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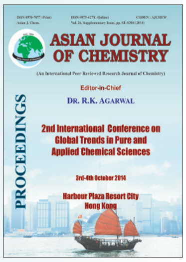

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Separation and Preconcentration for Determination of Ultra Trace of Chromium(III) and Zinc(II) Using Spectrofluorimetry Techniques

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Cloud point extraction has been used for the preconcentration of ultra-trace amount of chromium and zinc, after the formation of a complex with doxycycline hyclate as a drug in a surfactant solution yielding a hydrophobic complex, which then is entrapped in surfactant micelles and further determination by spectrofluorimetry. The main factors affecting the determination, such as pH, concentration of reagent and surfactant, equilibration temperature and time on cloud point extraction, were optimized for the best extract efficiency. The calibration graph was linear in the range of (0.025-1) and (10-100) ng mL^{-1} with detection limit of (0.01, 7.8) ng mL^{-1}. The proposed technique was applied to the determination of chromium(III) and zinc(II) in milk samples with satisfactory analytical results.

Keywords: Cloud point extraction, Chromium, Zinc, Spectrofluorimetry, Triton X-114, Deoxycycline hyclate.

INTRODUCTION

Doxycycline hyclate (Doxy), chemically formula is known as a $C_{22}H_{24}N_2O_8{\cdot}HC1{\cdot}0.5C_2H_5OH{\cdot}0.5H_2O$ (4S,4a*R*, 5S,5a*R*,6*R*,12a*S*)-4-(dimethylamino)-3,5,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide hydrochloride hemi ethanol hemihydrate[1] (Fig. 1).

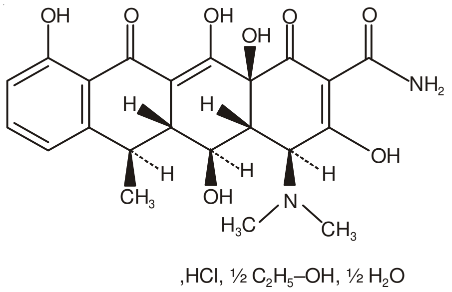


Fig. 1. Chemical structure of doxycycline hyclate

Different analytical method were used in the literature for the analysis of doxycycline hyclate such as spectrofluorimetry, because of its high sensitivity, easily operated, wide availability in most quality control laboratories, low cost and selective, is analytical techniques for the determination of drugs and elements[2,3].

Zinc is an essential trace element of very importance for humans, animals and plants[4,5]. Also zinc is made of superoxide dismutase, as it has a principle function in the protection of the organism against activated oxygen species[6]. Therefore, if there is any excess of its level, this metal can also play an important role in the progression of several damages to human body, including increasing in oxidative stress or disturbances in energy metabolism, also plays as a cofactor of over 200 enzymes and to its structural role in a large number of Zn finger proteins. The Zn deficiency consequences made a prematurity pregnancy, growth retardation, weight loss, altered immune response, anorexia[7,8].

Chromium is another important element because it is widely used in various industries, such as tanning, paint and pigment, production and metallurgy which contaminate the environment. Analysis of trace amounts of chromium(III) ion has become an important topic in environmental and biological sciences[9]. It is well known that the toxicological and biological properties of most elements depend on their chemical forms.

Chromium(III) compounds have an important role in the metabolism of certain lipids and glucose[10,11]. Consequently, the development of sensitive method, as well as this method of chromium(III) in environment is highly required[12].

Separation and preconcentration based on cloud point extraction were becomes an important and practical application of surfactants in analytical chemistry[13,14]. These techniques are based on the probability of most nonionic surfactants in aqueous solutions to made micelles and to transfers its separation into a surfactant-rich phase of a small volume when heated to a temperature of the cloud point temperature. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are have a many advantages are its simple experimental procedure, high preconcentration factors, low cost, low personal toxicity[15,16].

Several researchers proposed many and different mechanisms for the phase separation of non-ionic surfactants about the cloud point extraction. There are some of the normally accepted hypotheses for the cloud point extraction phenomena. One of these hypotheses is suggested by the micellar will interactions which are repulsive at lower temperature while become attractive at higher temperature[17,18]. Second hypotheses is the dehydration was occurs in the outer layer of the micelles at higher temperature[19,20]. And the third is the micellar size at higher temperature will increase and causing to phase separation[21].

In the present work, doxycycline hyclate as a novel reagent was used for cloud point extraction method for the estimation of chromium species and zinc ions by development method with satisfactory results.

EXPERIMENTAL

Spectrophotometer (Shimadzu-Model RF-5301PC) was used for all the measurements in this methods for the determine the concentration of the chromium(III) and zinc(II). A digital pH meter (inolab 720 model WTW Germany) was used for all pH measurements. A thermo stated bath (Thermo-Circulator England) maintained as the desired temperature was used for the cloud point extraction experiments, a UV-1800 (spectrophotometer Shimadzu) and phase separation was assisted using a centrifuge (PLC 03 USA).

All of the chemicals used were of analytical reagent grade, free from chromium traces. Stock solutions of Cr(III) and Zn(II) were prepared by dissolving appropriate amounts of Cr_2O_3 and $ZnCl_2$ in distilled water. The non-ionic surfactant, Triton X-114 was used without further purification. A(0.01) M solution of doxycycline hyclate stock solution was prepared by dissolving appropriate amounts of this reagent in distilled water. Doubly distilled water was used throughout the entire study. The pipettes and vessels used for trace analysis were kept in 5 % nitric acid for at least 24 h and subsequently washed three times with distilled water.

Cloud point extraction procedure: For the cloud point extraction procedure, aliquots of 5 mL of a solution containing the Cr(III), Zn(II), Triton X-114, doxycycline hyclate and a buffered solution at a suitable pH was kept in the thermostatic bath maintained at 40 °C for 20 min. Because the surfactant density, was 1.052 g L^{-1}, the surfactant-rich phase can settle through the aqueous phase, therefore needed to the centrifuging for 20 min at 4000 rpm accelerated the phase separation and then make a cooling in an ice bath, the surfactant rich phase became viscous and was still at the bottom of the centrifuge tube. Simply a syringe centered in the bottom of the tube can readily discard the aqueous phases. In order to decrease the viscosity and facilitate sample handling prior to the spectrofluirometer instrument, 3 mL of ethanol was added to the surfactant rich phase. The final solution was introduced into the spectrofluorimetry cuvate to complete its measurement.

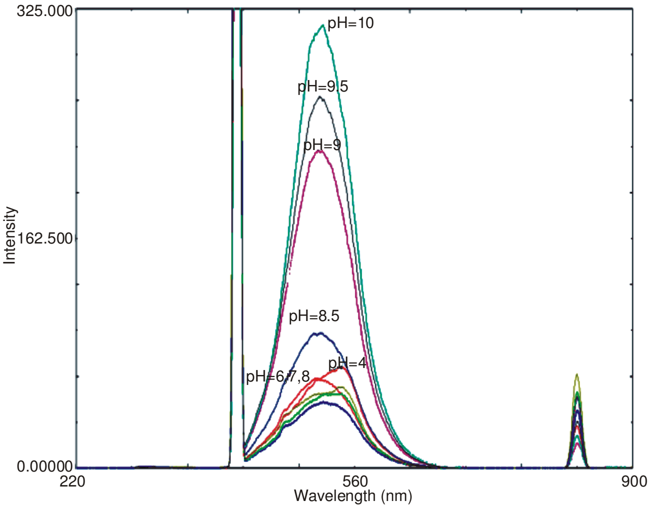
Fluorescence measurements: A spectrofuorimetric method was based on fluorescence enhancement of doxycycline hyclate with Cr(III) and Zn(II) for the determination of its metal ions in all the experimental. The fluorescence intensity of its Cr(III) and Zn(II) complexes was measured in the absorption solution at an excitation wavelength of 415 nm and an emission wavelength of 511 nm and calibration curve was constituted. The fluorescence intensity of its complexes is dissolved in ethanol after extraction was measured and the Cr(III) and Zn(II) were determined. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Under the optimum experimental conditions which are represented in the below results. Cr(III) and Zn(II) reacts with doxy to form hydrophobic complexes, which is subsequently trapped in surfactant micelles.

Effect of pH: Cloud point extraction of chromium and zinc species were prepared in different pH buffer solutions. The separation of metal ions by cloud point extraction involves prior formation of a complex with sufficient hydrophobic and the doxycycline hyclate to be extracted into the small volume of the surfactant-rich phase. The pH of the solution was optimized for the non-ionic cloud point extraction in order to obtain the optimum signal for the selected emission spectrofluorimetry, the pH was adjusted to the desired value by addition of buffer solution. Following the experimental process described, it was found that the extraction efficiency is almost dependent of pH conditions for the pH range of (8-9.5) for each element. Fig. 2 giving a plateau in the area of its value. This behaviour is anticipated due to the hydrophobic, non-ionizable nature of the analytes. Cr(III) and Zn(II) complexes were determined and chosen for subsequent work.

Effect of reagent concentration(drug) on the cloud point extraction: The effect of doxycycline hyclate concentration on the determination of chromium(III) and zinc(II) were



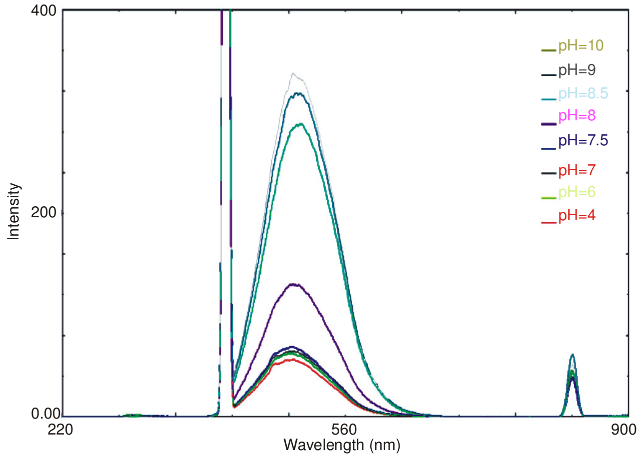


Fig. 2. Effect of pH on the complex of doxycycline hyclate with Cr(III) and Zn(II)

investigated by the changing in the volume of its drug in the range of 0.1-1 mL. The signal intensity will increased up to the doxycycline hyclate volume of (0.4, 0.6) for the chromium(III) and zinc(II), respectively reached near quantitative extraction efficiency. A volume of above value was therefore chosen as the optimum volume for the subsequent studies (Fig. 3).

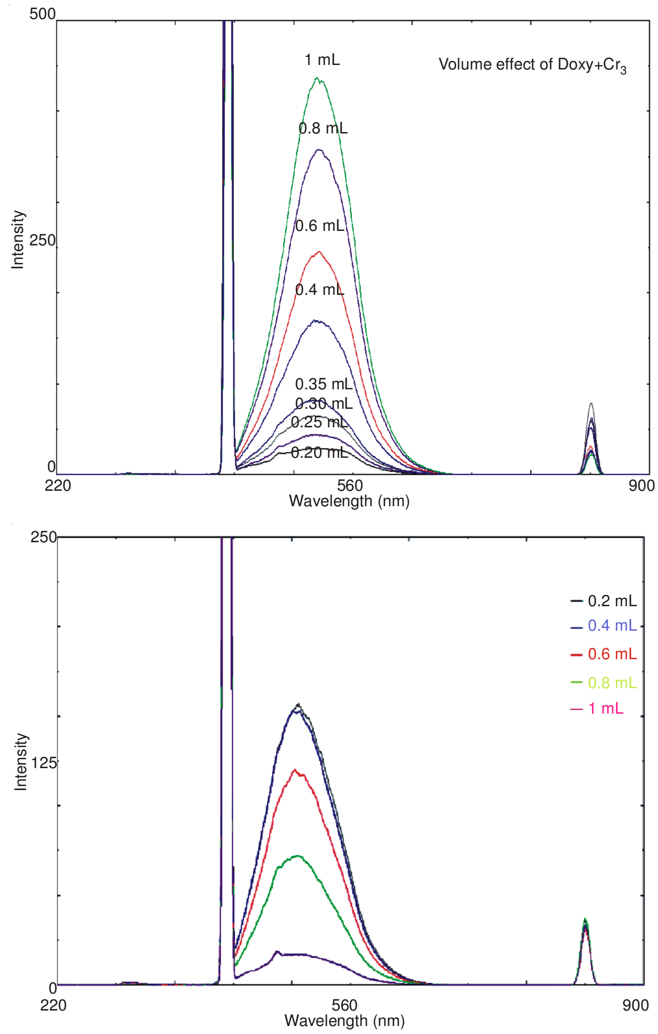


Fig. 3. Effect of doxycycline hyclate concentration on the its complexes of Cr(III) and Zn(II)

Effect of Triton X-114 concentration: A good cloud point extraction method would be that which maximizes the extraction efficiency through minimizing the phase volume ratio, thus maximizing its volume factor. Triton X-114 was chosen for the formation of the surfactant-rich phase due to its high density and low cloud point temperature of the surfactant-rich phase by which phase separation will be then by centrifugation. Extraction of chromium(III) and zinc(II) with the Triton X-114 volume was investigated within the range of 0.01-0.4 mL shown in Fig. 4. The optimum surfactant volume used for the Cr(III) was 0.35 mL and for the Zn(II) was 0.3 mL. So, the concentration of Triton X-114 was chosen as its above volume for each its elements in order to achieve the optimal surfactant concentration in conjunction with the highest possible extraction efficiency.

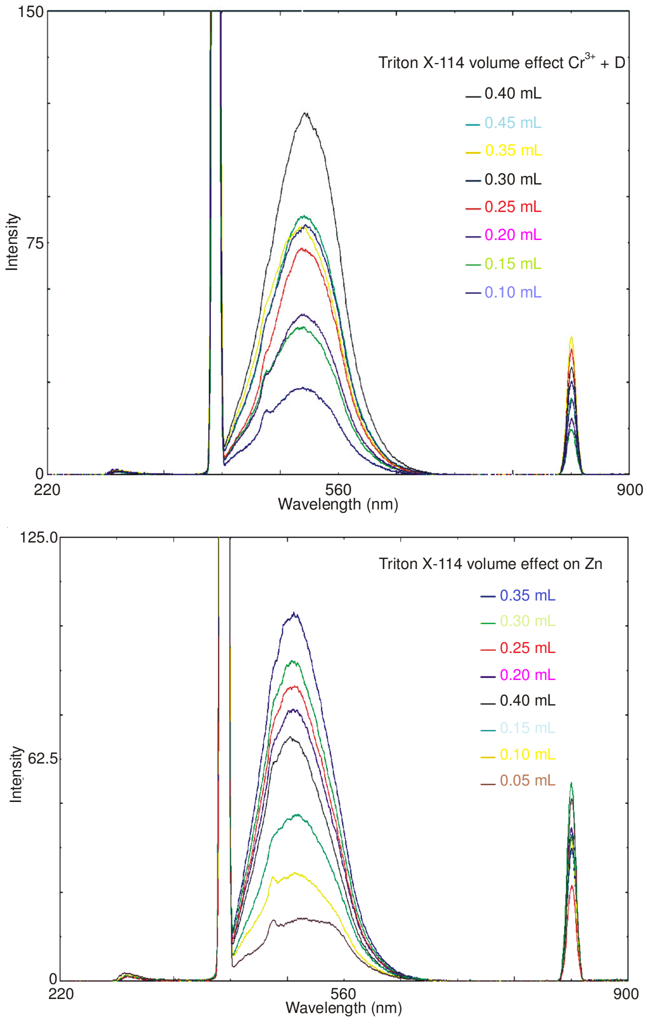


Fig. 4. Effect of Triton X-114 concentration on the its complexes of Cr(III) and Zn(II)

Effect of the equilibrium temperature and time: In the method of cloud point extraction system, temperature of extraction is very important parameter for micelle us occurring. The effect of equilibration temperature and time incubation in the cloud point extraction system was investigated at 30 to 80 °C. At lower temperatures than 30 °C the separation of the two phases was not complete. After 40 °C, the signal intensity was approximately same value (Fig. 5). The incubation time

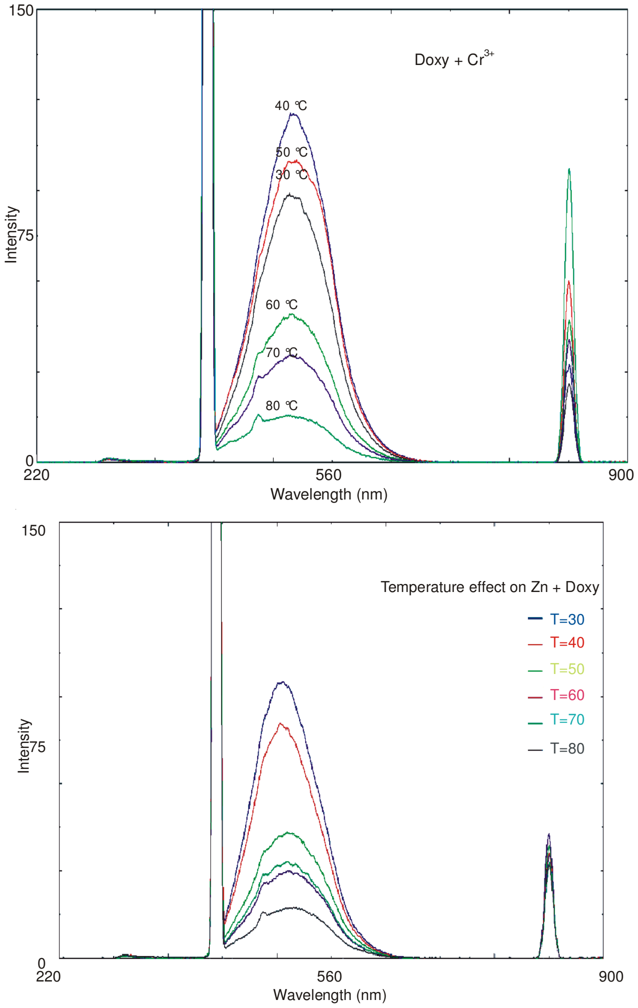


Fig. 5. Effect of temperature on the complexes of Cr(III) and Zn(II)

was kept at 20 min which is sufficient for the completion of the its processes. Thus incubation temperature was to determine at 40 to 30 °C, respectively.

Method validation of the spectrofluorimetric determination of Cr(III) and Zn(II) using cloud point extraction procedure are given in Table-1.

Conclusion

A simple spectrofluorimetric process for the determination of chromium(III) and zinc(II) was developed. Optimization of the parameters produced a stable and highly fluorescence intensity for its ions-doxycycline hyclate complex. This methodology resulted in a low value of LOD and LOQ shown in above table for its ions as simple and rapid method by sensitive value of spectrofluorimetric determination of its ions.

TABLE-1

Parameter	Value of Cr(III)	Value of Zn(II)
λ_{ex} (nm)	415	415
λ_{em} (nm)	511	510
Regression equation	y=142.7x+19.32	y=2.742x
Correlation coefficient (r)	0.996	0.998
Concentration rang (ng mL^{-1})	0.025-1	10-100
LOD (ng mL^{-1})	0.0034	0.182
LOQ (ng mL^{-1})	0.0106	0.552
Enrichment factor	70.42	43

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