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# Determination of Ge(IV) in rice in a mercury-coated glassy carbon electrode in the presence of catechol

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**Abstract**

Electrochemical adsorptive cathodic stripping voltammetry determination of Ge(IV) using the catechol complex on a mercury-coated (MC) electrode was prepared using a glassy carbon electrode (GCE), the peak potential of which was −0.5 V vs. Ag/AgCl on MCGCE. The various parameters of the catechol concentration, its pH, and others were optimized. The linear working ranges were obtained in the concentration of 2–700 μg $L^{-1}$ Ge(IV). The relative standard deviation at the Ge(IV) concentration of 50 μg $L^{-1}$ was 1.37% ($n = 15$) using the optimum condition, and the detection limit was found to be 0.6 μg $L^{-1}$ ($8.26 \times 10^{-9}$ M) (S/N = 3), with an adsorption time of 180 s. The Ge(IV) response was highly linear. This developed method was applied to Ge(IV) to determine the presence of rice grains.

*Keywords:* Stripping voltammetry; Mercury coated glassy carbon; Ge(IV); Catechol

## 1. Introduction

A highly sensitive method of determining Ge(IV) is required in biological, ore, electronic, and other forms of science. Ge(IV) is an important trace metal element in the human body, and an important semiconductor in industry, among its other uses. Its rare earth elements are composed in the atmosphere, seas, plants, and ore (Sri, Satoshi, Hiroshige, & Shigeru, 1997). In food science, its trace determination is important in the biological functions of anticarcinogenic and hygienic food (Li Zaijun, Pan Jiaomai, & Tang Jan, 2001), because its accumulation of and deficiency in germanium results in diseases and tumor formation or cancer (Jinhui & Kui, 1995). Thus, various analytical methods have been developed for its assay, such as, for example, the graphite furnace AAS method (De qiang & Zhe, 1996), the hydride generation atomic fluorescence spectrometry method (Shi, Tang, Tan, Chi, & Jin, 2002), the spectrophotometric method (Li Zaijun et al., 2001; Xiaoli, Yuanqian, Menglong, Bo, & Jingguo, 2004), the luminol chemilunescene flow method (Terufumi, Kiyomi, Takahiro, & Hiroyuki, 1996), and Raman spectroscopy with X-ray diffractometry (Bhagavannarayana, Dietrich, Zaumseil, & Dombrowski, 1999), which are applied in standard regents, food, cattle liver, seaweeds, reference materials, rice, wines, and electronic devices. All of these techniques, however, require very complicated systems, such as the pre-treatment separation system, high-temperature atomization system, fluid compression, photometric detection, and other data control systems. Faster as well as more inexpensive and sensitive analytical

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methods are now required in analytical science. The other hand-stripping voltammetric measurements are powerful methods for trace analysis (Abo El-Maali, Abd El-Hady, Abd El-Hamid, & Seliem, 2000; Joseph, Beatriz, Suw, Jianmin, & Jose, 2001; Suw et al., 2004; Suw, Duck, & Myung, 2002; Joseph Wang et al., 2000; Zhongmin, Carl, & William, 1998). The advantages of using voltammetry methods are their preconcentration procedure, their low cost, and their speed. Whichever of these systems is integrated with the three-electrode cell systems, its working electrode would be a major factor in the detection of trace elements. Thus, various working sensors have been developed, such as the hanging mercury drop electrode method (Chang, Qian, & LiLing, 1995; Jesus, Josefa, & Juan, 1999), the catalytic stripping and polarographic method, and the complex formation hanging mercury drop electrode method (Alan, Steven, Newman, & Michael, 1998; Bhagavannarayana et al., 1999; Jinhui & Kui, 1995). All these methods use the hanging mercury drop electrode, even though mercury is a very toxic element, and treatments using it are uncomfortable. The mercury-plated surface on the electrode, however, may influence response increase and lower narrow peak, although its preparation is simple. In this study, a more sensitive and accurate procedure for determining Ge(IV) was developed using the interfacial accumulation of the Ge(IV)-catalytic complex formations (Jesus et al., 1999; Jesus, Josefa, & Juan, 2001a, Jesus, Josefa, & Juan, 2001b) on the mercury-coated glassy carbon electrodes (Helena, Sandra, Luciana, & Armando, 2004; Othman, 2003; Pavel, Ludek, Hana, & Miroslav, 2003; Sandra, Helena, Joao, & Armando, 2004). A low detection limit was achieved, and although toxic dropping mercury was not used, similar detection limits were arrived at. These developed methods were applied in rice determination in specially cultured grains. The developed methods can be used in any other field, such as in those related to food, the environment, agriculture, medicine, and analytical science. Finally, the analytical results were compared with those of the other common methods of voltammetry and spectrophotommetry. Table 1 shows their sensitivity, working ranges, and detection methods. Other common voltammetric methods use only dropping mercury electrodes, which are toxic and uncomfortable. Moreover, another commonly used method, spectrophotommetry, is complicated. This developed method did not use mercury dropping, but arrived at similarly sensitive results.

## 2. Experimental section

### 2.1. Apparatus, reagents, and procedure

Experimental measurements were performed with a BAS 100 BW (bio-analytical system). A three-electrode system was used to monitor the voltammetric signal. The working electrode was an MCGCE. The reference electrode was an Ag/AgCl electrode (saturated KCl), and the auxiliary electrode was used as a platinum wire. The experimental solution was prepared from double-distilled water (18 M ohm cm$^{-1}$). The mercury-coated standard stock solution was obtained from Aldrich, and was diluted within the required time. A solution of 400-mg L$^{-1}$ mercury, which was used for the coated electrodes, was prepared by diluting the corresponding standard stock atomic absorption solution of 1 g L$^{-1}$. The 0.1-M acetate acid solution (pH: 2.0) served as the supporting electrolyte. The GCE was polished with a 0.05-μm $Al_2O_3$ slurry that was washed with double-distilled water. The three-electrode system was immersed in a 15-mL cell, which contained 400 mg L$^{-1}$ of standard mercury in a 0.1-M HCl solution. Its coating potential was −1.10 V, and its coating time, 180 s, while the solution was being stirred. The three-electrode system was then moved to the new cell, which contained a 0.1-M acetic acid solution with a pH of 1.7, following the pre-concentration step in which the usual time of 180 s was used, and the deposition potential [the initial potential of −0.2 V and the final potential of −0.7 V for measurements of Ge(IV)] was applied to the working electrode. A voltammogram was used to record a square-wave scan with a 12-Hz frequency, a 40-mV amplitude, and a 4-mV potential step.

Table 1
Comparison of the developed MCGCE method with the conventional voltammetry and spectrophotommetry methods

| Methods | Detection limit | Working ranges | Electrode or system | Reference |
|---|---|---|---|---|
| MCGCE | 0.6 μg L$^{-1}$ ($8.26 \times 10^{-9}$ M) | 2–700 μg L$^{-1}$ Ge(IV) | Catechol complex | (This method) |
| Catechol-$NaBrO_3$ | $1.0 \times 10^{-9}$ M | $1.0 \times 10^{-9}$–$7.0 \times 10^{-6}$ M | Mercury drop | Jinhui and Kui (1995) |
| DHB | $5 \times 10^{-11}$ M | $1 \times 10^{-10}$–$1 \times 10^{-8}$ M | Mercury drop | Changqing et al. (1995) |
| Pyrogallol complex | $1.2 \times 10^{-9}$ M | – | Mercury drop | Chang et al. (1995) |
| Hg-AFS | 0.11 μg L$^{-1}$ | – | Atomic fluorescence | Shi et al. (2002) |
| Chemiluminescence | 50.0 μg L$^{-1}$ | – | Ion chromatography | Terufumi et al. (1996) |
| HGAAS | 0.59 μg L$^{-1}$ | 4–140 μg L$^{-1}$ | Atomic absorption spectrometry | Elif and Murvet (2000) |
| UV–Vis | 0.4 μg L$^{-1}$ | 4–140 μg L$^{-1}$ | UV–Vis spectrophotometer | Ying et al. (2000) |

## 3. Results and discussion

### 3.1. Cyclic voltammetric mercury and catechol effects on glassy carbon electrodes

First, various electrolyte solutions of phosphate potassium, and other acid-based electrolyte solutions, were examined, and optimized solutions were obtained for the acetic acid solutions. The ionic activities of various electrolyte solutions were then tested, and the 0.1-M factors responded very actively. The effects of the cyclic voltammetric mercury-coated electrodes and the catechol complex were then examined. Fig. 1(a) shows the responses. First, in Fig. 1(a), no signal was detected in the glassy carbon-based voltammograms in the electrolyte solution; in Fig. 1(b), a small amount of the 200-mg $L^{-1}$ Ge(IV) standard was spiked, even though no signal was obtained and the area increased; in Fig. 1(c), the 1-mg $L^{-1}$ catechol solutions were spiked, and at this time, small peak signals of −0.5 V appeared, while no increase in peak current was obtained; in Fig. 1(d), the mercury-coated electrode was tested, and in this solution, to which catechols were not added, small peak signals of −0.7 V were obtained; and in Fig. 1(e), the 1-mg $L^{-1}$ catechol was spiked, and quickly increasing peak signals appeared, just as with the catechol-Ge(IV), in which catalytic peak currents appeared (Jesus et al., 1999). Moreover, the cyclic voltammetric scan rates were compared, and an optimum rate of 100 $mVs^{-1}$ was obtained. All other stripping optimizations and applications were used with these −0.7-V peak signals.

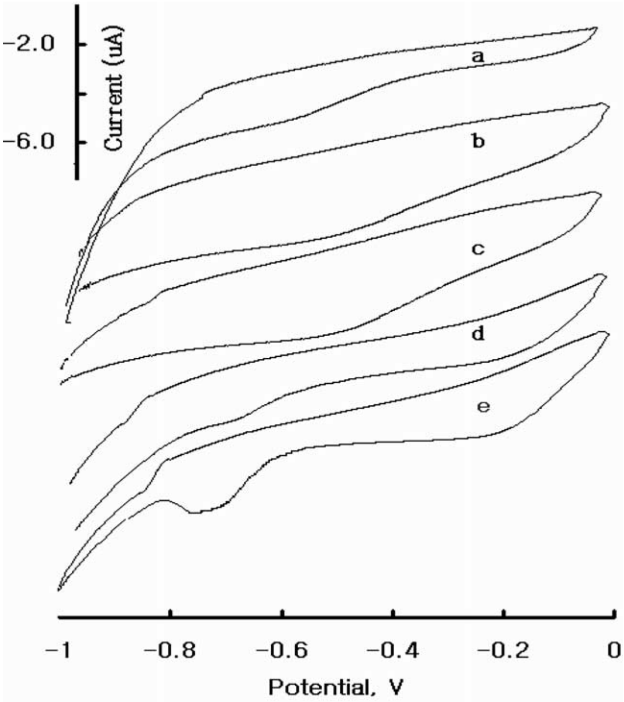

Fig. 1. Cyclic voltammetric effects for various conditions: (a) a glassy carbon base in an electrolyte solution; (b) at 200-mg $L^{-1}$ Ge(IV) on glassy carbon; (c) at b, and with 1-mg $L^{-1}$ catechol added; (d) at c, and an Hg(II)-coated electrode; and (e) at d, and with 1-mg $L^{-1}$ catechol added. The scan rate was 100 mV $s^{-1}$ for 0.1-M acetic acid (pH: 1.7).

### 3.2. Stripping voltammetric effects for the pH and catechol concentration

Fig. 2(a) illustrates the Ge(IV) peak current as a function of pH. The influence of the pH of the 20-g $L^{-1}$ Ge(IV) and the 0.1-M acetic acid solution was studied for the various pH values of 1, 1.7, 2, 3, 4, and 5. The peak current quickly increased at 1 pH, then remained within the range of 1.7–2, after which it decreased

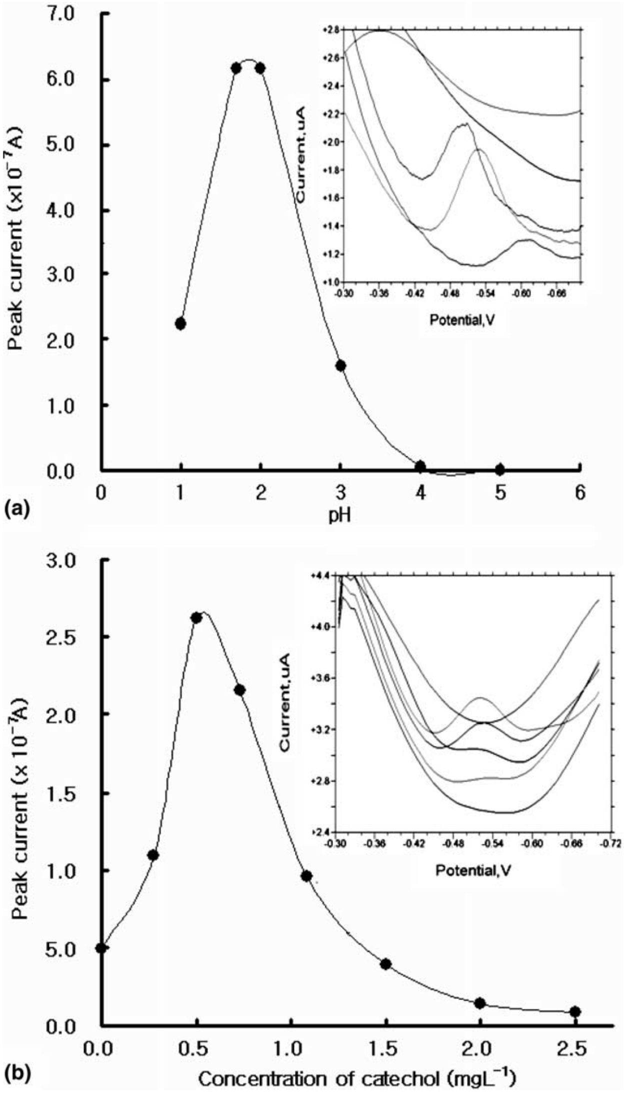

Fig. 2. (a) Dependence of the solution pH (1, 1.7, 2, 3, 4, and 5), and (b) catechol concentration (0, 0.2, 0.5, 1.1, 1.5, 2, and $2.5 \times 10^{-2}$ mol $L^{-1}$) on the 20-g $L^{-1}$ Ge(IV), at the accumulation potential of −0.40, frequency of 12 Hz, amplitude of 40 mV, and potential step of 5 mV. The other experimental parameters are as in Fig. 3.

sharply up to 4; and at the pH range of 4–6, the peak current disappeared. The raw voltammograms are shown in the inset in Fig. 2. Thus, the maximum increased current ratio for $6.14 \times 10^{-7}$ A was obtained. This was due to the increasing complex formation of Ge(IV) with catechol at the electrode surface, with the increasing pH. The most important effect was the pH of the analyte solution. Optimum formation of the target species occurred at the pH of 1.7. Other effects of the acetic acid electrolyte concentration were tested, and the same results as those at the pH of 1.7 were obtained. Therefore, this pH strength was used for all the other examinations. Afterwards, other parameters of the catechol concentration were investigated. For the optimal concentration of catechol in Fig. 2(b), it can be seen that the Ge(IV) peak was highest when the concentration of the catechol solution equaled $0.5 \times 10^{-2}$ M. Its raw voltammograms, which can be seen in the figure insert, correspond to the mole concentration ratio between the element of Ge(IV) and the ligand of catechol. At the other increased ranges, these peaks disappeared and did not respond, and registered only one good response: $0.5 \times 10^{-2}$ M.

### *3.3. Effects of varying the frequency, the step potential, and the amplitude*

Fig. 3(a) shows the results of this paper's test of the stripping voltammetric parameters of various frequencies for 20-g $L^{-1}$ Ge(IV). The experimental peak current shows a frequency range of 6–14 Hz. The well-defined sharp peaks are observed at 12 Hz, following the 180-s deposition. The peak current is strongly dependent on the frequency, and the best frequency value for increasing the peak current on the Ge(IV) stripping is 12 Hz. Moreover, at the other Hz ranges, the peak width increased broadly, and the peak height disappeared. Other high and low Ge(IV) concentration effects were examined, and the same results were achieved. At this time, a maximum increased ratio of $1.03 \times 10^{-6}$-A peak current appeared. Real voltammograms can also be seen in Fig. 3. Other parameters of amplitude were also tested. In Fig. 3(b), the dependence of the peak current on the amplitude for 10–70 mV as the amplitude increased is demonstrated. It was found that only 45 mV is enough to attain the accumulation of the metal chelate onto the electrode, which was dependent on the concentration of the complex adsorption equilibrium. An increasing peak current ratio was obtained for $6.07 \times 10^{-7}$ A. At this time, various other Ge(IV) concentrations, step potentials, and frequencies were examined, and the same results were achieved. At the optimized conditions, the stripping voltammetric parameters of various step potentials with 20-g $L^{-1}$ Ge(IV) were tested. The experimental peak current is not shown here, while the step potential rate increased to 1–6 mV $s^{-1}$. The well-defined sharp peaks were observed at 5 mV $s^{-1}$, following the 180-s deposition. The peak current was strongly dependent on the scan rate, and the best value for increasing the $4.20 \times 10^{-7}$-A peak current on the Ge(IV) stripping is 5 mV $s^{-1}$.

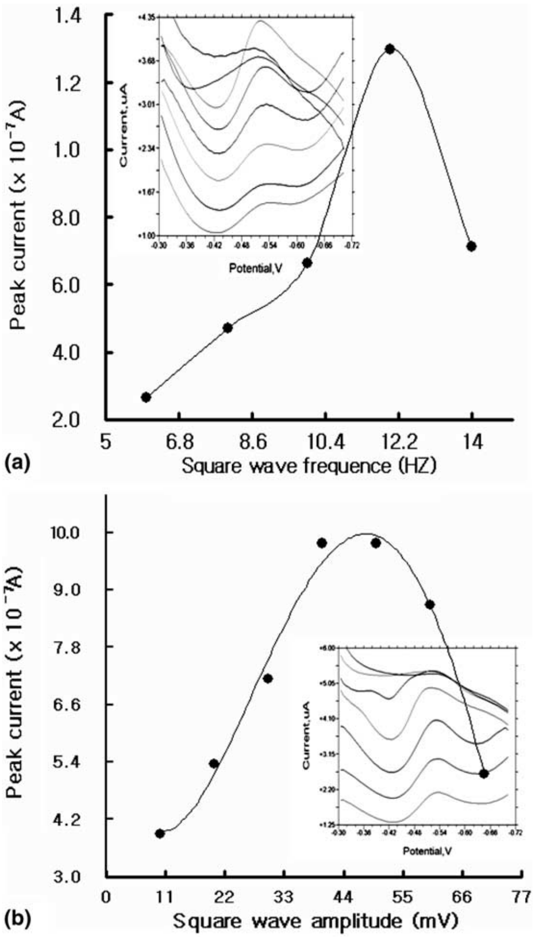

Fig. 3. (a) Stripping voltammograms of the frequencies of 6, 8, 10, 12, and 14 Hz, and (b) amplitudes of 10, 20, 30, 40, 50, 60, and 70 mV, at the 0.1-M acetic acid solution of 20 μg $L^{-1}$ Ge(IV). The other experimental parameters are as in Fig. 2.

### *3.4. Effects of varying the accumulation time and initial potential*

Fig. 4(a) demonstrates the dependence of the peak current on the accumulation times for 0 and −240 s. As the accumulation time increased, the response rose slowly. In general, the time required for the accumulation of the 20 μg $L^{-1}$ Ge(IV) chelate onto the electrode depended on the short accumulation time. It was also found that 180 s is enough to attain the adsorption equilibrium, so the maximum increasing peak current ratio of $6.07 \times 10^{-7}$ A was achieved. Various other concentrations were then studied, which yielded short adsorption times. Thus, 180 s was chosen as the best accumulation time, as in the quantitative estimations of Ge(IV). Fig. 4(b) shows the dependence of the peak current on the

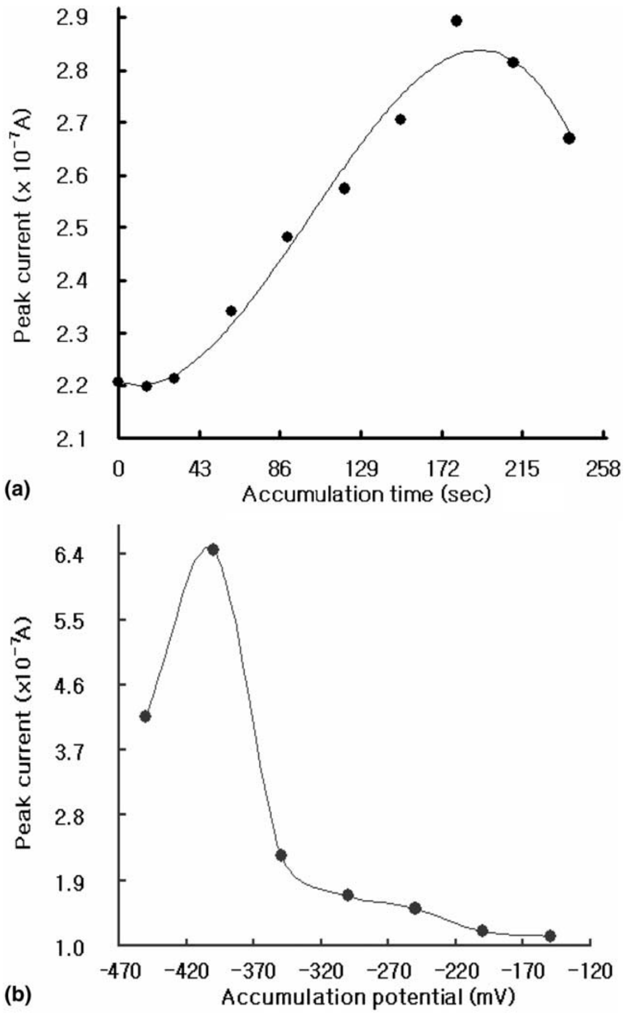

Fig. 4. (a) Response of the modified electrode as a function of the accumulation time (0, 10, 15, 30, 60, 90, 120, 150, 180, 210, and 240 $s^{-1}$) and (b) the accumulation potential (−150, −200, −250, −300, −350, −400, and −450 mV) for 20 μg $L^{-1}$ of Ge(IV) and $0.5 \times 10^{-2}$ M catechol. The other parameters are as in Fig. 3.

deposition potential, which was examined over the range of −450 to −150 mV. The peak current increased quickly as the pre-concentration potential became more negative at −330 mV, after which it quickly dropped as the accumulation potential approached −410 mV, and then dropped rapidly when the peak potential became lower than −420 mV. Thus, the maximum current of the ratio of $5.32 \times 10^{-7}$ A was achieved at about −400 mV in the acetate buffer electrolyte of 0.1 M. Therefore, the accumulation potential of −400 mV in the adsorptive stripping voltammetric determination of Ge(IV) can be chosen. Other positive potentials were examined, but no peak signals were detected.

### 3.5. Statistics and applications

In Fig. 5, at the optimum conditions, the various concentration effects of the calibration curve (a) and the raw voltammograms (b) were estimated. The figure of Ge(IV) was linear over the range of 2–700 μg $L^{-1}$ for a 180-s accumulation. For this range, the linear plot yielded a regression equation of $y$ = 1E-09$x$ + 2E-07 [$R$ = 0.992, 10 points, $y$ = current, A; X = Ge(IV) concentration, μg $L^{-1}$]. At this time, the reproducibility of the stripping peak current, as measured by the relative standard deviation (RSD) posted for 14 determinations of the 50 μg $L^{-1}$ Ge(IV) solution with 180-s accumulation, was 1.37%, and the detection limit was estimated to be 0.60 μg $L^{-1}$ on the basis of the signal-to-noise ratio (S/N = 3) at an accumulation within the same time. Moreover, the maximum increased peak current ($\Delta y$) ratio

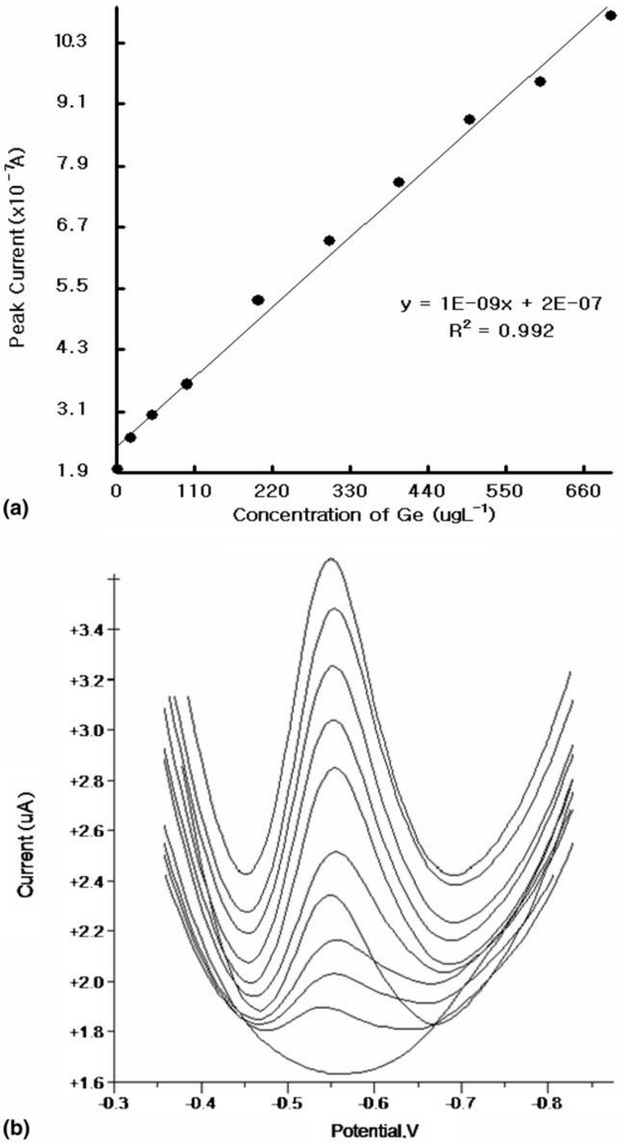

Fig. 5. (a) Stripping voltammetric working curves of increasing Ge(IV) concentrations (0, 2, 20, 50, 100, 200, 300, 400, 500, 600, and 700 μg $L^{-1}$) and (b) its real voltammograms at a pH of 1.7, an initial potential of −0.40, a final potential of −0.70 V, a square-wave frequency of 12 Hz, an amplitude of 40 mV, and a potential step of 5 mV. The other parameters are as in Fig. 4.

was obtained at $8.82 \times 10^{-7}$ A. The analytical-interference ions were then removed using the standard addition method. Analytical applications performed using specific cultured Korean rice samples, which contained fertilized soil germanium, and other generally selling rice samples, were tested. First, small amounts of commonly and specially cultured rice samples were grinded in a crystal milling port, some 10.0-g milled rice powders were added to the covered quartz cell, then 5 mL of concentrated $HNO_3$, 0.5 mL of $HClO_4$, and 5–10 drops of concentrated $H_2SO_4$, were added. The mixture was then placed on a hot plate, and was slightly boiled (Li Zaijun et al., 2001). The solutions were used to determine the presence of Ge(IV) concentration. The stripping voltammetric signals showed a distinct peak current of Ge(IV). The concentration of Ge(IV) in both rice samples was determined by the standard addition method of known concentrations. No Ge(IV) was detected in all the five other commercial rice samples. Other specific cultured rice samples were also examined. First, the standard peak currents of the blank solutions, samples, and 2-, 4-, and 6 μg $L^{-1}$ Ge(IV), were spiked, and the calibrated value of 1.3 μg/100 g was thus obtained. These samples were examined using common methods, such as the ICP-AA method. The results of 1.30–1.31 ppb $L^{-1}$ of identical concentrations were obtained.

The resulting concentration values are similar to those in other papers (Jinhui & Kui, 1995). Jinhui & Kui searched for Ge(IV) contents in food samples of grape (0.1 μg/100 g), cabbage (0.089.3 μg/100 g), spinach (0.086.4 μg/100 g) and cucumber (0.059.7 μg/100 g), but higher contents of Ge(IV) in rice samples were obtained in this study.

## 4. Conclusion

A mercury-coated modified stripping method has been developed using the catalytic current of catechol to determine Ge(IV). The electrode response was linearly related to the Ge(IV) concentration within the range of 2–700 μg $L^{-1}$, with a 180-s adsorption time in 0.1-M acetic acid (pH: 1.7) electrolyte solutions. The presented method had a lower detection limit of 0.6 μg $L^{-1}$ ($8.26 \times 10^{-9}$ M) (S/N = 3). Although toxic dropping mercury was not used, similar detection limits were arrived at. This method was applied to specially cultured rice, and can be used for trace Ge(IV) detection in any other measurement of food, water, agricultural produce, and minerals.

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