Comparison of Three Analytical Methods for Separation of Mineral and Chelated Fraction from an Adulterated Zn-EDTA Fertilizer

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Summary: Different analytical procedures are being employed in the world to quantify the chelated portion in a Zn-EDTA fertilizer. Agriculture Department, Government of the Punjab is following Shahid′s analytical method in this regard. This method is based on Ion-chromatography (IC) that separates the mineral zinc (Zn) from an adulterated Zn-EDTA fertilizer sample i.e. mixture of mineral and chelated Zn fractions. To find out its effectiveness and suitability, this comparative study was carried out by analyzing adulterated, non-adulterated Zn-EDTA standard and Zn-EDTA samples taken from market in thrice following three methods namely Shahid′s (IC) analytical method, Atomic Absorption Spectrophotometric (AAS) method based on the principle of precipitating the mineral Zn fraction at high pH value by using alkali solution of suitable concentration and analysis of filtrate containing only chelated fraction and Association of Official Analytical Chemists (AOAC) method FM-841 respectively. Adulterated Zn-EDTA samples were prepared by mixing of known quantity of mineral Zn with chelated Zn-EDTA standard. The results showed that Shahid′s analytical method and AAS method, both successfully estimated the chelated fraction. The AOAC FM-841 method was insensitive to put a ceiling on the mineral fraction hence did not furnish the reliable results. The Shahid′s analytical method was selected being equally effective to produce reliable results both for solid and liquid Zn-EDTA samples. The AAS method was comparable in only liquid samples.

Keywords: Mineral zinc ($ZnSO_4.7H_2O$), chelated zinc ($Na_2ZnEDTA.4H_2O$), atomic absorption spectroscopy (AAS) and ion chromatography (IC).

Introduction

Zinc is one of essential micronutrient needed by plants whose uptake is affected by different factors especially soil pH. The pH of most of Pakistani soils is alkaline and ranges from 7.5 to 8.5 [1]. Applied mineral zinc precipitates as the pH increases. Its solubility decreases and drops up to <0.1 % at pH level of 8.5 [Table-1]. In short at alkaline pH it becomes unavailable to plants. Contrary to this, chelated zinc remains 99.7% soluble even at pH level of higher than 8.5 [Fig. 1]. Therefore chelated zinc fertilizers are being used as a source of zinc in high pH (alkaline) soils. A number of chelated zinc fertilizers are available in the market. Department of Agriculture is monitoring the quality of these fertilizers through its divisional laboratories throughout the province, Punjab by following the Shahid′s analytical method [2]. The present study was conducted with the aim to find the suitable one by comparing currently followed method with other traditional methods for analysis of adulterated chelated zinc fertilizers.

Results and Discussion

Analytical results from Shahid′s method showed the effectiveness of method for all kind of samples. Last two columns in Table-3 shows the mathematically calculated percentage of mineral and chelated Zn fractions in adulterated Zn-EDTA samples prepared by mixing mineral Zn and Zn-EDTA standards in known ratios. It is clear that results obtained by Shahid's method are comparable with calculated values. Regarding samples collected from open market, results were repeatable and reproducible.

Atomic Absorption Spectrophotometric (AAS) method works on the principle of Zn insolubility at high pH values. Different salts like $NaHCO_3$, Na_2CO_3 and NaOH were used to raise the pH of solution [Table-2]. All were found equally effective to precipitate mineral zinc (non-chelated). Zinc in the form of Zn-EDTA remains in solution at pH range of 6.5 to 8.5. Sodium hydroxide solution of

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0.1molar strength was found to be the better option to avoid carbonate interference at wavelength of 213.9nm and slit width of 0.1nm during analysis of Zn through atomic absorption spectroscopy. Results obtained by following AAS method were higher than Shahid's method results and calculated values in all adulterated and liquid samples except sample No.5 [Table-3]. The possible reason may be that during filtration process fine precipitates of mineral Zn got entry into solution and increased the value when aspirated through AAS. Whereas for solid samples taken from market, this method failed to produce reliable results.

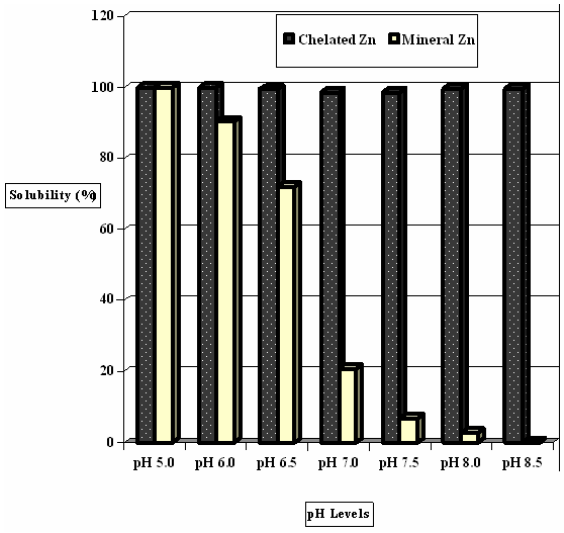

Fig. 1: Solubility of chelated and Minerals Zn at different pH levels.

Association of Official Analytical Chemists (AOAC) method FM-841 is an analytical procedure for determination of chelated metals (Mn, Cu, Fe, and Zn) in mixed fertilizers [4]. This method was found unsuitable for analysis of adulterated Zn-EDTA samples. Results produced were nearly equal to total Zn contents of the samples.

Experimental

Mineral zinc ($ZnSO_4.7H_2O$ Merck, 22.7% Zn), chelated zinc ($C_{10}H_{12}N_2Na_2O_8Zn.4H_2O$, Merck, zinc titriplex GR 471.63g / mol, 13.8% Zn) and their mixtures in different weight based ratios (adulterated samples) along with samples taken from market were analyzed by following Shahid′s (IC) analytical method, Atomic Absorption Spectrophotometric (AAS) method and Association of Official Analytical Chemists (AOAC) method FM-841.

Shahid's Analytical Method

Zinc was analysed isocratically by ion chromatography (Perkin Elmer series 200) using 1.5mM tartaric acid and 1mM oxalic acid 2-hydrate solutions as mobile phase. Cation column coupled with conductivity detector was used to convert signals into mv. Pump speed was set at $0.5mLmin^{-1}$. Peak area was used for calculation of mineral Zn [2].

Mineral Zinc% = sample peak area/standard peak area ×weight of standard/weight of sample ×purity of standard

Total zinc contents were determined by AAS (SpectrAA 250 plus, Varian) after digestion of samples and standard with concentrated H_2SO_4. Chelated Zn fraction was calculated as followings.

Chelated zinc = Total zinc (AAS) – Mineral zinc (IC)

Atomic Absorption Spectroscopy (AAS) Method

This method is based on masking principle of metals [3]. Chelated zinc fertilizer sample was ground and passed through 100 mesh sieve. One gram sample was taken in 250 ml volumetric flask. Appropriate amount of de-ionized water was used to dissolve the sample. Volume was raised upto the mark after adjusting the pH at 8.5 with 0.1M NaOH. At this pH level 99.9 % mineral Zn precipitates (Table-1, Fig. 1). Solution was filtered through 0.45µm pore size Sartorius filter. Filtrate was aspirated through atomic absorption spectrophotometer (AAS) following the standard operating procedure. Air acetylene flame was used for determination of Zn. Working standards were prepared from Certified Reference Material with certificate of analysis traceable to National Institute of Standards and Technology (NIST).

Table-1: Percent solubility of Mineral and Chelated Zn at various pH levels adjusted with 0.1M NaOH.

Description	pH 5.0	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0	pH 8.5
$ZnSO_4.7H_2O$* (Merck)	100	90.5	72.0	20.7	6.8	2.7	<0.1
Zn-EDTA.$4H_2O$** (14% Merck)	99.9	100	99.4	98.5	98.7	99.7	99.7

*0.880g $ZnSO_4.7H_2O$ in 100ml (2000 mg Zn L^{-1})
**1.4429g Zn-EDTA in 100ml (2000 mg Zn L^{-1})

Table-2: Effect of various bases on the solubility of $ZnSO_4$ and Zn-EDTA.

Description	$NaHCO_3$ (5%)	NaOH (0.1M)	Na_2CO_3 (5%)
		pH 8.5	
$ZnSO_4.7H_2O$* (22.7% Merck)	<1 %	<0.1 %	<0.1 %
Zn-EDTA.$4H_2O$** (14% Merck)	98 %	99.4 %	98.5 %

*0.880g $ZnSO_4.7H_2O$ in 100ml (2000 mg Zn L^{-1})
**1.4429g Zn-EDTA in 100ml (2000 mg Zn L^{-1})

Table-3: Results comparison of three analytical methods for analysis of chelated Zn samples.

Description	Shahid's Analytical Method			AAS method	AOAC (FM-841)	Standard Analysis	
	Total Zn %	Mineral Zn %	Chelated Zn %	Chelated Zn %	Chelated Zn %	Mineral	Chelated
Mineral Zinc Standard (22.7%)	22.7	22.7	0	0	22.6	22.7	0
Zn-EDTA Standard (13.8%)	13.7	0	13.7	13.9	13.6	0	13.8
Adulterated Sample-1, Chelated Zn : Mineral Zn (1:1)*	18.5	11.7	6.8	7.0	18.2	11.3**	6.9**
Adulterated Sample-2, Chelated Zn : Mineral Zn (1:2)*	20.8	16.7	4.1	4.8	19.7	15.1**	4.6**
Adulterated Sample-3, Chelated Zn : Mineral Zn(1:3)*	21.4	17.6	3.8	4.0	20.7	17.0**	3.4**
Adulterated Sample-4, Chelated Zn : Mineral Zn (2:1)*	17.1	8.7	8.4	9.4	16.6	7.6**	9.2**
Adulterated Sample-5, Chelated Zn : Mineral Zn (3:1)*	16.3	5.6	10.7	10.4	15.7	5.7**	10.3**
Market Sample-1 (solid) 5% Zn-EDTA claimed	8.0	3.2	4.8	0.20	6.9	--	--
Market Sample-2 (solid) 5% Zn-EDTA claimed	6.0	3.2	2.8	0.18	5.6	--	--
Market Sample-3 (liquid) 12% Zn-EDTA claimed	12.2	0.6	11.6	12.0	11.8	--	--
Market Sample-4(liquid) 5% Zn-EDTA claimed	8.0	0.2	7.8	8.0	7.9	--	--
Market Sample-5 (liquid) 5% Zn-EDTA claimed	14.0	8.5	5.5	5.7	13.8	--	--

*Ratios on weight basis. ** Calculation on actual weight basis,
Mixture-1, Mineral Zinc = 1/2 × 22.7 = 11.3 %., Chelated Zinc = 1/2 × 13.8 = 6.9 %
Mixture-5, Mineral Zinc = 1/4 × 22.7 = 5.7 %., Chelated Zinc = 3/4 × 13.8 = 10.3 %
Results are average of 3 replicates of each sample.

Association of Official Analytical Chemists (AOAC) Method FM-841

Chelated zinc sample (1.25g) was dissolved in 125ml of chelate buffer (extraction solution) in 250ml volumetric flask. 18ml of 2% Sodium hypochlorite solution and 18ml of 1% Diammonium phosphate (DAP) solution was added. Volume was made upto the mark using de-ionized water. After shaking the samples were given the precipitate settling time of 10 minutes. Filtrate was obtained using 0.45µm pore size filter paper. With appropriate dilutions samples were analysed by AAS. Chelate buffer solution was prepared by dissolving 1g of sodium acetate and 25 ml of glacial acetic acid in 700ml de-ionized water, making the final volume 1 liter. Similarly 1% DAP and 2% sodium hypochlorite solutions were prepared by dissolving 1g of DAP and 2ml of commercial bleach in 100ml deionized water, respectively [4].

Conclusion

Shahid′s analytical method (Ion chromatography) showed reliability, repeatability and reproducibility of results for both solid and liquid Zn-EDTA samples.

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