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# Development of an optical sensor for determination of zinc by application of PC-ANN

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ABSTRACT

A very sensitive and reversible optical chemical sensor based on dithizone as chromoionophore immobilized within a plasticized carboxylated PVC film for $Zn^{2+}$ determination is described. At optimum conditions (i.e. pH 5.0), the proposed sensor displays a linear response to $Zn^{2+}$ over $5.0 \times 10^{-8}$–$5.0 \times 10^{-6}$ mol $L^{-1}$ range. This range was improved to $2.5 \times 10^{-8}$–$5.8 \times 10^{-5}$ mol $L^{-1}$ range by applying principle component-feed forward artificial neural network with back-propagation training algorithm (PC-ANNB). Detection limit of $8.0 \times 10^{-9}$ mol $L^{-1}$ was obtained. The sensor is fully reversible within the dynamic range and the response time ($t_{95\%}$) is approximately 4 min under batch conditions. In addition to its high stability and reproducibility, the sensor shows good selectivity towards $Zn^{2+}$ ion with respect to common metal cations. The sensor was successfully applied for determination of $Zn^{2+}$ ion in hair sample.



## 1. Introduction

Zinc is essential in human metabolism, being of importance in biochemical processes [1], because it plays a vital role in the operation of more than 200 enzymes, for the stabilization of DNA and the transference of a nervous stimulus [2]. Deficiency of zinc leads to retarded growth, lower feed efficiency, inhibits the general well-being, causes ulcers, scaling of the skin, besides affecting the bones and joints [3].

Some analytical methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), differential pulse polarographic, and stripping potentiometry have been proposed for the determination of zinc ion [4]. These methods need relatively high cost apparatus. Therefore, a growing interest showed up to develop metal ion chemical sensors. Chemical sensors based on optical signal have some advantageous such as easy fabrication, low cost, good selectivity, and sensitivity [5]. The sensing phase consists of reagent dyes immobilized in organic or inorganic matrices. Reaction with the analyte changes the absorbance or fluorescence behavior of the sensitive layer. Several methods have been used to immobilize reagents in optical sensors such as covalent binding [6], electrostatic attraction to a resin [7] and entrapment inside hydrophobic matrices [8]. Physical immobilization has been used where lipophilic chromoionophores and selective neutral ion carriers were dissolved in plasticized poly(vinylchloride) (PVC) layers and referred to membranes [9,10]. Optodes for a variety of analytes such as cations, anions and gaseous have been reported [11–16]. In comparison with cation optodes, zinc optodes are few in number [17–20].

Optical sensors usually suffer from low sensitivity and narrow linear range. A number of signal processing techniques, for instance polynomial curve-fitting [21], have also been applied for modeling the sensor response. Over the last several years, the number of studies on application of artificial neural network (ANN) for solving modeling problems in analytical chemistry and especially in optical sensors technology has substantially increased. Optical sensors show a sigmoidal response curve and a narrow range of this curve can be taken as linear [22]. ANN is a computing system made up of a number of simple and highly interconnected processing elements which processes information by its dynamic state response to external inputs [23]. The range of scope of applications of ANN comes from their capability to estimate complex functions that make them compatible for modeling non-linear relationships. Thus, the range of chemical applications of ANN [24,25] is very large and it includes fields as diverse as modeling structure of protein, molecular dynamics, process control, interpretation of spectra, calibration, pattern recognition, optimization of the linear signal range and signal processing [26]. Meanwhile, in optical sensor

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technology, ANN is used in signal processing, data reduction and optimization, interpretation and prediction of spectra and calibration [27].

Search for new sensing materials that can respond reversibly, selectively and sensitively to the analyte in a short time is the key step in sensor design. Selectivity, sensitivity, and response time of the chemical sensors highly depends on the type of recognition elements used in the detection system. Dithizone (diphenylthiocarbazone, $H_2Dz$) is an organic colorimetric reagent that provides the basis of sensitive methods for the spectrophotometric determination of heavy metals. Metal ions combine with dithizone to yield nonpolar colored complexes whose colors differ significantly from dithizone [28].

In this paper, we described an optode for sensitive and selective determination of zinc. This optical chemical sensor is prepared by immobilizing dithizone lipophilic sensing reagent in PVC membrane according to a simple method. A PC-feed-forward ANN with back-propagation training algorithm was employed for treatment of the data, to model relationship between the concentration values and the spectra of optode. The membrane has a good sensitivity, a short response time, and a broad dynamic range. It is also fully reversible in a short time.

## 2. Experimental

### 2.1. Reagents

All reagents were of the highest grade commercially available and were used without further purification. Carboxylated poly(vinylchloride) (PVC), dibutyl phthalate (DBP), orthonitrophenyl octyl ether (o-NPOE), dimethyl sebacate (DMS), dibutyl sebacate (DBS), diethyl sebacate (DES), tetrahydrofurane (THF), and potassium tetrakis-(4-chlorophenyl) borate (KTpClPB) all were obtained from Fluka or Merck chemical companies. The chromoionophore dithizone was purchased from Merck Company. The 0.01 mol $L^{-1}$ potassium hydrogen phthalate buffer (pH 5.0) was prepared by dissolving 0.2 g potassium hydrogen phthalate salt in 100.0 mL distilled water and its pH was then adjusted. Reagent-grade nitrate or sulphate salts of all cations were obtained from Merck. The stock solution of $Zn^{2+}$ was prepared by dissolving 0.075 g $Zn(NO_3)_2{\cdot}6H_2O$ in deionized water containing 1 mL concentrated nitric acid in a 250 mL volumetric flask and diluting to mark with deionized water. Deionized distilled water was used throughout the experiment.

### 2.2. Apparatus

All absorbance measurements were carried on an Ultraspec 4000 UV-VIS spectrophotometer. The sensing membrane was placed in a quartz cell and the spectra's were recorded between 325 and 800 nm. All measurements were performed in a batch mode. These data were partitioned to training, validation and, test sets with size of 18, 6, and 6, respectively.

The results of ANN were obtained from ANN toolbox of MATLAB (version 7, Math Work Inc.). All programs were run on a personal computer (Pentium IV) with Windows XP operating system. Measurement of pH was performed with a Metrohm pH meter (model 780) calibrated with Merck pH standards of pH 4.0 and 7.0.

### 2.3. Membrane preparation

Membrane cocktails have been prepared by typically mixing 65.0 mg of DES (plasticizer), 32.0 mg carboxylated PVC and 3.0 mg dithizone as chromoionophore in a glass vial with 1.5 mL of THF. The solution was immediately shaken vigorously to achieve complete homogeneity. A glass plate (13 mm × 24 mm and 1 mm thickness) was cleaned with pure THF to remove organic impurities and dust. A membrane of 2–5 μm thickness has been obtained by depositing 100.0 μL of the cocktail onto the glass plate with a spin-on device during 30 s at 600 rpm. The membrane was then located in ambient air and allowed to dry in air for about 2 h. Before measurements, the sensing membrane was conditioned by immersing in zinc solution of $5.0 \times 10^{-6}$ mol $L^{-1}$, 0.1 mol $L^{-1}$ HCl solution, and KHP buffer solution (pH = 5.0, 0.01 mol $L^{-1}$) for about 4, 15, and 2 min, respectively, for three times.

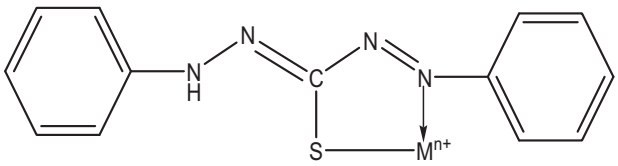


**Fig. 1.** Structure of primary metal dithizonate.

### 2.4. Analytical procedure

The membrane was placed vertically inside the sample cuvett containing 2.0 mL KHP buffer solution of pH 5.0, and a blank membrane (without chromoionophore) was put in the reference cuvett containing the buffer solution. Appropriate amounts of the standard $Zn^{2+}$ solution were injected followed by recording absorbance spectrum after about 4 min, required to reach the equilibrium.

### 2.5. Procedure for the determination of zinc in hair sample

The hair sample was first soaked in deionized water for 10 min. This was followed by soaking in 1% triton X-100 solution for 20 min [29]. The hair sample was then rinsed five times with deionized water and air-dried. 0.250 g of dried hair sample was digested with 5.0 mL pure concentrated nitric acid for 2 h at ~120 °C. Finally 3.0 mL of $H_2O_2$ was added to the sample and digested. The residue was diluted with KHP buffer (pH 5.0) to 50.0 mL. This solution was analyzed by standard addition method.

## 3. Results and discussion

### 3.1. Sensing reagent and spectral characteristics

Dithizone is a weak acid and dissolves in alkaline aqueous media (>20 g $L^{-1}$) but is practically insoluble in water at pH < 7 ($(5.0-7.2)\times10^{-5}$) [21,30]. The complexation reactions of dithizone with metal ions are well known to be strongly dependent to the pH. Structural investigations of these complexes have shown that the metal is bonded to the sulphur atom and coordinately bonded to the nitrogen, as shown in Fig. 1 [31].

When dithizone reacts with a metal as the anion of monobasic acid ($HDz^-$), these complexes called primary or normal dithizonates.

$$M^{n+} + 2HDZ^- \rightarrow M(HDZ)_2^{(n-2)+}$$

However, some metal ions (Cu, Hg, Ag, Pt, Au, and Pd) form secondary dithizonates, which have found no real application in spectrophotometric analysis.

Fig. 2 shows the response of the optode membrane to various concentrations of $Zn^{2+}$ ions under optimal experimental conditions. As seen, upon addition of $Zn^{2+}$ ion, the absorbance of free of chromoionophore is decreased (at $\lambda_{max}$ = 430 and 620 nm) in the expense of increasing absorbance of the complexed chromoionophore (at $\lambda_{max}$ = 530 nm). The calibration curve was linear in the range of $5.0 \times 10^{-8}$–$5.0 \times 10^{-6}$ mol $L^{-1}$. The dynamic range