

ANALYSIS OF SELENIUM SPECIES USING CATHODIC STRIPPING VOLTAMMETRY

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Abstract. Differential pulse cathodic stripping voltammetry of an inorganic selenium (selenite, Se(IV)) and organic selenium (dimethyl diselenide, DMDS_e) was investigated using hanging mercury drop electrode (HMDE). The reduction peaks of selenite and dimethyl diselenide were obtained at -472 mV and -304 mV vs Ag/AgCl electrode respectively in acidic media. Various voltammetric parameters such as supporting electrolyte, accumulation potential and accumulation time were studied to establish the optimum condition for the determination of selenite and dimethyl diselenide. The detection limit of selenite and dimethyl diselenide was 8.175×10^{-9} M and 9.487×10^{-8} M respectively when an accumulation potential of 100 mV was applied for 90 seconds. Simultaneous determination of selenite and dimethyl diselenide was also carried out. The effect of selenite on the determination of dimethyl diselenide and vice versa was studied. The influence of metal ions such as lead, copper, cadmium and zinc on the reduction signals for selenite and dimethyl diselenide was also investigated.

Keywords: Cathodic stripping voltammetry, Se(IV), dimethyldiselenide

Abstrak. Voltammetri perlucutan katodik denyut perbezaan bagi selenium tak organik (selenit, Se(IV)) dan selenium organik (dimetil diselenida, DMDS_e) telah dikaji menggunakan elektrod titisan merkuri tergantung (HMDE). Hasil kajian mendapati bahawa puncak penurunan bagi selenit dan dimetil diselenida masing-masing adalah pada keupayaan -472 mV dan -304 mV melawan elektrod Ag/AgCl dalam medium berasid. Pelbagai parameter voltammetri contohnya elektrolit penyokong, keupayaan pengumpulan dan masa pengumpulan dikaji untuk mendapatkan suatu keadaan optimum bagi penentuan selenit dan dimetil diselenida. Had pengesanan selenit dan dimetil diselenida masing-masing adalah 8.175×10^{-9} M dan 9.487×10^{-8} M diperolehi apabila keupayaan pengumpulan 100 mV dikenakan selama 90 saat. Penentuan serentak bagi selenit dan dimetil diselenida juga dilakukan. Kesan kehadiran selenit dalam penentuan dimetil diselenida dan sebaliknya juga dikaji. Kesan gangguan ion logam seperti plumbum, kuprum, cadmium dan zink terhadap isyarat penurunan bagi selenit dan dimetil diselenida juga dikaji.

Kata kunci: Voltammetri perlucutan katodik, Se(IV), dimetil diselenida

1.0 INTRODUCTION

Selenium is an essential trace element with only a small difference between its toxic and essential level. It has been reported that selenium has an anti-cancer effect, protecting the human body from radicals and the recommended intake is between

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of 50-200 mg/day. Out of this range, diseases due to its deficiency or poisoning can occur [1]. Selenium functions as an essential part of antioxidant enzymes that protect cells and their lipid membrane against oxidative damage, catalyze the reactions of the intermediate metabolism, inhibits free radical peroxidation of lipids and also inhibit the toxicity of heavy metals such as arsenic, cadmium, lead and tin [2].

Selenium has unique photoelectrical and semi-conducting properties. It is used in mining, fuel production and photocopying technology. Industrial processes release selenium into the environment mainly as inorganic species, such as selenite, Se(IV) and selenate Se(VI), which are bioconverted to organometallic species through biomethylation processes.

Selenium naturally exists in several oxidation states in inorganic and organic forms. The inorganic selenium has four oxidation states which are 6, 4, 0 and -2. The main organic forms of selenium are selenoamino acids and their derivatives, volatile methylated compounds such as dimethyl selenide and trimethylselenonium [3].

A variety of methods to determine selenium have been reported over the years [4]. For the speciation analysis of selenium, several analytical methods have been developed; most of them refer to inorganic selenium (Se(IV) and Se(VI)). The total concentration of selenium can be determined by instrumental neutron activation analysis (INAA) [5,6], atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry (ICP-AES) [7-9]. For the determination of inorganic as well as organic selenium species, hyphenated techniques based on liquid chromatography (LC) coupled with UV spectrophotometry, hydride generation atomic absorption spectrometry (HG-AAS), hydride generation atomic fluorescence spectrometry (HG-AFS), or other detection techniques have been used [10-14]. Voltammetric techniques, however, are inexpensive, sensitive and selective and they can also be used for speciation analysis [15]. Most of the voltammetric techniques reported for Se refer to inorganic selenium species such as Se(IV) and Se(VI) after reduction [16]. In this work, determination of inorganic and organic selenium species, which are selenium oxide (selenite, Se(IV)) and dimethyl diselenide (DMDS_e) were carried out using cathodic stripping voltammetry technique. The optimization of the technique was achieved by varying the main voltammetric parameter such as supporting electrolyte, accumulation potential and accumulation time to seek the optimum conditions for the determination of selenite and DMDS_e. The limit of detection of selenite and DMDS_e was determined under optimized conditions. Simultaneous determination of selenite and DMDS_e was then carried out. The influence of cations such as lead, copper, cadmium and zinc on the determination of selenite and DMDS_e was also investigated.

2.0 EXPERIMENTAL

2.1 Reagents

All reagents used throughout this research were analytical grade chemicals and were used without further purification. All solutions were prepared using deionized water except the DMDS_e solution which was prepared using methanol (Merck). The solutions of selenite, lead, copper, cadmium and zinc were respectively obtained from selenium dioxide (Merck), lead nitrate (Emory), cupric sulphate crystals (GCE), cadmium sulphate (BDH) and zinc sulphate (Comak). DMDS_e, hydrochloric acid and perchloric acid stock solutions were prepared by dimethyl diselenide (98%, Aldrich), hydrochloric acid (37%, Merck) and perchloric acid (70-72%, Merck) respectively. Working solutions were prepared by dilution of suitable volume of stock solutions in deionized water except for DMDS_e which was prepared in methanol. Pure nitrogen gas (MOX) was used to deaerate solutions prior to measurements.

2.2 Instrumentation

A Eco-Tribo Polarograph voltammetric analyzer equipped with a Polar Pro Version 1.0 software was used for the voltammetric determination of selenite and DMDS_e. The working electrode was a hanging mercury drop electrode (HMDE), the reference was a Ag/AgCl electrode filled with 3 M KCl and the auxiliary electrode was platinum. All the potential reported are compared to the reference electrode.

2.3 Procedures

For the investigation of the voltammetric behavior of selenite and DMDS_e, the general procedure used to obtain cathodic stripping voltammograms was as follows: 20 mL of hydrochloric acid as supporting electrolyte was placed in the voltammetric cell and the solution was purged with nitrogen for 10 minutes with the stirrer on. After an initial blank run, the required volumes of the compounds studied were spiked into the cell and the solution was deoxygenated for a further 15 seconds. After the formation of a new mercury drop, the accumulation was performed on HMDE and the solution was stirred at the accumulation potential of 0 mV for 30 seconds. At the end of the accumulation period, the stirrer was switched off and after 5 seconds had elapsed to allow the solution to become quiescent, the voltammogram was recorded cathodically with a scan rate of 20 mV/s and a pulse amplitude of 50 mV.

3.0 RESULTS AND DISCUSSION

3.1 Cyclic Voltammetric of Se(IV) and DMDS_e

The cyclic voltammetric behavior of Se(IV) and DMDS_e was studied in the aqueous phase using HCl as the electrolyte. Both cyclic voltammograms (Figure 1(a) and (b))

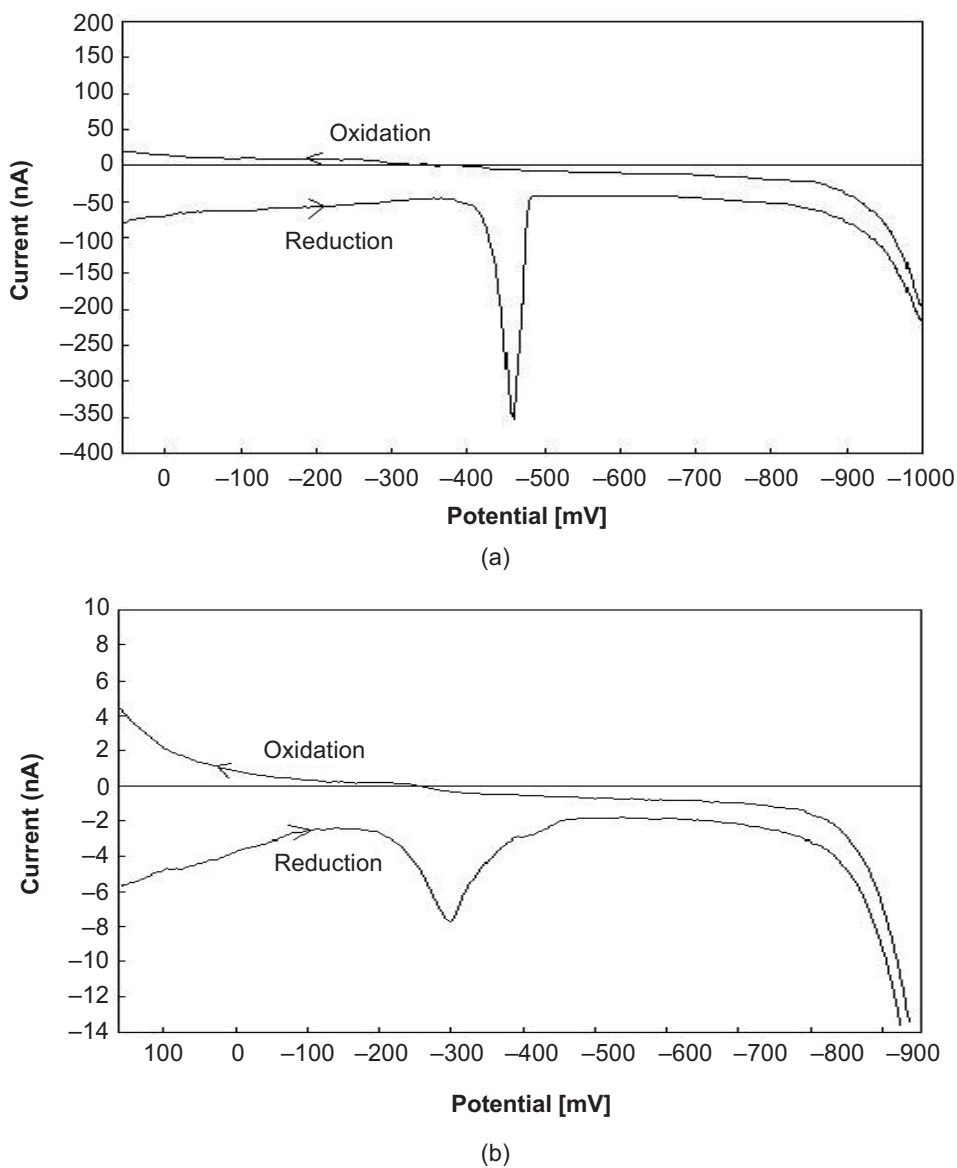


Figure 1 Cyclic voltammogram of (a) 0.2 mg/L Se(IV) and (b) 1.0 mg/L DMDSe in 0.05 M HCl. Scan rate was 50 mV/s

showed a clear defined reduction peak at -460 mV and -300 mV for selenite and DMDSe respectively. No peaks were observed on the reverse scan, indicating the irreversibility of both electrode processes.

The cathodic stripping voltammogram for selenite and DMDSe are shown in Figures 2 and 3 respectively. The reduction peak increases quantitatively with the

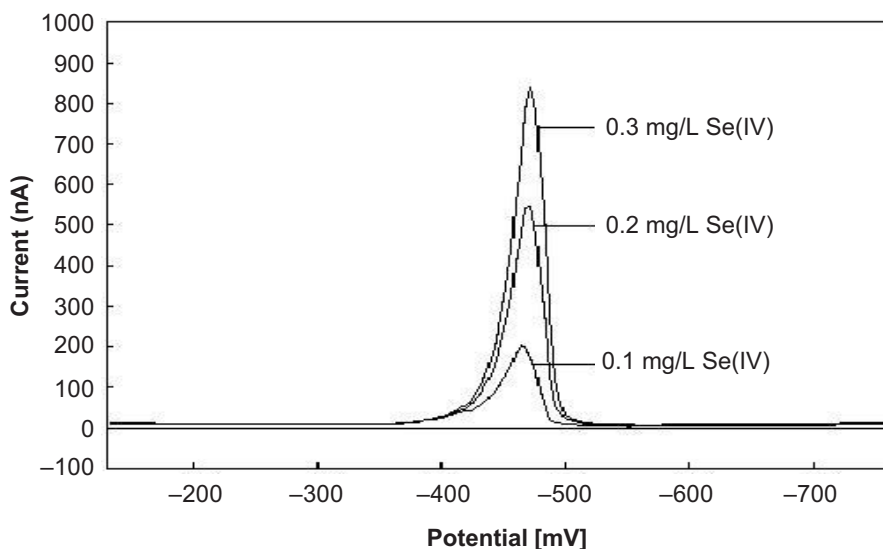


Figure 2 Cathodic stripping voltammogram of Se(IV) at different concentrations using 0.05 M HCl as supporting electrolyte. $E_i = 0$ mV, $E_{acc} = 100$ mV, $t_{acc} = 30$ s, scan rate = 20 mV/s

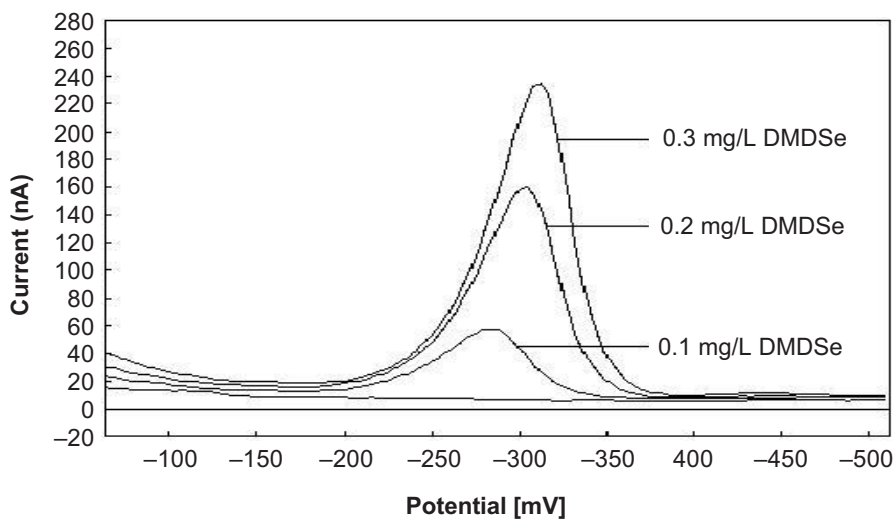
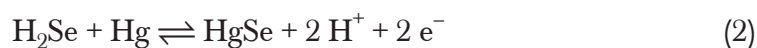


Figure 3 Cathodic stripping voltammogram of DMDSe at different concentrations using 0.05 M HCl as supporting electrolyte. $E_i = 0$ mV, $E_{acc} = 100$ mV, $t_{acc} = 30$ s, scan rate = 20 mV/s

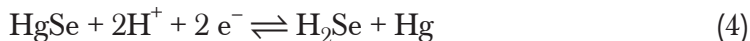
amount of selenite and DMDSe present. In acidic solution, reduction of Se(IV) occurs in two stages [16], the first involves the formation of hydrogen selenide (H₂Se),



With the net reaction:



The HgSe is then reduced to H₂Se during the stripping step at -0.54 V.



The voltammetric behaviour of organic selenium species, such as DMDS_e has not yet been investigated [15].

3.2 Optimization of the Analytical Parameters

Various voltammetric parameters were studied to establish the optimum condition for the determination of Se(IV) and DMDS_e.

3.2.1 Selection of Electrolyte

For the optimization of the voltammetric parameters, the effect of HCl and HClO₄ on the CSV peak current of Se(IV) and DMDS_e were initially tested. From the results, the peak current of Se(IV) decreased with increasing concentration of HCl as the supporting electrolyte. However, when HClO₄ was used, the height of the Se(IV) peak initially increased with increasing HClO₄ concentration up to 0.10 M, and no peak was observed at higher concentration (Figure 4). The height of the DMDS_e peak increased with increasing hydrochloric acid concentration up to 0.1 M and does not increase further at higher concentration (Figure 5). There was an abrupt decrease of peak current when higher concentration (>0.01 M) of HClO₄ was used. By increasing the concentration of acids, the reduction peaks of Se(IV) and DMDS_e were shifted to less negative potentials [15].

We observed that at higher concentration of HClO₄, the CSV peak shapes and height of Se(IV) became distorted and were accompanied by another small peak at more negative potential, which was around -570 mV.

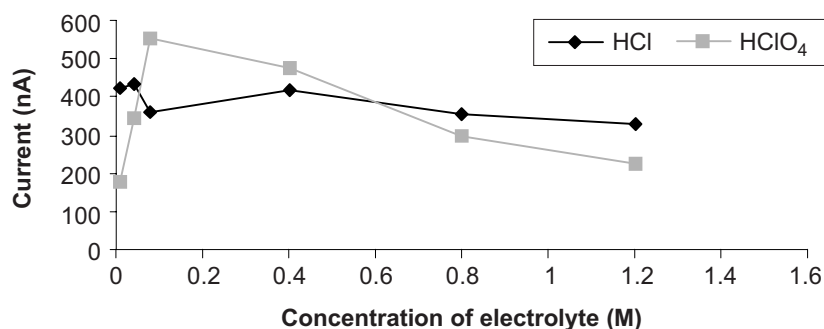


Figure 4 Effect of varying the HCl and HClO₄ concentration on the peak current of 0.2 mg/L Se (IV)

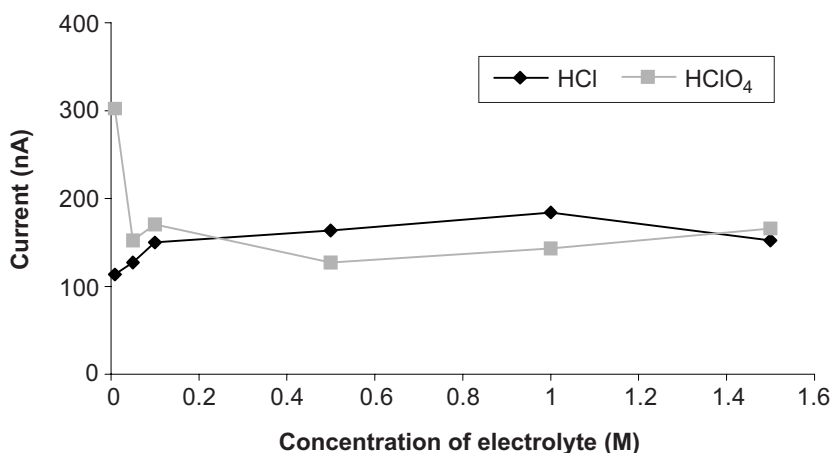


Figure 5 Effect of varying the HCl and HClO₄ concentration on the peak current of 0.2 mg/L DMDSse

Since the peak current of DMDSse was independent of concentration of HCl, thus 0.05 M HCl was chosen for further studies for both Se(IV) and DMDSse.

3.2.2 Effect of Accumulation Potential (E_{acc})

The accumulation was carried out for 30 seconds at selected potential between 150 mV and -150 mV. The dependence of peak current on the E_{acc} for 0.1 mg/L Se(IV) and 0.2 mg/L DMDSse is shown in Figure 6. Generally, the peak current for both Se(IV) and DMDSse decreased when the E_{acc} became more negative (<100 mV). This may be related to the charge on the electrode, which changes from positive to negative [16].

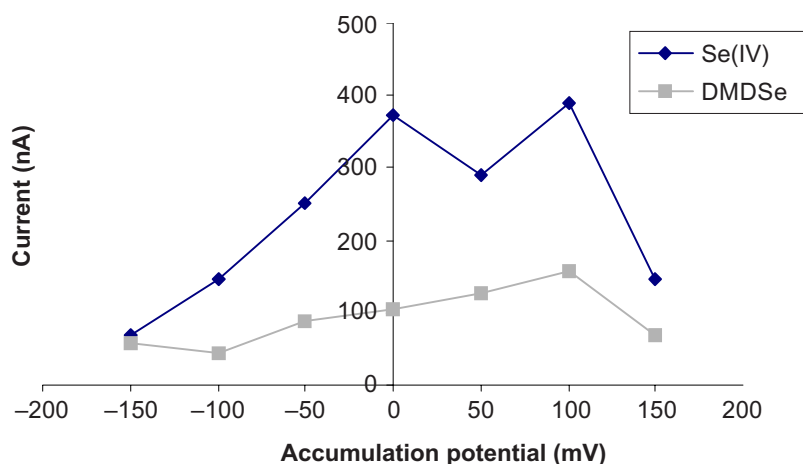


Figure 6 Effect of E_{acc} on the peak current of 0.1 mg/L Se(IV) and 0.2 mg/L DMDSse

The peak currents obtained at E_{acc} more positive than 100 mV could be low due to incomplete reduction of selenium species on the mercury surface. Hence an E_{acc} of 100 mV was chosen as the optimum E_{acc} for both Se(IV) and DMDS_e.

3.2.3 Effect of Accumulation Time (t_{acc})

The peak current for Se(IV) and DMDS_e were measured using CSV as a function of accumulation time using the optimized analytical procedure. Theoretically, the observed peak current should be directly proportional to the accumulation time. However, this is not the case in practice.

Variation of the accumulation time showed that the peak current for 0.1 mg/L Se(IV) increased linearly with accumulation time for $t_{acc} < 90$ seconds, after which the peak current remained constant (Figure 7). However, there is not much difference in the effect of accumulation time on the peak current of DMDS_e. Hence for analytical purposes, 90 seconds was employed as the optimum t_{acc} for the analysis of both Se(IV) and DMDS_e.

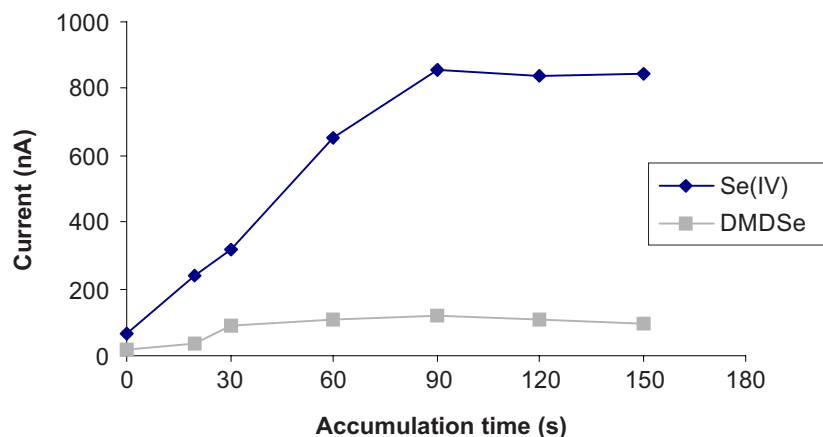


Figure 7 Effect of accumulation time on the peak current of 0.1 mg/L Se(IV) and 0.2 mg/L DMDS_e

3.3 Linear Range and Limit of Detection (LOD)

The LOD of Se(IV) was found to be lower than DMDS_e. Under the optimized condition, linear calibration graph for Se(IV) and DMDS_e were obtained within the ranges of 1.27×10^{-8} M to 12.67×10^{-8} M and 1.27×10^{-7} M to 12.66×10^{-7} M respectively (Table 1). The detection limit, defined as three times the signal-to-noise ratio, was found to be 8.18×10^{-9} M and 9.49×10^{-8} M for Se(IV) and DMDS_e respectively. The slope of the calibration graph of the Se(IV) was steeper than the DMDS_e's reflecting that CSV technique was more sensitive to Se(IV) compared to DMDS_e under the optimum condition.

Table 1 Characteristics of the calibration graphs for Se(IV) and DMDS_e

Species	Range of linearity ($\mu\text{g/L}$)	Correlation coefficient	Slope ($\text{nA}\mu\text{mol}^{-1}$)	Intercept (nA)
Se(IV)	$1.27 \times 10^{-8} - 12.67 \times 10^{-8}$	0.9995	4.1126	2.5488
DMDS _e	$1.27 \times 10^{-7} - 12.66 \times 10^{-7}$	0.9940	1.3604	5.3867

3.4 Interferences

3.4.1 Simultaneous Determination of Se(IV) and DMDS_e

The stripping peaks of the individual Se(IV) and DMDS_e (as shown in Figures 2 and 3) having the potentials at -472 and -304 mV respectively proves that Se(IV) and DMDS_e can be determined simultaneously by CSV. Figure 8 shows the voltammogram for the mixture of 0.1 mg/L Se(IV) and 0.1 mg/L DMDS_e. The potentials of Se(IV) and DMDS_e were at -476 mV and -272 mV respectively. Although the measured concentration of Se(IV) and DMDS_e were the same, the resulting peak current of Se(IV) was much higher than DMDS_e showing that the sensitivity for the Se(IV) is higher than DMDS_e under the same condition. The peak current of Se(IV) was 351.9 nA and 69.54 nA for DMDS_e. The peak current for DMDS_e was much broader compared to that of Se(IV).

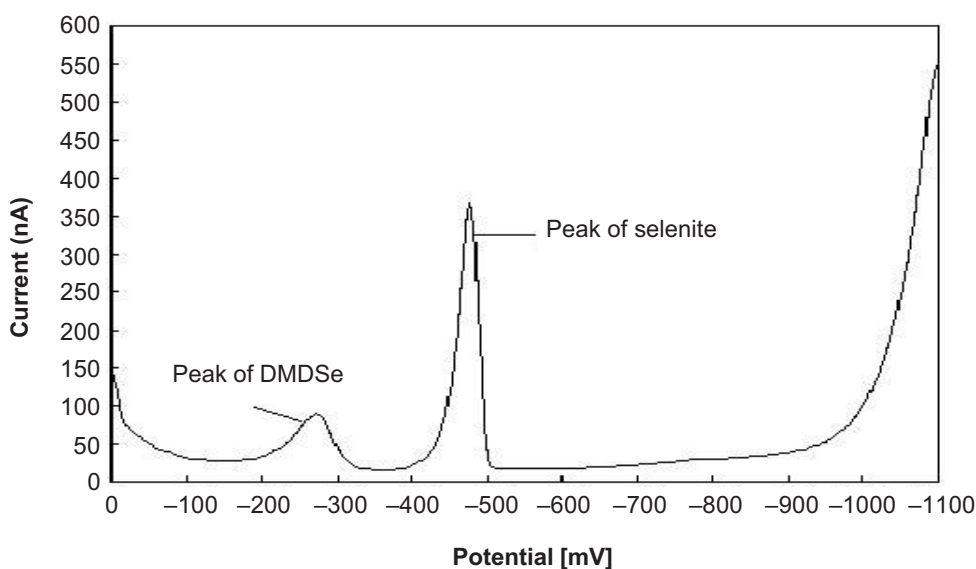


Figure 8 Cathodic stripping voltammogram of Se(IV) and DMDS_e using 0.05 M HCl as supporting electrolyte. $E_i = 0$ mV, $E_{acc} = 100$ mV, $t_{acc} = 30$ s, scan rate = 20 mV/s, 0.1 mg/L Se(IV) and 0.1 mg/L DMDS_e

The effect of Se(IV) on the peak current of DMDSe and vice versa was studied. By varying the concentration of Se(IV) from 0.1 to 0.4 mg/L in the presence of 0.5 mg/L DMDSe, the peak current of DMDSe was reduced by more than 90% (Figure 9). The peak potential of DMDSe was also slightly shifted to more positive values when the concentration of Se(IV) was increased. At a concentration of 0.5 mg/L Se(IV), the DMDSe peak was not detected.

The effect on the peak current of Se(IV) in the presence of different concentrations of DMDSe was also investigated (Figure 10). The concentration of DMDSe was

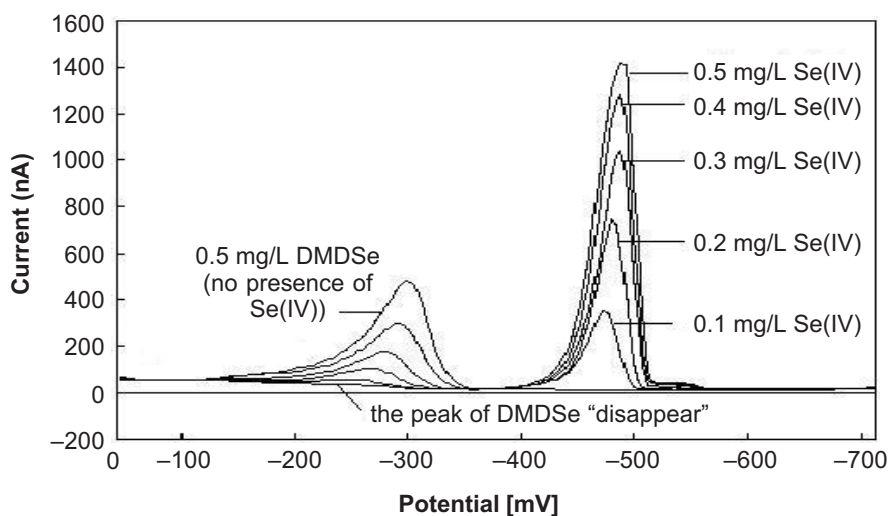


Figure 9 Effect of Se(IV) (0.1 – 0.5 mg/L) on the CSV of DMDSe (0.5 mg/L) using 0.05 M HCl as supporting electrolyte. $E_i = 0$ mV, $E_{acc} = 100$ mV, $t_{acc} = 30$ s, scan rate = 20 mV/s

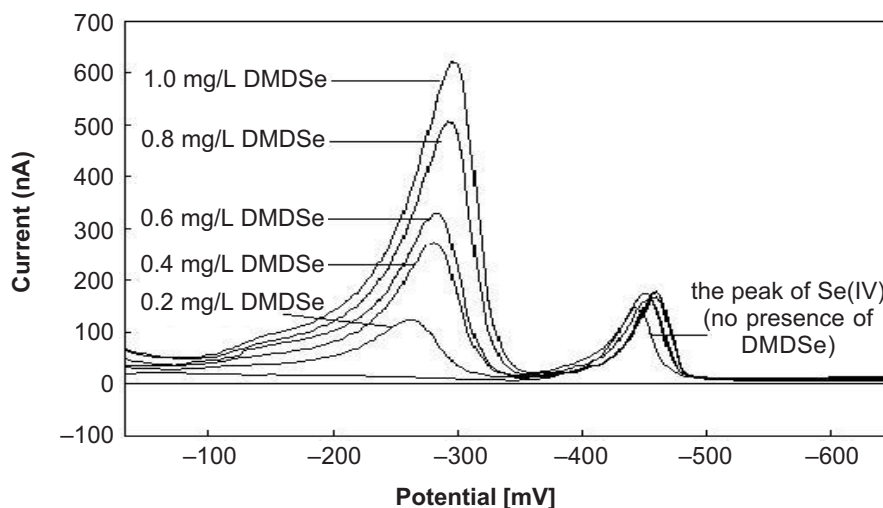


Figure 10 Effect of DMDSe (0.2 – 1.0 mg/L) on the CSV of 0.05 mg/L Se(IV) using 0.05 M HCl as supporting electrolyte. $E_i = 0$ mV, $E_{acc} = 100$ mV, $t_{acc} = 30$ s, scan rate = 20 mV/s

increased from 0.2 to 1.0 mg/L in the presence of 0.05 mg/L Se(IV) and results showed that the peak current of Se(IV) was slightly increased even when the concentration of DMDS_e was 20 times in comparison to the Se(IV).

3.4.2 Cations Interference

The interference of some cations in the determination of Se(IV) and DMDS_e by CSV was also studied. The various ratios of the selenium species to interfering ions (Pb(II), Cu(II), Cd(II) and Zn(II)) were studied to determine the effect of these cations on the determination of the selenium species.

It was observed that all the cations interfered in the determination of DMDS_e. The CSV peak of DMDS_e completely disappeared in the presence of the cations even at low concentration. On the other hand, at low concentration of interferents, there was no significant difference in the peak height of Se(IV). However, higher concentration of interferents will cause greater changes in the peak current of Se(IV). The increment in peak current of Se(IV) was observed in the presence of Pb²⁺, whereas for the other cations, the peak current of Se(IV) was reduced (Figure 11).

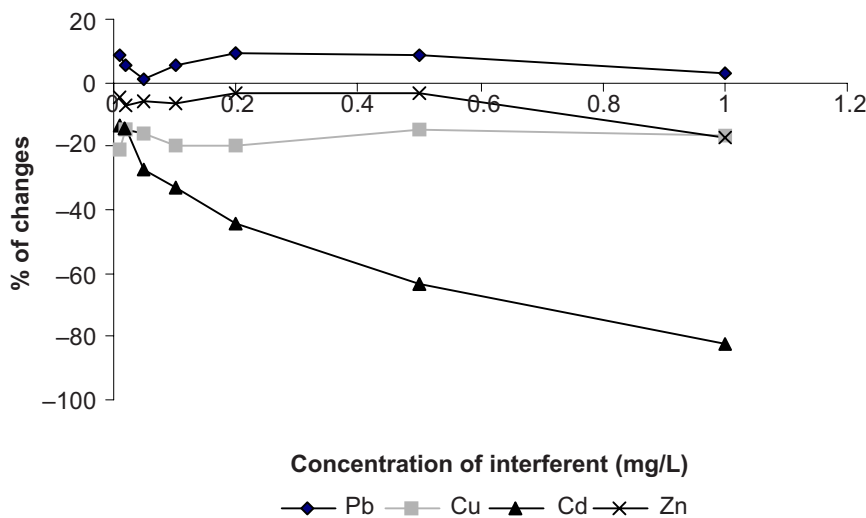


Figure 11 The percentage of changes in peak current of Se(IV)

4.0 CONCLUSIONS

Determination of selenite and DMDS_e can be achieved by cathodic stripping voltammetry in acidic media. The reduction peak of selenite and DMDS_e can be seen approximately at -472 mV and -304 mV respectively. The limits of detection of selenite and DMDS_e under optimized conditions were 8.175×10^{-9} M and 9.487

$\times 10^{-8}$ M respectively. The presence of selenite interferes in the determination of DMDS_e whereas DMDS_e does not interfere in the determination of selenite. Therefore, studies on the separation of the selenium species should be done before the voltammetric techniques can be applied for the determination of the speciation of Se compound in environmental samples. Cations such as lead, copper, cadmium and zinc interfere in the determination of DMDS_e. The presence of lead enhanced the sensitivity of the selenite while other cations reduced the peak current of selenite.

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