A New Adsorptive Square-Wave Stripping Voltammetric Method for the Trace Analysis of Germanium

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Abstract

The adsorptive stripping voltammetric determination of trace amounts of germanium(IV) based on the adsorptive accumulation of the germanium(IV)-N-(2-hydroxyphenyl)-3-hydroxysalicylaldimine complex on the hanging mercury drop electrode is reported. The cathodic current of the adsorbed complex was measured by square wave adsorptive stripping voltammetry. The peak potential is at -0.44 V vs. Ag|AgCl|KCl$_{(sat)}$. The effects of various parameters such as ligand and supporting electrolyte (H_3PO_4) concentrations, accumulation potential and deposition time were investigated. After all optimization processes, the reduction peak was exploited for analytical purposes. The detection limit is 4.7×10^{-9} M and coefficient of variation is 7.5%. The possible interferences in soil and biological samples by some ions were evaluated in detail.

Key Words: Trace analysis of germanium, square wave stripping voltammetry, N-(2-hydroxyphenyl)-3-hydroxysalicylaldimine complex.

INTRODUCTION

Germanium is rare element in the earth's crust. Since germanium is significantly used in the semiconductor industry and has biological importance, a highly sensitive method is required for its reliable measurement. It has been reported [1] that UV-spectrophotometric method is not sufficiently sensitive and also requires very specific reagents. The determination of germanium by using electrochemical methods has advantages of accuracy, sensitivity and simplicity. Several electrochemical methods for the determination of germanium (IV) have been reported [1-8] but only some of them are sensitive enough for germanium analysis. Decreasing of over potentials required for metal ion reductions yielded by adsorbed ligands has been widely studied at the dropping mercury electrode [9-11]. Recently, this type of electro catalytic processes has been studied at the hanging mercury drop electrode [11-14].

Germanium (IV) normally cannot be reduced in acidic media prior to hydrogen evolution, but when complexed a well-defined electrochemical response is observed [10]. Several complexing agents have been used in the adsorptive stripping voltammetric determinations of germanium [1,4,6-8]. The

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complexing agents are generally 1,2-diphenol derivatives which have small molecular structure. Our previously work we synthesized a new 1,2-diphenol derivative N-(phenyl)-3-hydroxysalicyl aldimine and used for determination of germanium (IV) as a complexing agent. Since it has bigger molecular structure it showed very fine adsorptional and complexing behaviors [15].

In this paper, a new sensitive adsorptive stripping square wave voltammetric method for the determination of traces of germanium is described. Using N-(2-hydroxyphenyl)-3-hydroxysalicylaldimine (Ligand) synthesized as a complexing agent (Figure 1). The optimum analytical conditions were investigated for germanium (IV) determination in H_3PO_4 solution. Possible interferences are evaluated and calibration graphs are established by regression analysis.
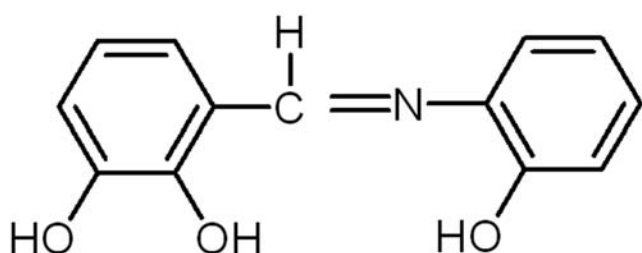

Figure 1. The molecule formula of N-(2-hydroxyphenyl)-3-hydroxysalicylaldimine (Ligand).

EXPERIMENTAL

Synthesis of N-(2-hydroxyphenyl)-3-hydroxysalicylaldimine (Ligand)

Ligand was prepared from 2,3-dihydroxy benzaldehyde and 2- hydroxy aniline according to the literature method [16]. The compound was purified by crystallizing from ethanol. The structure of the resulting compounds was elucidated by using UV, IR, ^{1}H-NMR, molecular weight determination and melting point analysis. A stock solution of 1.0 x

10^{-2} M Ligand was prepared weekly by dissolving an appropriate amount of Ligand in doubly distilled on CaO ethanol and was stored at 4°C in refrigerator.

Reagents

Unless otherwise specified, all reagents were of analytical reagent grade. Phosphoric acid (Merck), germanium dioxide (Merck) and sodium hydroxide (Merck) were used without further purification. A standard solution of germanium(IV) was prepared from the pure GeO_2 by weighing appropriate amount and dissolved in 2% NaOH solution to adjust the concentration to 10^{-2} M. Water was distilled and deionized by ELGASTAT water purification system and was used for the preparation of solutions and solvent systems.

Apparatus

The voltammograms were recorded on a BAS100B Electrochemical Analyzer. The working electrode was a PAR model 303A static mercury drop electrode. An Ag|AgCl|KCl$_{(sat)}$ and platinum wire served as reference and auxiliary electrode, respectively. The voltammograms were received to a computer by BAS100W.EXE software and evaluated one by one or along. All solutions were deaerated for 5-10 min with pure nitrogen and a nitrogen atmosphere was maintained over the solutions during the experiment.

RESULTS AND DISCUSSION

Germanium (IV) is not electroactive in phosphoric acid media in the absence of any complexing agent because it cannot be reduced before the hydrogen ion reduction. Ligand has two cathodic peaks at - 0.30 V and - 0.58 V in the same medium. Addition of Ligand to solutions of Ge (IV) in these media results in the appearance of a new peak at -0.44 V. The peak current increases with increasing Ge (IV) concentration. Figure 2 shows cyclic voltammo-

grams for solutions without and with Ge (IV) in the presence of different cocentrations. In the absence of Ge (IV) there is not any peak at - 0.44 V (Figure 2a)". When 5×10^{-6} M Ge (IV) was added to the solution only a small peak was observed (Figure 2b). In the presence of 1×10^{-4} M Ge (IV) this peak significantly increased indicating the dependence on the amount of Ge (IV). In addition to the well-defined cyclic voltammetric response in the square wave voltammetric experiments the wave increased considerably because of the addition of anodic response to the cathodic one in this technique (Figure 3).

In order to check the applicability of the adsorption preconcentration behavior of germanium(IV)-Ligand complex at the HMDE for the determination of Ge (IV) by SWAdSV, different parameters such as supporting electrolyte concentration, accumulation potential, accumulation time, ligand and Ge (IV) concentration, as well as the operational parameters of the technique were investigated.

Phosphoric acid was selected as a supporting electrolyte because of its facilitative feature in the germanium complexing reactions [17]. By comparing the peak currents of Ge (IV)-Ligand complex at different phosphoric acid concentrations, we found that the germanium (IV)-Ligand complex peak was highest in 0.8 M H_3PO_4 solution and slowly decreased as the concentration of phosphoric acid was increased. Therefore the optimum concentration of phosphoric acid was 0.8 M.

The concentration of Ligand has a significant effect on the adsorptive stripping peak current. It can be seen from Figure 4 that the peak current increases with the Ligand concentration below 1 mM, above which it remains constant. Both to obtain sufficient Ligand concentration for total complexing of Ge (IV) and to avoid the negative effects of the free Ligand on the adsorption of the complex, 1 mM of Ligand was selected as the optimum concentration.
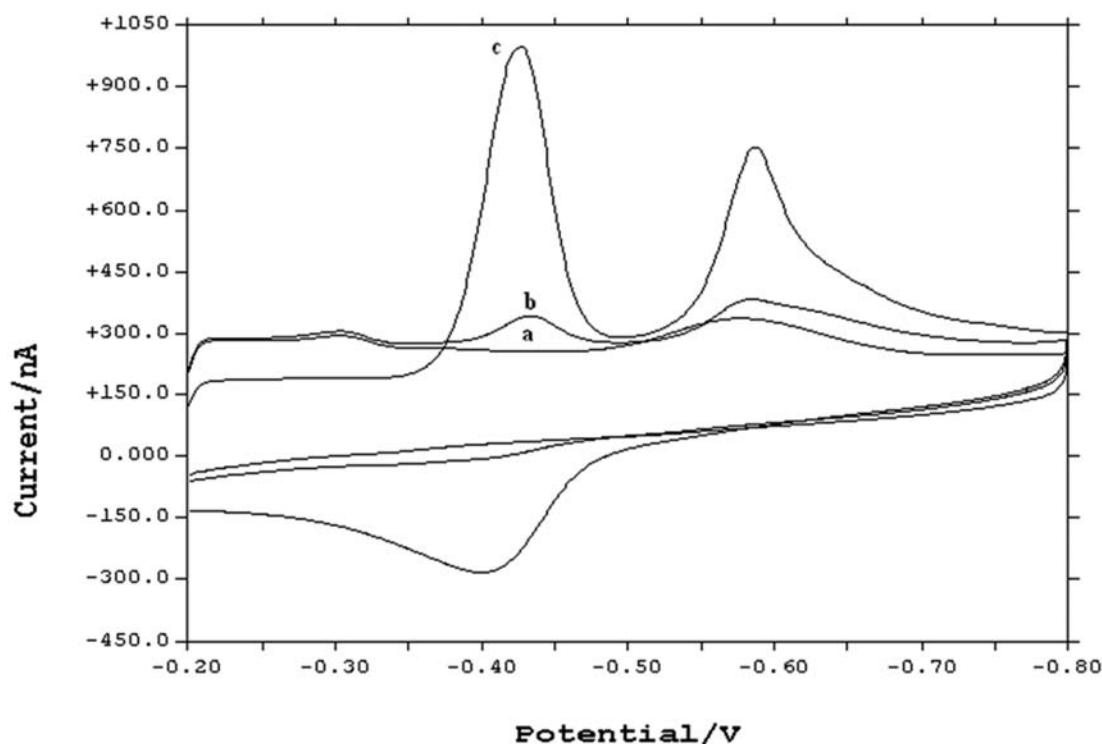

Figure 2. Cyclic voltammograms of 0.7 M H_3PO_4 solutions containing 1 mM Ligand a) in the absence of Ge(IV) b) in the presence of 5.0×10^{-6} M Ge(IV) c) in the presence of 1.0×10^{-4} M Ge(IV) (1:6 [v/v] Ethyl alcohol+0.7 M H_3PO_4, vs. Ag|AgCl). Scan rate: 0.20 V/s.
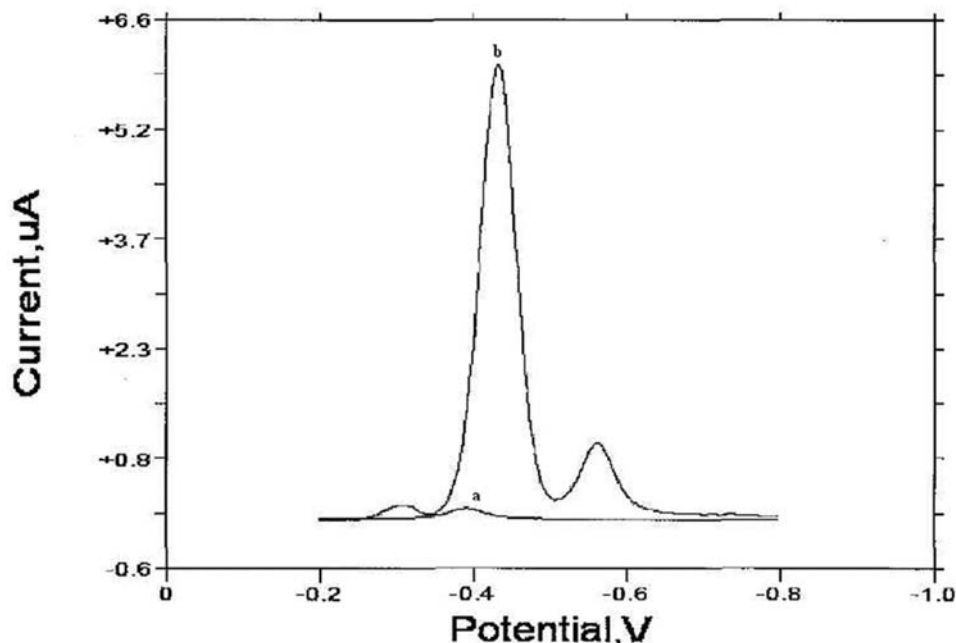
Figure 3. Square wave voltammograms of 1.0×10^{-4} M Ge(IV) in the presence of 0.1 mM (a) and 1 mM (b) Ligand (1:6 [v/v] Ethyl alcohol+0.7 M H_3PO_4, vs. Ag|AgCl). S.W. Amp:17 mV, Frequency: 80 Hz, Step: 3 mV, t_q:30 s.

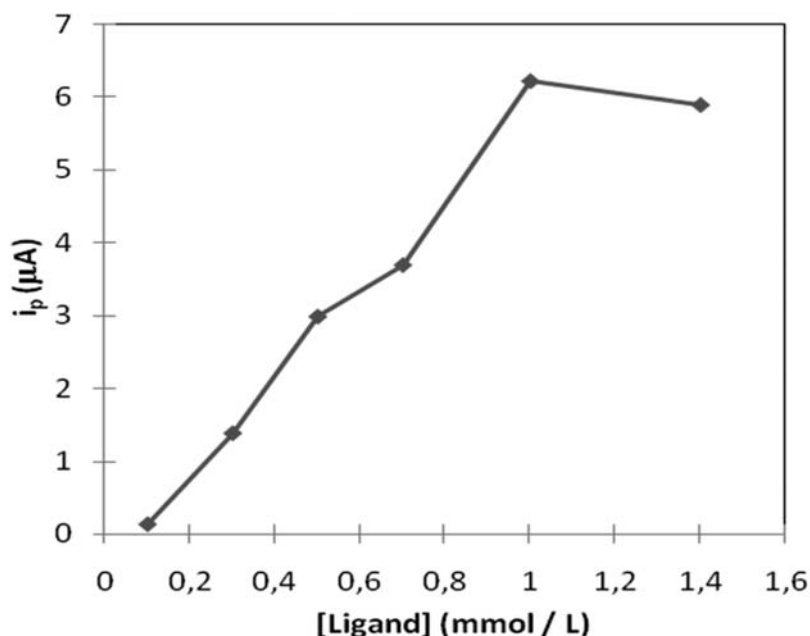Figure 4. Dependence of the reduction peak current of the adsorbed Ge(IV) complex on the concentration of Ligand. (1:6 [v/v] Ethyl alcohol+0.8 M H_3PO_4, 5×10^{-6} M Ge(IV), vs. Ag|AgCl). S.W. Amp: 17 mV, Frequency: 80 Hz, Step: 3 mV, t_q:30 s.

The effect of the accumulation potential on the square wave stripping peak current of the germanium complex was examined over the potential range from 0.0 to -0.40 V in 0.8 M H_3PO_4, 1 mM Ligand and 5.0×10^{-6} M Ge(IV) at a quiet time of 30 s. The peak height increased when the accumulation potential became more negative until the potential of -0.150 V and it tended to remain constant between -0.150 to -0.250 V. After the interval the current decreased slowly at more negative potentials. The competition between free Ligand and Ge (IV)-Ligand complex for adsorption to HMDE may be responsible for the observed effect. The results are shown in Figure 5. As understood from the figure the potentials of -0.150, -0.200 and -0.250 V can be used as the accumulation potential in the recommended procedure. Therefore, -0.200 V was selected from among.
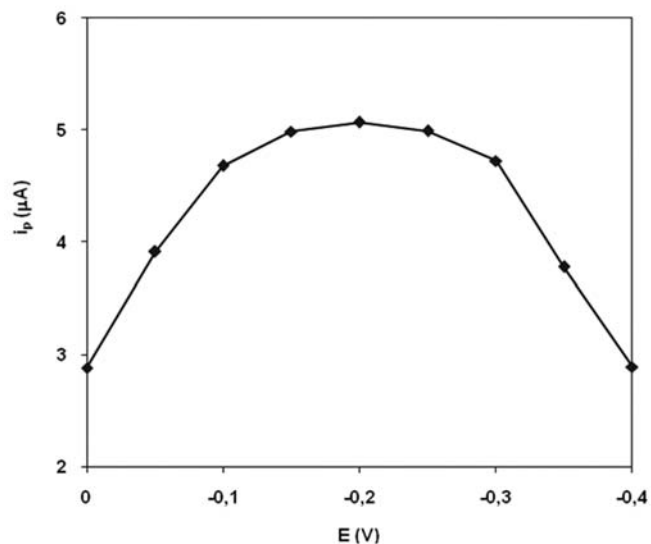
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Figure 5. Dependence of the reduction peak current of the adsorbed Ge (IV) complex to the accumulation potential. (1:6 [v/v] Ethyl alcohol+0.8 M H_3PO_4, 5×10^{-6} M Ge(IV), 1 mM Ligand, vs. Ag|AgCl). S.W. Amp: 17 mV, Frequency: 80 Hz, Step: 3 mV, t_q: 5 s.

From the results above, the optimum experimental conditions were as follows: 0.8 M H_3PO_4, 1 mM Ligand. The accumulation potential was -0.200 V vs. Ag|AgCl|KCl$_{(sat)}$.

STATISTIC EVALUATION OF CALIBRATION CURVES

The greatest advantage of the determination of Ge (IV) by the proposed adsorptive square-wave stripping voltammetric method is the inherent sensitivity. The operational parameters for square-wave techniques were determined as 80 Hz, 17 s and 3 mV for frequency, amplitude and step potential, respectively. Under the optimum conditions and using these parameters, a linear relationship was obtained between the peak current and the Ge(IV) concentration in the range of 1.0-9.7×10^{-7} M (Figure 6a) and 1.0-9.7 x 10^{-8} M (Figure 6b) when the collection time was 60 s and 120 s, respectively. When the collection time was 120 s, the detection limit of the method was 4.7 x 10^{-9} M. The results of the evaluation of the calibration curves are shown in Table 1.
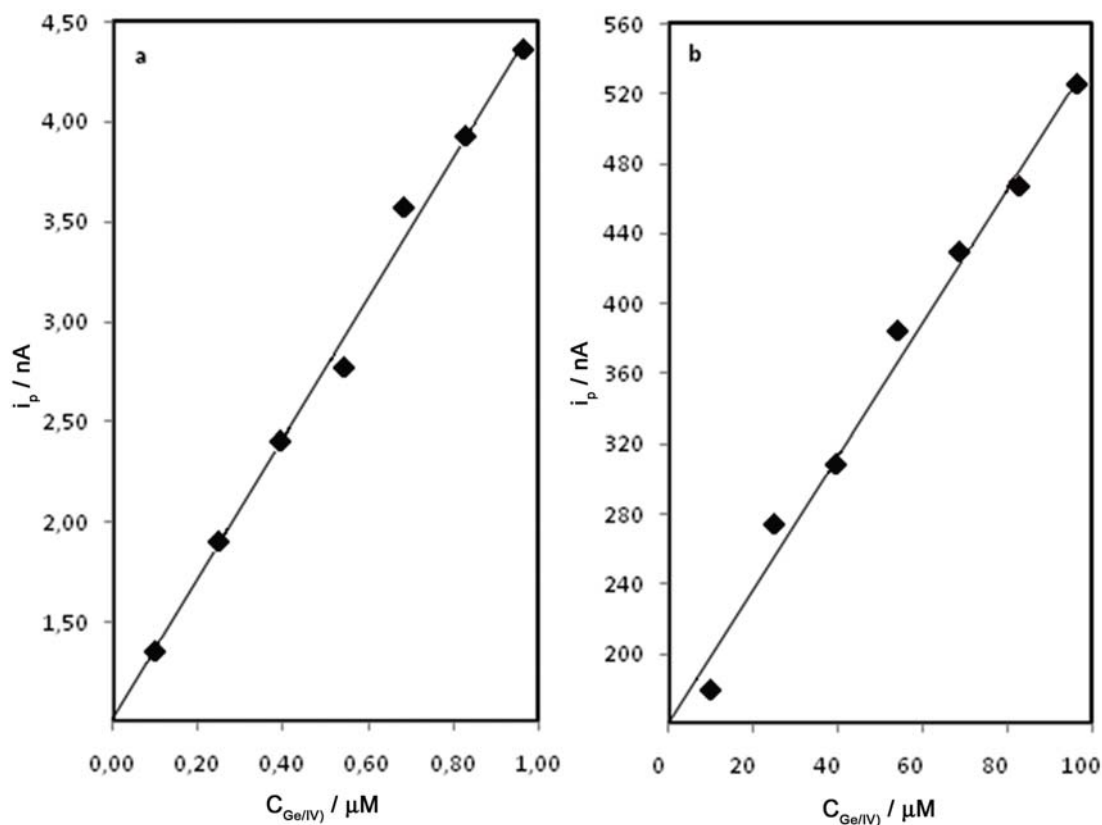

Figure 6. Dependence of the reduction peak current of the adsorbed Ge(IV) complex on the concentration of Ge(IV). (a) 1.0-9.7x 10^{-7} M Ge(IV); (b)1.0-9.7x 10^{-8} M Ge(IV). Under the optimum conditions with accumulation time of 60 s (a) and 120 s (b).

Table 1. The Results of The Statistical Evaluation of Calibration Curves

Working Range (M)	Slope (b)	Intercept (a)	Residual Standart Deviation (S_y)	Standard Deviation of the method (S_{xo})	Relative Standard Deviation (V_{xo})	Detection Limit (C_L)
$1.0 \times 10^{-8} - 9.7 \times 10^{-8}$	$3.8 \pm 0.2^*$	1.6×10^{-7}	1.6×10^{-8}	4.1×10^{-9}	7.5	4.7×10^{-9}
$1.0 \times 10^{-7} - 9.7 \times 10^{-7}$	$3.5 \pm 0.1^*$	1.0×10^{-6}	9.7×10^{-8}	2.8×10^{-8}	5.2	3.9×10^{-8}

* Standard deviation

INTERFERENCES

In order to test the selectivity of the method the effects of various foreign ions that may be coexist in geological samples on the determination of Ge (IV) was studied. The results showed that the determination of 5.0×10^{-8} M germanium was not affected by the presence of 1000-fold of Ca^{2+}, Mg^{2+}, Al^{3+}, Co^{3+}, Zn^{2+}, Ni^{2+}, Sn^{4+} and Fe^{3+} and 10-fold Cu^{2+}, Cd^{2+}, In^{2+} ions under the experimental conditions. Since the square-wave peak of Pb^{2+} are close to that of the Ge (IV) complex, the wave form was distorted by even 10-fold excess of Pb for the technique. Therefore, it is necessary to remove Pb ions from the sample prior to analysis.

CONCLUSIONS

This study proved that an alternative method can use for the determination of trace analysis of Ge (IV) by using a Schiff base bearing o-diphenols. The results above demonstrate that the feasibility of the square wave adsorptive stripping method for the trace analysis of germanium in the presence of N-(2-hydroxy phenyl)-3-hydroxysalicyl aldimine. The detection limit is 4.7×10^{-9} M. The method is not only sensitive but also highly simple and rapid.

ACKNOWLEDGEMENTS

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