A Modified Carbon Paste Sensor for Determination of Zn in Vitamin and Waste Water using Thiosemicarbazide and Acetaldehyde Thiosemicarbazone Complexes

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Abstract

A novel carbon paste Zinc (II) ion-chemically modified carbon paste sensors highly selective and sensitive (CMCPE) based on the metal complexes Zn- incorporating thiosemicarbazide, [Zn(TS)2(ac)2].C2H5OH (Zn-TSC) and Zn-acetaldehyde thiosemicarbazone [Zn(ATS)2].4H2O (Zn-ATSC) dissolved in tricresyl phthalate (TCP) as binder liquid. The chemically modified sensors were developed for determination of Zinc (II) in vitamin and waste water. The constructed sensors showed good linear response of Nernstian slopes 32.5 ± 0.5 and 28.5 ± 0.5 mV per decade over the concentration range of 5.0×10-9-2.0×10-2 and 6.3×10-9 - 7.9×10-9 M with a detection limit of 0.25 and 0.50 nM for (Zn-TSC) and (Zn-ATSC) ions respectively. The selectivity coefficients of the proposed sensors revealed very good selectivity with respect to alkali, alkaline earth and some transition metal ions and could be used in pH range of 3.5-8.0. As a result the proposed sensors were successfully applied to (Zn-TSC) or (Zn-ATSC) ions determination in mixture solutions, multivitamins and wastewater samples and as an indicator sensors for potentiometric titration of Zn2+ with EDTA. The isolated complexes, (Zn- TSC) or (Zn-ATSC) were synthesized by the anodic dissolution of Zinc metal in an anhydrous acetone solution of the ligands where TSC is thiosemicarbazide, ATSC is acetaldehyde thiosemicarbazone ligand and ac = aceton. Applications of the proposed sensors to the determination of zinc as an indicator sensor for potentiometric titration of Zinc (II) ion with EDTA are successfully applied. The obtained results were compared using the US Pharmacopoeia method and there is no significant difference was observed.

Keywords: Carbon paste sensor; Zinc complexes; Zinc vitamin; Waste water; Thiosemicarbazide; Acetaldehydedithiosemicarbazone; Potentiometric

Introduction

Zinc is one of the most functioning metals necessary for more than three hundred different enzymes [1], so plays a very vital role in a large number of biological processes. As it is a cofactor for the antioxidant enzyme superoxide dismutase (SOD) with a number of enzymatic reactions involved in carbohydrate and protein metabolism. Its natural killer cells and interleukin-2 immune-enhancing activities include regulation of T lymphocytes, CD4 cells, so possesses antiviral activity. In addition, controls the release of stored vitamin A from the liver so, regulates insulin activity and promote the conversion thyroid hormones thyroxine to triiodothyronine. Zinc plays a role in wound healing, especially following burns or surgical incisions, Wilson’s disease, herpes, taste or smell disorders, diabetes, and diabetic neuropathy and use in the prevention of the common cold. The over dose can consider as toxicity which may cause severe anemia, stomach cramps, nausea, and vomiting, renal failure, pulmonary manifestations while deficiency in the diet cause slow wound healing, decreased immune function, loss of appetite, poorly sperm production in male organ and stimulate the formation of a-amyloid which causes Alzheimer’s disease so it’s very important to determine and detect trace quantities of zinc. Several analytical methods has been used for the determination of zinc ion, as flame atomic absorption [2], spectrometry UV-Vis spectroscopy [3], potentiometry [4], fluorescence [5,6] and inductively coupled plasma atomic emission spectrometry (ICP AES) [7]. These techniques have some limitations due to the completely filled d-orbital of zinc ion, which results in an absence of suitable spectroscopic or magnetic signals. Beside other analytical tools, different zinc ion selective sensors based on many ionophores have been reported [8]. Although all ISE methods used for determination of Zn are acceptable but most of them suffer from have poor selectivity [9-18], sensitivity and stability, long response time and short life time [19-28]. In addition, there is no method in the literature for the analysis and determination of Zn by chemical modified carbon paste sensor (Zn-CMCP). The advantages of CMCPs are short measurement time, adequate precision, wide analytical ranges, high accuracy, low cost, small size sensors, low detection limits and simple to design.

In this work, suggested new types of an octahedral structure of zinc (II) complexes based on thiosemicarbazide and acetyl thiosemicarbazone as shown in Figure 1. (Zn-TSC) or (Zn-ATSC) were synthesized for the determination of zinc in pure state, vitamin and waste water by construction of Zn-CMCP which were dissolved in tricresyl phthalate (TCP) as liquid binder mediator and the electrochemical performance characteristics of the proposed sensors were studied.

Materials and Methods

The electrochemical system

Laboratory potential measurements were performed using Jenway

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**Preparation of modified carbon paste sensors**

A modified carbon paste sensor is a Teflon holder (12 cm length) with a hole at one end (3.5 mm deep, 7 mm diameter) filling with carbon paste served as the sensor body. Chemically modified pastes of carbon were prepared by weighed amounts of several pastes of varying nature and ratios of (Zn-TSC) and/or (Zn- ATSC)/graphite/binder for the systematic investigation of each paste composition mixed with high purity graphite with aceton. Mix the mixture homogenized, left at room temperature to evaporate aceton, and then the impregnated carbon powder was added to weighed amount of tricresyl phthalate (TCP). The prepared paste was packed into the hole of the sensor holder body. The CP was smoothed onto paper until it had a shiny appearance and was used directly for potentiometric measurements without preconditioning requirements.

**Calibration of sensor**

Standard zinc solutions was added to 50 ml doubly distilled water to cover the concentration range from 1.0×10⁻⁷ to 1.0×10⁻² M. Lower concentrations were prepared by appropriate dilutions. The new (Zn-TSC) and/or (Zn- ATSC) CMCPes sensor and the reference sensor were immersed in conjunction with the solution at 25 ± 1°C and the emf value was recorded, after each addition, the values were plotted versus the negative logarithmic value of the zinc concentration (pZn) and the resulting graph was used for subsequent determination of unknown zinc concentration from the liner part of the curve (calibration curve method).

**Effect of pH on the sensor potential**

The influence of pH of the zinc solution on the potential response values of the paste sensor for (Zn-TSC) and/or (Zn- ATSC) was studied. Aliquots of the Zn solution (50 ml) were transferred to 100 ml titration cell and the tested Zn-CMCPs in conjunction with the glass electrode for measuring pH, calomel reference electrode, and a combined cell and the tested Zn-CMCP in conjunction with the glass electrode for measuring pH. The pH and mV readings were simultaneously recorded. The pH of the solution was varied over the range of 1.0-10.0 by addition of very small volumes of 0.1M HNO₃ and/or (0.1-1.0M) NaOH solution. Plot the mV-readings against the pH-range of 1.0-10.0 by addition of very small volumes of 0.1M HNO₃ and/or (0.1-1.0M) NaOH solution.

**Selectivity of the sensors**

The selectivity coefficients of different interfering ions for the studied sensors, was determine according to the MPM [29,30], a reference solution (s₀) is added an amount of the drug to give a final concentration of (sₓ), the shift in potential change (ΔE) is thus dissolution of 63.5 mg of Zn during 60 min. (E = 0.5 mol.F⁻¹). The insoluble material was collected and analyzed as [Zn (TSC) (TS) (ac) ]\[^{(C_{2}H_{5}OH)}\].

\[ [\text{Zn (ATSC)}]_{(ac)} (H_{2}O). (H_{2}O) \] was prepared by the same procedure.

**Elemental, spectral and thermal measurements**

Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer CHN 2400 at Micro analytical Center, Cairo University, Egypt. Infrared spectra for the samples were recorded by Perkin Elmer FTIR 1605 using KBr pellets. Thermo gravimetric analysis (TGA and DTG) were carried out in dynamic nitrogen atmosphere (30 ml/min) with a heating rate of 10°C/min using a Schimadzu TGA-50H thermal analyzer.

**The organic compounds**

Thiosemicarbazide and Acetyl thiosemicarbazone (3505 and 3510) digital pH/mV meters. The ruggedness and pH were done using the same pervious system at 25 ± 1°C. An external reference electrode is a saturated calomel electrode (SCE). All EMF measurements were carried out with the following assembly: Hg, HgCl₂(s), KCl (sat.) solution carbon paste sensor. A calibrated microcomputer conductivity meter [Jenway, 4310 digital] was used for conductance measurements.

**Theoretical and materials**

All chemicals used were of analytical reagent grade. Doubly distilled water was used throughout all the experiments. Grade pure graphite powders, tricresyl phthalate (TCP), dioctyl phthalate (DOP), tributyl phthalate (TBP), dibutyl phthalate (DBP), as well as all metal salts such as chlorides, nitrates and sulphates were purchased from Aldrich. The metal (Alfa Inorganics) used; Zn was purchased in the form of rods (~2 cm × 2 cm, 2-3 mm thick). Octozinc (25 mg /capsule) were provided by October Pharma S.A.E. - Egypt. The oxide surface was removed by treating the metal with conc. HNO₃ for several minutes and then washed with distilled water.

**Electrochemical synthesis of thiosemicarbazide and acetaldehyde thiosemicarbazone Zinc complexes**

Thiosemicarbazide (0.46 g, 5 mM) was dissolved in at least amount (5 ml) of 96% Ethanol and then 55 ml of anhydrous acetone were added in presence of 1.5 mg Et₄NClO₄ dissolved in two drops of water. Electrolysis of Copper metal into 60 ml of the previous thiosemicarbazide solution (HTS) at 20 V current was started led to...
measured. To a reference solution containing the same concentration (a), a certain amount of interference ion that cause the same (ΔE) value is thus determined (A).

$$K^\text{MOT} = \frac{(a - a_t)}{a_t}$$

**Potentiometric determination**

The standard additions method: An increment of certain volumes of standard Zn solution was added to 50 ml water containing different volumes of the zinc in its pure state, pharmaceutical preparation (Octozinc capsules), and in spiked samples of wastewater with known volumes of the zinc. The jump in mV reading was recording for each increment and used to calculate the concentration of the drug in sample solution using the following equation [31].

$$C_x = C \left( \frac{V_x}{V_x + V_y} \right) = 10^{\frac{100(\Delta E/S)}{S}} \left( \frac{V_x}{V_x + V_y} \right)^{-1}$$

Where, Cx: the calculated concentration, Vx: the volume of the original sample solution, Vs and Cs: the volume and concentration of the standard solution added to the sample to be analyzed, respectively, ΔE: the change in potential after addition of certain volume of standard solution, and S: the slope of the calibration graph.

**In the potentiometric titrations:** Different weights ranged from 1.79-17.95 mg of zinc were dissolved in 50 ml by bi-distilled water. Different volumes of this solution (1.0-5.0 mL) were taken and subjected against 0.01N EDTA using the sensor(s). Conventional S-shaped curves with first and second plots were used to determine the end points.

**Analysis of octozinc capsule**

20 capsules of (Octozinc 25 mg/ capsule) were powdered and weighed (200-250 mg) portion from each was mixed with 50 ml doubly distilled water. Different volumes of this solution (1.0-5.0 mL) were taken and subjected against 0.01N EDTA using the sensor(s). Conventional S-shaped curves with first and second plots were used to determine the point.

**In spiked waste water**

The concentrations of different quantities from 1.0 × 10⁻² to 5.0 × 10⁻¹ M zinc were putted in volumetric flask 100 ml spiked with five ml waste water and shaking for 5 min, then completed with doubly bidistilled water to the mark. A small volume of 0.01M HCl (0.1- 2.0 ml) was putted to adjust the pH from 4 to 5. The spiked waste water was containing zinc was determined by the standard addition method.

**Content uniformity assay of octozinc capsule**

Ten individual capsules were placed in separate beaker 100 ml and dissolved in distilled water. The different concentration of the solutions was determined by the standard addition method, as described above.

**Dissolution test**

The test was carried out according to the USP XXX method apparatus II [32]. One tablet (Octozinc capsule 25 mg) was placed in the vessel, and the dissolution medium (900 ml bidistilled) was maintained at 37 ± 0.5°C. The vessel was rotated at 50 rpm. For the potentiometric determination, after an appropriate time interval (1.0-2.0 sec), the potential values were recorded, and the amount of the zinc was calculated from the calibration graph. For the conductimetric measurements, introduce the conductimetric electrode in the vessel every two seconds without hindering the motion and take the reading by μ.

**Results and Discussion**

Measurements of the electrochemical efficiency, E, defined as moles of metal dissolved per Faraday of electricity, for the Zn /L system (where L=ligand) gave $E_0 = 0.5 ± 0.05 \text{ molF}^{-1}$. The mechanism for Zinc anode dissolution is compatible with the following equations 1 and 2 [32,33].

Mechanism for Zn (II) anodic dissolution:

Cathode: 2HATS + 2e → 2(ATS)⁻ + H₂ (g) (1)

Anode: 2(ATS)⁻ + Zn → Zn (ATS)₂ + 2e (2)

The elemental analysis of:

[Zn (TS)₄(ac)₄].(C₂H₅OH) (M.wt 407.9) (yellowish white), is:

{\%C = 28.9 (29.4), \%H = 6.14 (6.42) and \%N= 20.3 (20.6)} while,

[Zn(ATS)₂(H₂O₂)].(H₂O) (M.wt 369.8) (Buff) is: {\%C = 18.67 (19.49), \%H = 4.98 (5.45) and \%N= 22.37 (22.73)}.

The complexes are air-stable, hygroscopic, with higher melting points, insoluble in H₂O and most of organic solvents, but soluble in DMSO and DMF. The analytical data are in a good agreement with the proposed stoichiometry of the complexes.

**Characteristics of the sensor**

The electrochemical characteristics of the sensors were determined its sensitivity, linear range, detection limit, response time and selectivity coefficients. The graphite (G)/ binder (B) ratio, the nature and amount of the complex, are reported to significantly influence the sensitivity and selectivity of the sensor. Firstly, the sensor was preconditioned in stirred water until a steady potential was obtained before measurement. The influence of the binder type with its concentration on the characteristics of the studied sensors was investigated by using four binders with different polarities including TCP, DOP, DBP, and TBP.

![Figure 3: Effect of different binders on the response of ZnTSC and ZnATSC sensor.](image-url)
Different binder/graphite (w/w) ratios were studied as shown in Figure 3, among the different compositions studied, a paste containing 1.0 wt% Zn-TSC or 1.0 wt% Zn-ATSC complexes, 55.0 wt% graphite, and 44.0 wt% TCP exhibited the best response characteristics also the lowest detection limit. Therefore, these compositions were used to study various operation parameters of the Zn-sensors and the optimum compositions for the best sensors were given in Table 1. These sensors were chosen in this study and its electrochemical performance characteristics were systematically evaluated according to IUPAC recommendation [34,35].

Reproducibility of the sensor

The sensor surface of the modified sensor is the main attraction that can be renewed after every use. The surface of modified sensor can be renewed by a little carbon paste squeezing out of the tube and a fresh surface is smoothed on a piece of weighing paper whenever needed. Accordingly, a suitable weight (~2.0 g) of paste can be used at optimum composition.

The examination of the potential reading was taken for the repeatability of the Zn-TSC and Zn-ATSC sensors by the subsequent measurements in 1.0×10⁻³ M Zn sulphate solution then followed by measuring the first set of solution at 1.0×10⁻³ M Zn solution. The standard deviation values are given in Table 2 for each Zn-sensor by measuring five replicate measurements emf. The values obtained indicate the repeatability is excellent of the potential response of the sensors.

![Table 1: Effect of binders on composition and characteristics of sensors (Zn-TSC) and (Zn-ATSC).](image-url)
Effect of pH

The potential pH profile obtained indicates that the pH covering the range 3.5–8.0 responses of the sensors are fairly constant where in this range the sensor can be safely used for Zn determination. Therefore, for quantitative measurements with CMCP sensors, to reach the optimum experimental conditions the pH range from 3.5-8.0 was assumed to be the working pH range of the sensors. From Figure 4, it can be seen that there is no need to adjust the pH or use buffer solution at that pH values while, the pH lower than 3.5, the readings of potential increase which can be related to hydronium ion interfering. In addition, at pH values higher than pH 8, the potential readings decrease gradually due to the formation of free base of zinc and decrease of the protonated species in lipophilic nature and polarity of their molecules relative to zinc ion. As can be seen, the selectivity coefficients determined by MPM is sufficiently smaller than 1.0 indicating that the (Zn-TSC, Zn-ATSC) sensors are significantly selective to zinc ion over all the interfering ions.

Validation of the proposed method

Linearity and detection limit (LOD): For the optimal experimental CMCP conditions, exists a linear relationship between the sensor potential /mV and the logarithm of corresponding concentration of the zinc ion. The accuracy of the proposed Zn-CMCPS method was investigated by the determination of Zn in its pure state and its vitamin and waste water using another model of pH-meter (Jenway, 3505) the results obtained were listed in Table 1. While the ruggedness or the reproducibility was examined by repeating the proposed CMCPs method for analysis of the investigated Zn-CMCPS conditions, exists a linear relationship between the sensor potential /mV and the logarithm of corresponding concentration of the zinc ion. The correlation coefficient (r) and other statistical parameters were listed in Table 1.

Accuracy: The accuracy of the proposed Zn-CMCPS method was investigated by the determination of Zn in its pure state and its vitamin and waste water using another model of pH-meter (Jenway, 3505) the results obtained were listed in Table 1. While the ruggedness or the reproducibility was examined by repeating the proposed CMCPs method for analysis of the investigated Zn-CMCPS conditions, exists a linear relationship between the sensor potential /mV and the logarithm of corresponding concentration of the zinc ion. The correlation coefficient (r) and other statistical parameters were listed in Table 1.

Robustness and ruggedness: The examination of robustness method for Zn-CMCPS was found by changed the aqueous solution to acetate buffer pH 4 ± 0.5 and the percentage result of robustness as in Table 1.

Precision: The precision measured as percentage relative standard deviation (% RDS) for the Zn-CMCPS method and was tested by repeating the proposed CMCPs method for analysis of the investigated zinc ion in intra-day (within the day) and inter-day (consecutive days) to five replicates. The obtained %RSD values were listed in Table 1 for the Zn-CMCPS sensors. The% RSD values are less than 2%, indicating good precision.

Selectivity of the sensor

The potential–time plot for the response of the sensor Zn-CMCPS is shown in Figure 5. Table 3 is the selectivity coefficients which reflected the relative response of the paste sensor for the primary ion over other ions present in the solution and indicated highly selective and sensitive to zinc ion. Most of inorganic cations do not interfere due to the difference in their mobility and permeability as compared to zinc ion. In the case of amino acids and sugars the high selectivity is related to the difference in lipophilic nature and polarity of their molecules relative to zinc ion. As can be seen, the selectivity coefficients determined by MPM is sufficiently smaller than 1.0 indicating that the (Zn-TSC, Zn-ATSC) sensors are significantly selective to zinc ion over all the interfering ions.
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Table 4: Determination of Zn-CMCPs applying the standard addition method, potentiometric titration in pure solution, Octozinc (25 mg), spiked waste water and its statistical data treatments in comparison with official methods.

Table 5: Comparison of response characteristic of Zn-CMCP sensor with some previous reported electrode.

Figure 6: Potentiometric titration of (A) 2.69 (B) 4.49 and (C) 6.28 mg respectively of 1.0×10⁻²M ZnSO₄.H₂O with standard solution of 1.0×10⁻²M of EDTA.

was indicated the high robustness and ruggedness as percentage in Table 1.

Content uniformity assay of octozinc: The proposed Zn-CMCP sensors method described good validation with accuracy and precision for the quality control tests, the content uniformity assay showed accurate and reproducible results so the sensors can be employed for quantification of zinc and the recovery of zinc ion is almost quantitative.

Analytical applications

The standard addition method for the determination of zinc ion was proved to be successfully applied in its pure solutions, Octozinc (25 mg/capsule) and biological waste water using its prepared Zn-chemically modified carbon paste sensors.

Determination of octozinc (25 mg/capsule): In order to assess the validity of the proposed sensor, the proposed Zn-CMCP sensors were used successfully using the standard additions method [30] and the potentiometric titration method for the determination of Zn ion in its pure solutions, capsule and the waste water. It is clear from the results, given in Table 4, that there is good agreement between the results of the proposed sensor and those obtained from US Pharmacopeia method.

Determination of Zn in spiked waste water: The proposed Zn-CMCPS method was successfully applied for determination of Zn in spiked waste water and the results obtained with high precision and accuracy as summarized in Table 4. In spiked waste water samples the standard addition technique was applied to overcome the matrix effects
in these samples. In addition, the response times of the proposed sensors are instant (within 10 s), so the sensors are rapidly transferred forth and back between the samples and the bi-distilled water for washing between the measurements to protect the sensing component from adhering to the surface of some matrix components. It is concluded that the proposed Zn-CMCP sensors can be successfully applied in spiked waste water samples and this confirms that the sensitivity and limit of quantification (LOQ) are adequate for determination of zinc ion.

Potentiometric titration of zinc ion with a standard EDTA solution using Zn-TSC and Zn-ATSC sensors: The Zn-TSC and Zn-ATSC sensors were successfully applied as an indicator in titration of (1-10) ml ZnSO_4.H_2O (1.0×10^-2 M) with a standard EDTA solution (1.0×10^-3 M). The resulting titration curve is shown in Figure 6. The amount of Zn ions in its solution could be accurately determined with the sensors Zn-TSC and Zn-ATSC very well. The end point of the titration is sharp and the amount of Zn ions in solution can be accurately determined with the sensors. The fast and sharp end point can be explained by the fact that these sensors contain carbon particles surrounded by a very thin film of TCP and acting as a conductor and the absence of the internal reference solution.

Statistical treatment of results

The results of the recoveries of Zn applying the standard additions method and the potentiometric titration were evaluated statistically and compared with the values obtained with the pharmacopeia method by applying the F-tests [34,35]. As shown in Table 4 that the present methods had a precision comparable to that of the pharmacopeia method. However, the proposed methods were more practical regarding time of analysis, consumption of solvents and sample pretreatment requirements for ion selective electrode for the analysis of zinc ion.

Potentiometric monitoring of octozinc dissolution

The dissolution test showed that zinc capsule released immediately after capsule was ruptured. More than 75% zinc was released within 15 sec and complete dissolution was achieved in 20 sec.

The potentiometric method, the potential values were continuously recorded at 1-2 sec time intervals and compared with a calibration graph. For the conductimetric measurements, introduce the conductometric electrode in the vessel every two seconds without hindering the motion and take the reading by us and compared with a calibration graph. Figure 7 showed the dissolution profiles of zinc capsule using both measurement techniques. The results obtained by two methods are almost identical. The use of the potentiometric method sensor, however, has the advantage of in situ monitoring.

Comparison of the zinc selective sensors

The comparison of the performance characteristics of the proposed sensors and those of some reported ISE method were presented in Table 5. It is clear that the proposed sensor CMCPS was the most wide linear range and the response time improved with respect to those the previously reported in zinc-selective electrodes. Its detection limit was lower than found for the other electrodes those in the reference.

Conclusion

The proposed potentiometric methods based on the construction of CMCP sensors with Zn-complexes might be useful analytical characteristics for the determination of zinc in its pure solutions, pharmaceutical dosage form and waste water. The good recoveries and low relative standard deviations observed reflect the high accuracy and precision of the proposed method. Moreover, the CMCPS is simple in fabrication and construction, high sensitivity sensor, easy to operate in mechanism, and fast static response dynamic time, reasonable selectivity for variables ions, long term stability for zinc ion solution and applicability over a wider concentration range with minimal sample pretreatment and inexpensive making it an excellent tool for the routine determination of Zn in quality control laboratories. The sensor developed is superior as compared with the zinc selective sensor described in the literature.

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