigated using the spiked amounts of Zn (II) ions to the water samples at several concentrations.

The results are summarized in Table 1. The obtained recoveries in the ranges 97.76%–103.16%, confirm satisfactorily applicability of the proposed method for determination of zinc in solid and solution samples.
**Conclusion**

Using of solvent impregnated resin (SIR) as adsorbent Solid phase in the extraction of metal ions from plant samples help we to determine trace amount of them in these samples. Furthermore it exhibits some advantages such as faster rate of equilibrium, high capacity and sorption rate to some extent. It could be used for 80-100 cycle without any lowering its sorption capacity. It is very useful in the measurement amount of Zn (II) at neutral water samples with the recovery factor higher than 90%.

**References**


Prabhakaran D, Subramanian MS. 2003. A column system for the selective extraction of U(VI),Th(IV) using a new chelating sorbent. Talanta, 61, 423-430. http://dx.doi.org/10.1016/S0039-9140(03)00308-4

Prabhakaran D, Subramanian M S. 2004. selective extraction of U(VI),Th(IV),La(III) from acidic matrix solutions and environmental samples using chemically modified Amberlite XAD-16 resin. Journal of Analytical and Bio Analalytical Chemistry 379, 519-525.
Praveen RS, Daniel S, Rao TP. 2005. Flame atomic absorption spectrophotometric determination trace amount of nickel in water samples after solid-phase extraction and preconcentration on to IR-120 amberlit resin modified with 5-(4-dimethyl amino-benzyliden)-rhodamin, Talanta 66, 513.


http://dx.doi.org/10.1016/j.microc.2009.05.002