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Determination of ultra trace of thiosemicarbazide by adsorptive stripping voltammetric method

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ABSTRACT

In the present work, an adsorptive stripping voltammetric method using a hanging mercury drop electrode (HMDE) was described in order to determine the ultra trace of thiosemicarbazide in different real samples. The method is based on accumulation of thiosemicarbazide on mercury electrode. The potential was scanned to the negative direction and the differential pulse stripping voltammograms were recorded. The instrumental and chemical parameters were optimized. The optimized conditions were obtained in pH of 10.0, accumulation potential of 0.00 mV, accumulation time of 60 s, scan rate of 80 mV/s and pulse height of 50 mV. The relationship between the peak current versus concentration was linear over the range of 0.50-100.00 ng/ml. The limits of detection were 0.03 ng/ml and the relative standard deviation at 5.00 and 50.00 ng/ml of thiosemicarbazide ion were obtained 2.1 and 1.7%, respectively (n = 8).

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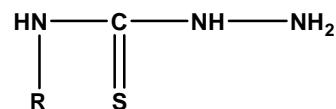
KEYWORDS

Thiosemicarbazide;
Adsorptive stripping
Voltammetry;
Real sample.

INTRODUCTION

Thiosemicarbazide (TSC, see the general formula below) could be considered as derivatives of thiourea, where a hydrogen atom of an NH₂ group is substituted with an amino group and a similar atom from another amino group is substituted with a group R (hydrocarbon or substituted hydrocarbon)^[1].

The technological application of thiosemicarbazide or hydrazinecarbothioamide (TSC) as a corrosion inhibitor of steel, Cu, Al and Ni is well known^[2-6]. Moreover, TSC and some of its derivatives have other im-



portant properties that make this molecule extensively studied in the field of medical chemistry^[7].

TSC is the main parent compound of a series of thiosemicarbazone derivatives of aromatic or aliphatic ketones and aldehydes with potentially beneficial biological activity^[8,9].

Since a number of metal complexes of the compound are known, suitable analytical techniques are essential for estimating TSC in the pure state as well as

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in its complexes. The analytical procedures reported so far for its estimation are based on its oxidation by alkali metal hypohalites^[10], lead tetraacetate^[11], and some of the arylhalosulfonamides, also determination of TSC alone and in its metal complexes with Arylhalosulfonamides^[12].

This paper describes a sensitive and selective adsorptive stripping voltammetric procedure for determination of thiosemicarbazide in synthetic and water samples. This method is based on the effective accumulation of the thiosemicarbazide on a hanging mercury drop electrode (HMDE) and then the reduction of thiosemicarbazide.

EXPERIMENTAL

Reagents

All solutions were prepared from double distilled water. All the reagents were of analytical grade and were used without further purification. A 1000 µg/ml thiosemicarbazide (Merck, Darmstadt, Germany) was prepared by dissolving 0.1000 g of thiosemicarbazide in water and diluting to 100 ml in a volumetric flask. Working standard solutions were obtained by appropriately diluting the stock solutions before use. 0.1 M Britton-Rabinson buffer (pH=10.0), was prepared by mixing appropriate amounts of CH₃COOH, H₃PO₄, H₃BO₃ and NaOH, and was used to prepare solutions of the supporting electrolyte.

Apparatus

All polarographic measurement was carried out using a polarographic processor model 746 VA (Metrohm) in combination with a polarographic stand model 747 VA (Metrohm). This electrode stand consists of a Hanging Mercury Drop Electrode (HMDE) as working electrode, a silver-silver chloride (KCl 3M) as reference electrode and a platinum wire with a considerably larger surface area than that of HMDE as auxiliary electrode. Stirring was carried out by a large Teflon rod with 2000 rpm speed. A 780 pH Meter (Metrohm) equipped with a combine Ag/AgCl glass electrode was used for pH measurement. Solutions were deoxygenated with high-purity nitrogen for 5 min prior to each experiment, and it was performed under a nitrogen atmosphere.

Eppendorf Vary-pipettes (10-100, 100-1000 µL) were used to deliver accurate volume. All glassware and storage bottle were soaked in 10 % nitric acid overnight and thoroughly rinsed with deionized water prior to use.

Recommended procedure

A 10 ml sample solution, containing 0.1 M Britton-Rabinson buffers (pH=10.0) and different concentrations of TSC was transferred to the voltammetric cell and purged with nitrogen for 5 min. The accumulation potential (0.00 V) was applied to a fresh mercury drop for 60 s while the solution was stirred. Following the accumulation period, the stirring was stopped, and after 10 s the voltammograms were recorded by applying a negative-going potential. Each scan was repeated four times with a new drop for each analyzed solution and the mean of these voltammograms were obtained. The reduction peak for TSC occurred at about -0.65 V and their current was used as a measure of TSC concentration. All data were obtained at room temperature.

Real sample analysis

Determination of TSC in water samples

The water samples such as Ilam university laboratory water, Ilam city water, mineral water and river water (Zayandehrood river, Isfahan, Iran) were collected, filtered, centrifuged at 2000 rpm for 5 min. In order to remove the possible cations that could complex the TSC, the water samples were passed through a Dowex 50X8 cation exchanger column. Then, they were stored on cooled place and analyzed by using the recommended procedure. The results are presented in TABLE 2.

Determination of TSC in blood sample

Exactly 2.0 ml of whole blood sample was transferred to each test tube and was left to equilibrate in a water bath for 1 h at 37° C. After that, 1.0 ml water was used to quantitatively transfer the samples into Teflon high-pressure microwave acid-digestion vessels for the digestion. A 2.0 ml of portion of concentrated nitric acid and a 4.0 ml of 30% H₂O₂ were added. After digestion of blood samples the closed vessels were cooled, the digest were quantitatively transferred to a 10.0 ml volumetric flask, neutralized with NH₃ 1.0 M

and diluted to volume with distilled water. Volumes of 1.0 ml of each of the aliquots were taken for the determination of copper via the recommended procedure. The results are presented in TABLE 2.

RESULTS AND DISCUSSION

Formation of stripping peaks

It seems that the presence of S donor function in the ligand molecule favors the chemisorptions on the Hg electrode, while the presence of π -electrons increases the adsorption process^[13].

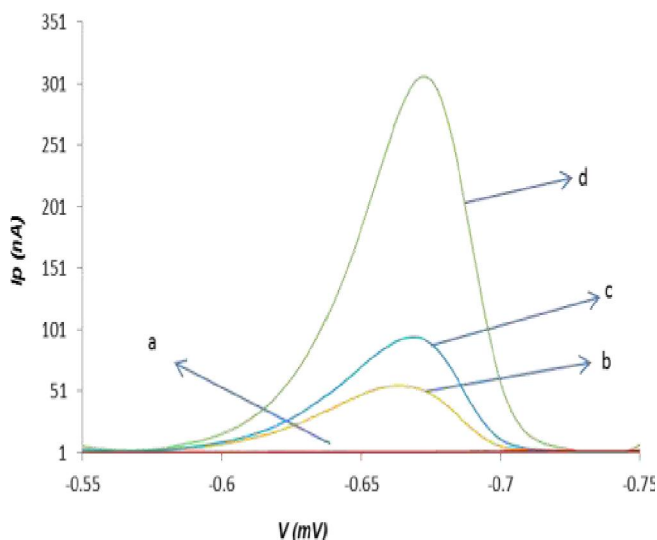


Figure 1 : Differential Pulse Voltammograms (DPVs) for 50.00 ng/ml of TSC in different accumulation times: b) 0 s, c) 20 s, d) 50 s and a) only buffer. Condition: 0.1 M Britton-Robinson buffer (pH=9.5) at -0.55 to -0.7 V, accumulation potential: -0.1 V and scan rate 60 mV/s.

Figure 1 shows differential pulse voltammograms (DPVs) of TSC between -0.55 and -0.75 V (vs. Ag/AgCl). Curve (a) shows obtained buffer alone. Curves (b, c, d) shows differential pulse voltammograms for TSC in supporting electrolyte that produced peak currents at about -0.65 V. All the above facts indicate that TSC was electroactive and could be produced by a reduction peak current at -0.65 V (vs. Ag/AgCl). This peaks (a, b, c) obtained in different accumulation times for TSC. The peak current was increased with increasing accumulation time). In addition, when 10 mg/ml Triton X-100 was added to the solution, the cathodic peak current was reduced. This phenomenon shows the adsorptive characteristic of the TSC in the HMDE sur-

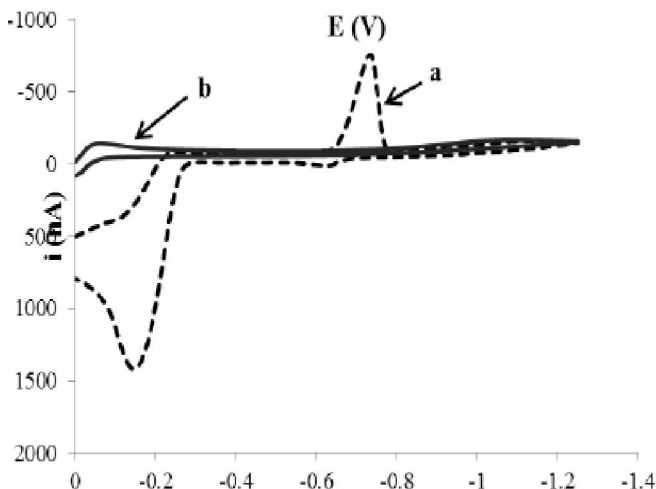


Figure 2 : Cyclic voltammograms obtained for a HMDE in 0.10 M Britton-Robinson buffer (pH = 10.0) containing (b) supporting electrolyte alone (b) 2.0 mg/L of TSC and supporting electrolyte.

face. Triton X-100 is a surface active agent, and its presence in solution can decrease adsorption and accumulation of the thiosemicarbazide on the HMDE^[14].

Cyclic voltammetry of 2.0 mg/ml TSC at deposition potential -0.10V in the presence of 0.10 M Britton-Robinson buffer at pH=10.0 shows that the TSC reduction peak is located at -0.7 V (Figure 2). There is a 0.5 V difference in the cathodic and anodic peak potentials. Thus, reduction of TSC is irreversible as demonstrated by cyclic voltammetry. The effect of scan rate on the current and potential of adsorbed TSC species is shown in Figure 3. The cathodic and anodic peak increase linearly with increasing scan rate. The shift of the peak potential with the scan rate indicates some irreversibility of the redox process, which is also char-

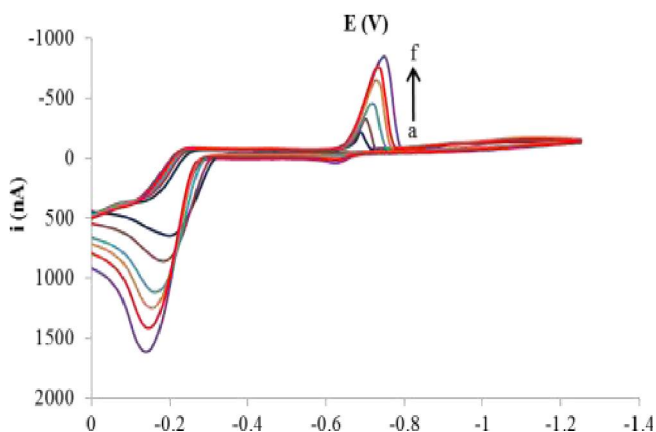


Figure 3 : Effect of scan rate on peak current and peak potential of TSC in various scan rate (50, 100, 200, 300, 400 and 500 mV/s).

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acterized by stronger separation of the cathodic and anodic peak. These are characteristics of the reaction of the adsorbed reactants on the electrode^[15, 16] and indicating an effective interfacial accumulation of the TSC.

For finding the optimum experimental conditions, the effect of chemical and instrumental factors on the height and shape of reduction peak current were studied.

Optimization of operational parameters

Effect of supporting electrolyte and pH

The effect of several supporting electrolytes such as acetate, Britton-Robinson, phosphate, carbonate and ammonia buffer was tested. The peak height and the peak shape were taken into consideration, when choosing the supporting electrolyte. Of these, Britton-Robinson gave the best response. The effect of pH on the pre-concentration stripping process in a solution containing 50.00 ng/ml of TSC was investigated in the pH range of the study between 5.0-11.0. It was found that at the pH 10.0, the peak currents of TSC were at maximum values. Thus pH 10.0 was adopted for further studies. Furthermore, different concentrations of supporting electrolyte (Britton-Robinson buffer) in the range of 0.01- 0.10 M were tested at constant TSC concentration. At 0.1M, Britton-Robinson buffer gave the highest signals for reduction peak and was selected for subsequent uses.

Effect of accumulation potential

The effect of accumulation potential on the stripping peak current of TSC was examined over the potential range of- 300 to 300 mV. The results shown that 0.00 mV was the optimum condition and it was adopted in all subsequent experiments.

Effect of accumulation time

The effect of accumulation time on peak current was also studied. The results indicate that, upon increasing the accumulation time up to 60 s, the peak current linearly increased. The peak current shows little increase when accumulation time is more than 60 s. As expected for adsorption processes, the dependence of the peak current on the accumulation time is limited by the saturation of the electrode, resulting in the current reaching a plateau at high accumulation times. Thus a deposition

time of 60 s was used throughout, as it combines good sensitivity and short analysis time. However, we selected 60 s as an optimum accumulation time for experiments.

Effect of scan rate

Based on the Randles–Sevcik Eq. 1, the stripping peak current (i_p) increases with the square root of scan rate ($v^{1/2}$)^[17];

$$I_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2} \quad (1)$$

Therefore, an optimum scan rate providing a maximum 'analytical signal' is desirable. So the effect of scan rate on the stripping peak currents was examined. For this purpose, the stripping voltammograms were recorded for 50.00 ng/ml of TSC with various scan rates of electrode potential ranging between 20 and 100 mV s⁻¹, while accumulation potential and accumulation time were 0.0 mV and 60 s respectively. According to the results, the maximum values for the analyte signals appeared at scan rate of 80 mV s⁻¹, so this scan rate was selected as optimum experimental conditions.

Calibration graph and reproducibility

Calibration plot were recorded under the optimized conditions as described above (0.1 M Britton-Robinson buffer of pH=10.0, $E_{acc} = 0.00$ mV, $t_{acc} = 60$ s and scan rate = 80 mV/s). The corresponding voltammograms are shown in Figure 4. The linearity of the calibration curves were maintains in the range of 0.50-100.00 ng/ml TSC with regression equation of $I = 8.2217 C + 2.3775$ ($R^2 = 0.9989$) where I is the net peak current in nA and C is concentration in ng/ml (Figure 5). The de-

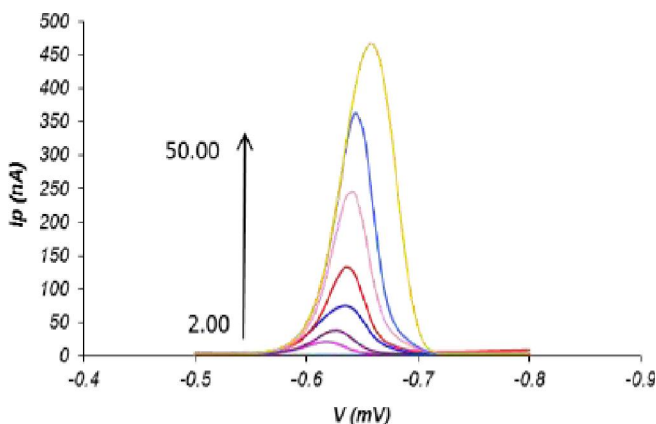


Figure 4 : Differential pulse adsorptive stripping voltammetry of different concentrations of TSC in optimized conditions. Concentration of thiosemicarbazide: (1) 2.00 ng/ml, (2) 5.00 ng/ml, (3) 10.00 ng/ml, (4) 20.00 ng/ml, (5) 30.00 ng/ml, (6) 40.00 ng/ml, (7) 50.00 ng/ml.

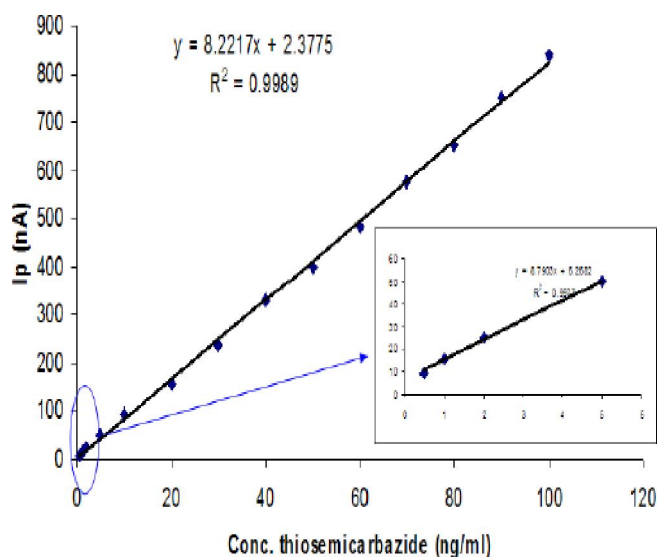


Figure 5 : Calibration graph under the optimized conditions.

tection limits which were calculated from three times the standard deviation of blank divided by the slope of the calibration graph were 0.03 ng/ml. The repeatability of the method was estimated by eight successive measurements of two solutions containing 5 and 50.00 ng/ml TSC under the optimized conditions. The relative standard deviation of 2.1 % and 1.7 % were obtained, respectively

Interference study

To study the selectivity of the proposed method, the effect of foreign species on the determination of 50.00 ng mL⁻¹ TSC was tested. The maximum tolerable concentrations of foreign species are shown in TABLE 1, where the tolerance limit was defined as the concentration of foreign species that produce a

TABLE 1 : Effect of selected potential interfering compounds on thiosemicarbazide determination.

Species	Tolerance ratio ($w_{ion}/w_{Cu^{2+}}$)
Ca ²⁺ , Na ⁺ , K ⁺ , Mg ²⁺ , Mn ²⁺ , Ag ⁺ , Ba ²⁺ , La ³⁺ , Sb ³⁺ , Li ⁺ , NO ₃ ⁻ , CH ₃ COO ⁻ , ClO ₄ ⁻ , Br ⁻ , I ⁻ , Cl ⁻ , HCO ₃ ⁻ , PO ₄ ³⁻ , CN ⁻ , SCN ⁻ Ascorbic acid, Methanol, Citric acid, Tartaric acid, Fructose, Sucrose, Oxalic acid,	1000
Glucosa, Ethanol	800
Cr ³⁺ , Al ³⁺ , Ni ²⁺ , Cd ²⁺ , SCN ⁻	500
Fe ³⁺ , Zn ²⁺ , Co ²⁺	200
Pb ²⁺ , Thiourea	50
Cu ²⁺	1

change in height peak currents less than 5 %. The results are given in TABLE 1 which shows that except Cu²⁺, most of the coexisting substances had no interference on the determination of TSC. Therefore, the method has a good selectivity. The interference of Cu²⁺ can be greatly diminished by addition of 0.1% EDTA (0.25 ml) solution.

TABLE 2 : Determination of thiosemicarbazide in various water samples.

Sample	Amount added (ng ml ⁻¹) TSC	Amount found (ng ml ⁻¹) (n = 7) TSC	Average recovery (%) TSC
city water	2	1.98±0.27	99.0
	30	29.91±0.23	99.7
	70	70.12±0.21	100.1
Zayandehrood river water	2	2.1±0.25	105.0
	30	29.82±0.22	99.4
Mineral water	70	70.14±0.22	100.2
	2	2.11±0.19	105.5
Laboratory water	30	30.17±0.24	100.6
	70	69.89±0.28	99.8
Blood sample	2	1.94±0.26	97.0
	30	29.87±0.23	99.6
	70	69.91±0.24	99.9
	2	1.99±0.30	99.5
	25	24.87±0.28	99.4
	50	50.91±0.29	101.8

TABLE 3 : Determination of thiosemicarbazide in synthetic samples.

Sample	Amount added (ng ml ⁻¹) TSC	Amount found (ng ml ⁻¹) (n = 7) TSC	Average recovery (%) TSC
1	0	19.71±0.21	-
	20	39.4±0.28	98.45
	40	60.11±0.31	101
2	0	20.13±0.19	-
	20	39.7±0.24	97.85
	40	60.14±0.28	102.52
Potassium nitrate (Merck)	2	1.97±0.29	98.5
	30	29.83±0.27	99.43
	70	70.14±0.22	100.2

Sample 1 containing: Ag(I), Ni(II), Mg(II), Cr(II), Ca(II), Ba(II), Zn(II) (1 ppb) and 20 ppb TSC, Sample 2 containing: K(I), Fe(III), Mn(II), Cd(II), Ca(II), Na(I), Co(II) (1 ppb) and 20ppb TSC

Analysis of real samples

To evaluate the validity of the proposed method for real sample analysis, the proposed procedure was applied in synthetic, blood and water samples. The TSC contents of synthetic, blood and water samples were

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determined by standard addition method using the recommended procedure under optimum conditions. The results in TABLE 2 and TABLE 3 show that the method is accurate and gives good recoveries of added TSC.

CONCLUSION

A highly sensitive and selective, rapid and low cost electroanalytical method was developed for the determination of ultra trace levels of thiosemicarbazide. The method does not require any separation steps and was directly applied to the determination of TSC in water samples. The method has very excellent linear dynamic range and low limit of detection. The proposed method is suitable for determination of trace amounts of TSC in synthetic, blood and water samples in presence of other ions at natural levels with satisfactory results.

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