

硒的伏安行为及测定的研究进展

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摘 要:综述了 1990 年以来国内外伏安法测定硒的进展情况, 特别是对硒的互化物和硒的络合物的伏安特性进行了讨论; 并对文献中电极反应机理、电极的类型, 支持电解质的组成, 检测限总结和归纳, 对进一步深入研究硒的电化学反应特性和探索测定硒的新体系有重要参考价值。

关键词:硒; 阳极溶出伏安法; 阴极溶出伏安法

中图分类号: O657.1

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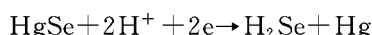
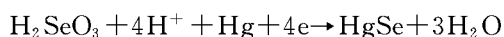
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0 引 言

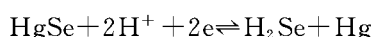
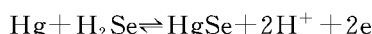
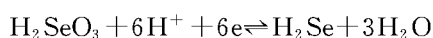
硒是人体必需微量元素之一, 具有预防和抑制肿瘤的作用. 硒为电子及冶金工业领域所使用, 所以硒的分析显得特别重要. 硒和碲都是多价元素, 对于碲的电化学行为笔者已作综述^[1-2]. 由于硒变价的多样性, 导致电化学反应的复杂性. 它们表现出特殊的电化学性质. 硒可以与某些金属生成金属互化物, 也可以生成硒的络合物, 还可以生成 H₂Se 等氢化物, 溶出伏安法^[3]就是利用这些特性建立起硒的电化学分析法. 笔者在此对硒的阳极和阴极溶出伏安法的行为作出评述.

1 硒同金属离子形成互化物的伏安行为

用伏安法(悬汞电极作工作电极)测定 Se(IV)^[4]时, 一般是先在一定电位下富集, 然后溶出, 产生溶出电流. 电极反应式为:

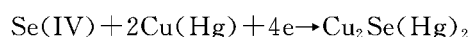


文献[5]用玻碳汞膜电极作为工作电极, 在 0.1 mol/L HClO₄-0.1 mol/L KCl 介质中, Se(IV)在-0.1 v(vs·SCE)电解, 硒形成难溶的 HgSe, 阴极溶出时, 富集在电极上的 HgSe 还原电极反应如下:

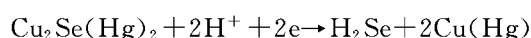


其他工作见文献^[6-15]和表 1.

为了提高测定灵敏度, 利用硒与其他金属离子生成金属互化物的性质, 在测定体系中引入金属离子(如 Pb²⁺, Cu²⁺, Hg²⁺ 等), 如在测定体系中加入 Cu²⁺^[16], Cu²⁺与 Se(IV)生成金属互化物, 反应如下:



然后再溶出:

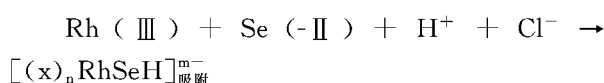


这种方法灵敏度大大提高. 文献[16]的检测限达 9×10^{-10} mol/L. 除了加上上述金属离子外, 还可以加入稀有金属离子, Wang^[25]在 0.1 mol/L H₂SO₄-10 μg/L Rh(Ⅲ)体系中, 在-0.2 V 集时, 发生下述电极反应:

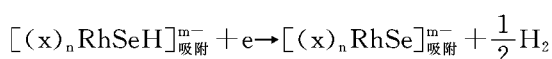


产生的伏安响应在-0.97 V 检测限达 6×10^{-12} mol/L.

在 0.3 mol/L HCl-75PPbRh(Ⅲ)体系中, 由于变价硒的复杂性, Se(IV)的伏安行为与 Wang 不一样. 硒与介质的组分生成混合络合物, 并产生氢催化波^[17]. Se(IV)于-0.2 v(vs·Ag/AgCl)沉积, Se(IV)被还原成 Se(-Ⅱ), 接着 Se(-Ⅱ)与 Rh(Ⅲ)等生成混合络合物:



当电位扫描-1.15 V(vs·Ag/AgCl), 发生下面电极反应:



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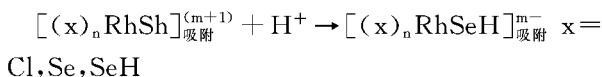
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表 1 硒的伏安行为

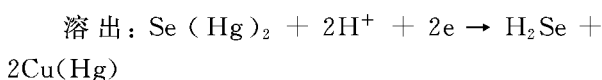
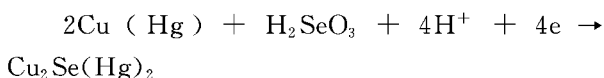
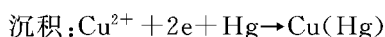
Table 1 Voltammetric behavior of selenium

底液组成	电极	反应机理	检测限	参考文献
酸性介质	悬汞电极	$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + \text{Hg} + 4\text{e}^- \rightarrow \text{HgSe} + 3\text{H}_2\text{O}$ $\text{HgSe} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{Se} + \text{Hg}$		[4]
0.1 mol/L HClO_4^- 0.1 mol/L KCl	玻碳汞 膜电极	$\text{H}_2\text{SeO}_3 + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{H}_2\text{Se} + 3\text{H}_2\text{O}$ $\text{Hg} + \text{H}_2\text{Se} \rightleftharpoons \text{HgSe} + 2\text{H}^+ + 2\text{e}^-$ $\text{HgSe} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{Se} + \text{Hg}$	3×10^{-9} mol/L	[5]
酸性介质	悬汞电极	$\text{SeO}_3^{2-} + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{H}_2\text{Se} + 3\text{H}_2\text{O}$ $\text{H}_2\text{Se} + \text{Hg} \rightarrow \text{HgSe} + 2\text{H}^+ + 2\text{e}^-$	1×10^{-3} $\mu\text{mol/L}$	[6]
0.1 mol/L HCl	悬汞电极	$\text{H}_2\text{SeO}_3 + \text{Hg} + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HgSe} + 3\text{H}_2\text{O}$ $\text{HgSe} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Hg} + \text{H}_2\text{Se}$	6×10^{-8} mol/L	[7]
0.1 mol/L HCl	悬汞电极	$\text{Se(IV)} + 4\text{e}^- + \text{Hg} \rightleftharpoons \text{HgSe}$ $\text{Se(0)} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{Se}$		[10]
0.1 mol/L HNO_3	悬汞电极	$\text{SeO}_3^{2-} + 8\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{H}_2\text{Se} + 3\text{H}_2\text{O}$ $\text{H}_2\text{Se} + \text{Hg} \rightleftharpoons \text{HgSe} + 2\text{H}^+ + 2\text{e}^-$ $\text{HgSe} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{Se} + \text{Hg}$	1×10^{-10} mol/L	[11]
0.1 mol/L HCl - 60 μL 1 mg/mL Cu^{2+}	悬汞电极	$\text{Se(IV)} + 2\text{Cu(Hg)} + 4\text{e}^- \rightarrow \text{Cu}_2\text{Se(Hg)}_2$ $\text{Cu}_2\text{Se(Hg)}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{Se} + 2\text{Cu(Hg)}$ $\text{Se(II)} \rightarrow \text{Se(-II)}$	9×10^{-10} mol/L	[16]
0.3 mol/L HCl - 75 PPbRh(III)	静汞电极	$\text{Rh(III)} + \text{Se(-II)} + \text{H}^+ + \text{Cl}^- \rightarrow [(\text{x})_n\text{RhSeH}]_{\text{吸附}}^{m-}$, $[(\text{x})_n\text{RhSeH}]_{\text{吸附}}^{m-} + \text{e}^- \rightarrow [(\text{x})_n\text{RhSe}]_{\text{吸附}}^{m-} + \frac{1}{2}\text{H}_2$ $[(\text{x})_n\text{RhSe}]_{\text{吸附}}^{(m+1)-} + \text{H}^+ \rightarrow [(\text{x})_n\text{RhSeH}]_{\text{吸附}}^{m-}$ 沉积: $\text{Cu}^{2+} + 2\text{e}^- + \text{Hg} \rightarrow \text{Cu(Hg)}$	2.4×10^{-12} mol/L	[17]
0.1 mol/L HCl	铜汞 齐电极	$2\text{Cu(Hg)} + \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Cu}_2\text{Se(Hg)}_2$ 溶出: $\text{Se(Hg)}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{Se} + 2\text{Cu(Hg)}$	2.5×10^{-10} mol/L	[18]
0.5 mol/L NaNO_3	玻碳金 膜电极	$\text{H}_2\text{SeO}_4 + 4\text{e}^- + 4\text{H}^+ + \text{XA}_U \rightleftharpoons \text{Se(A}_U)_x$	5×10^{-10} mol/L	[19]
R-B 缓冲溶液 pH2.1	悬汞电极	$\text{Se(IV)} + \text{O-PDA} \rightleftharpoons \text{Se(IV)}-\text{O-PDA}$ $\text{Se(IV)}-\text{O-PDA} + \text{Hg} \rightleftharpoons \text{Se(IV)}-\text{O-PDA}_{(\text{ads})}(\text{Hg})$ $\text{Se(IV)}-\text{O-PDA}_{(\text{ads})}(\text{Hg}) + 4\text{e}^- \rightarrow \text{Se(0)}-\text{O-PDA}_{(\text{ads})}(\text{Hg})$	5.0×10^{-10} mol/L	[20]
0.1 mol/L HCl - 1.0×10^{-3} mol/L DAN	悬汞 电极	$\text{Se(IV)} + \text{DAN} \rightarrow [\text{Se(IV)}-\text{DAN}]_{\text{吸附}}$ $[\text{Se(IV)}-\text{DAN}]_{\text{吸附}} + 4\text{e}^- + \text{Hg} \rightarrow \text{HgSe} + \text{DAN}_{\text{吸附}}$ $\text{HgSe} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{Se} + \text{Hg}$	1×10^{-8} mol/L	[21]
0.1 mol/L HCl - 4N ₀ PD	汞膜电极	$\text{H}_2\text{SeO}_3 + \text{NH}_2\text{-C}_6\text{H}_4\text{-NO}_2 \xrightarrow{\text{HCl}} 3\text{H}_2\text{O} + \left[\text{O}_2\text{N-C}_6\text{H}_3\text{(NH}_2\text{)-N=N-Se} \right]_{\text{吸附}}$ $\left[\text{O}_2\text{N-C}_6\text{H}_3\text{(NH}_2\text{)-N=N-Se} \right]_{\text{吸附}} \xrightarrow{\text{HCl}} \left[\text{O}_2\text{N-C}_6\text{H}_3\text{(NH}_2\text{)-N=N-Se} \right]_{\text{吸附}} + \left[\text{Hg} \right]_{\text{吸附}}$ $\left[\text{O}_2\text{N-C}_6\text{H}_3\text{(NH}_2\text{)-N=N-Se} \right]_{\text{吸附}} + \left[\text{Hg} \right]_{\text{吸附}} + 4\text{H}^+ + 4\text{e}^- \xrightarrow{\text{HCl}} \left[\text{NH}_2\text{-C}_6\text{H}_4\text{-NO}_2 \right]_{\text{吸附}} + \text{HgSe}$ $\text{HgSe} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{Se} + \text{Hg}$	7.6×10^{-10} mol/L	[22]
0.1 mol/L HNO_3	悬汞 电极	$\text{Br-C}_6\text{H}_3\text{(Br)-N=N-Se} \rightleftharpoons \text{Br-C}_6\text{H}_3\text{(Br)-N=N-Se}_{\text{吸附}}$ $\text{Br-C}_6\text{H}_3\text{(Br)-N=N-Se}_{\text{吸附}} + \text{Cu}^{2+} + \text{Hg} + 4\text{H}^+ + 6\text{e}^- \rightarrow \text{Cu(Hg)Se} + \text{Br-C}_6\text{H}_3\text{(NH}_2\text{)-N=N-Se}_{\text{吸附}}$ $\text{Cu(Hg)Se} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cu(Hg)} + \text{H}_2\text{Se}$	6×10^{-12} mol/L	[23]
HAc-NaAc pH2.9	铋膜玻 碳电极	$2\text{ABSA} + \text{H}_2\text{SeO}_3 + 2\text{H}^+ \rightarrow \text{ABSA-Se-ABSA} + 3\text{H}_2\text{O}$ $\text{Se(IV)}(\text{ABSA})_2 + \text{Bi} \rightarrow \text{Se(IV)}(\text{ABSA})_2(\text{ads})(\text{Bi})$ $\text{Se(IV)}(\text{ABSA})_2(\text{ads})(\text{Bi}) + 4\text{e}^- \rightarrow \text{Se(0)}(\text{ABSA})_2(\text{ads})(\text{Bi})$	1.3×10^{-8} mol/L	[24]

产生的电流是催化氢波引起的,产生催化氢波的原因是混合络合物吸附在汞电极表面,使电极表面得到修饰, H^+ 放电电位正移. 又因为下列反应发生:

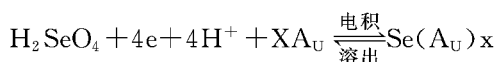


产物又回到电极上放电,形成催化循环而增大电流,产生灵敏的催化氢波,检测限达 2.4×10^{-12} mol/L. 用铜汞齐^[18]作工作电极,测定硒时发生下述电极反应:



检测限达 0.25 nmol/L.

文献[19]考虑到汞害和环境污染的问题,用碳金膜电极微分阳极溶出伏安测定水中痕量 $Se(IV)$ 和 $Se(VI)$, 在 0.5 mol/L HNO_3 底液中,于 -0.4 V(vs · SCE) 电积,然后溶出,其过程如下:



该方法检测限达 5×10^{-10} mol/L.

其他工作见表 2^[26-33].

表 2 在不同物质存在下硒的阴极溶出伏安测定

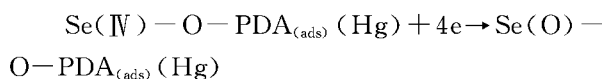
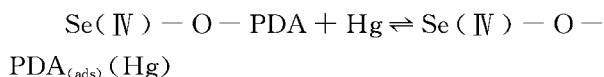
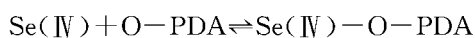
Table 2 CSV methods for the determination of selenium in the presence of various metals

M^{2+}	电极	电极产物	检测限	参考文献
Hg^{2+}	HMDE	$HgSe$	1.4×10^{-9} mol/L	21
Cu^{2+}	HMDE	Cu_2S	2×10^{-12} mol/L	22
Cu^{2+}	HMDE	Cu_2Se	2.5×10^{-10} mol/L	23
			6.0×10^{-11} mol/L	24
			1.3×10^{-11} mol/L	25
			9×10^{-12} mol/L	26
Ag^+	Ag 电极	Ag_2Se	6.9×10^{-9} mol/L	27
Cu^{2+}	汞膜石墨电极	$CuSe$	5×10^{-9} mol/L	28

2 硒络合物的伏安行为

$Se(IV)$ 与 Na_2SO_3 反应可以生成硒代硫酸根 ($SeSO_3^{2-}$), 我国利用 $SeSO_3^{2-} - IO_3^-$ 体系建立了稳定测定微量硒的极谱方法. 硒还可以与有机试剂生成络合物, 由于这种络合物有电活性, 在电极上发生电化学反应, 以达到测定微量硒的目的.

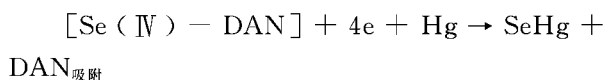
如文献[20]研究了在 R-B 缓冲溶液中, 硒(IV)与邻苯二胺(O-PDA)体系的示差脉冲吸附伏安行为. $Se(IV)$ 在溶液中先与 O-PDA 生成络合物, 该络合物吸附在汞电极上, 然后溶出, 其电极反应式如下:



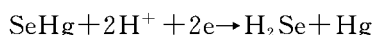
该方法灵敏度高, 检测限可达 5.0×10^{-10} mol/L, 用此法测定了人发中微量硒.

文献[21]在 0.1 mol/L $HCl - 1.0 \times 10^{-3}$ 二氨基萘(DAN)体系中, $Se(IV) - DAN$ 络合物在 $+0.05$ V(vs · SCE) 富集, $Se(IV) + DAN \rightarrow [Se(IV) - DAN]_{\text{吸附}}$

在 -0.06 V(vs · SCE) $Se(IV)$ 还原成 $Se(0)$, 与汞生成金属互化物.

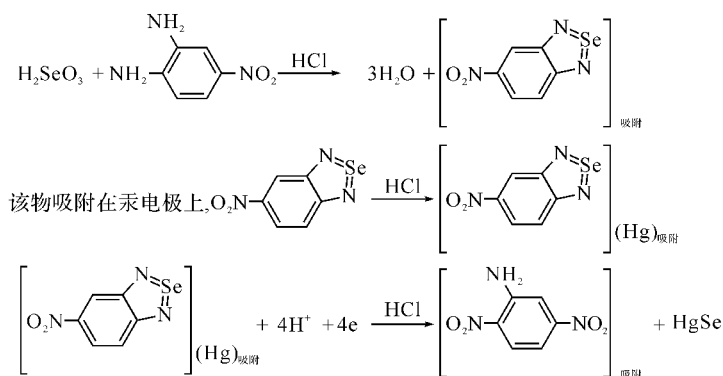


在 -0.46 V(vs · SCE) 进一步还原成 $Se(-II)$.

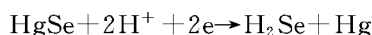


该方法的检测限达到 1×10^{-8} mol/L.

文献[22]报道了在 0.1 mol/L $HCl - 4$ -苯二胺(4N₀PD)溶液中, $Se(III)$ 与 4N₀PD 发生反应.



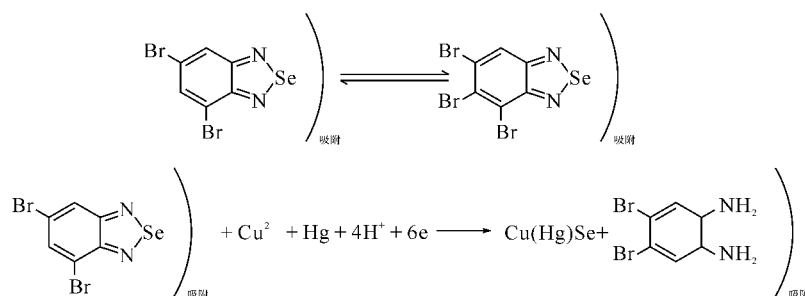
汞电极上 $HgSe$ 进一步还原为:



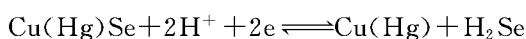
该方法的检测限 7.6×10^{-10} mol/L.

文献[23]利用 3,5-二溴代邻苯二胺在弱酸

(0.1 mol/L HNO_3) 介质中与硒反应生成 4,6-二溴代苯硒胺,该络合物有电活性,电极反应机理为:



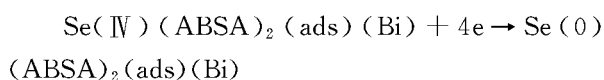
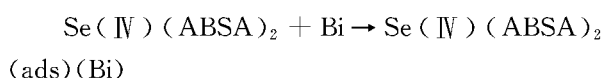
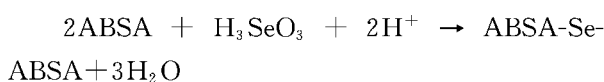
得出:



由于汞(膜)电极对人体有害,而镀金膜电极要耗掉贵重的黄金。

而铋膜玻碳电极电位窗口宽,溶出峰分辨率强,对溶解氧不敏感,实验时不必除 O_2 ,方便了实验操作。而且铋膜电极是对环境友好的电极,铋膜电极的使用,使溶出伏安的技术得到改进和发展,近几年各种修饰电极在溶出伏安法中的应用^[33-35],使得该方法具有更多的实际应用价值和良好的发展空间。文献[24]采用铋膜玻碳电极作为工作电极在 $\text{HAC-NaAc} \sim$ 氨基苯(ABSA)(pH2.9)的体系中测定硒。测定的原理是 Se(IV) 与 ABSA 生成络合物,由于该络合物具有强烈的吸附性,吸附在铋膜电极上的络合物进行电还原,产生溶出电流。检测限达 $1.3 \times 10^{-8} \text{ mol/L}$ 。

电极反应机理如下:



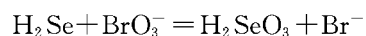
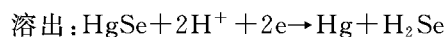
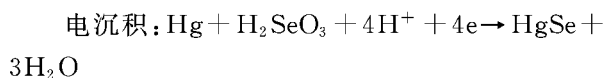
文献利用在 0.5 mol/L HCl -0.5 mol/L KI 溶液中, Se(IV) 与 I^- 作用生成 Se-I_2 络合物^[37],该络合物富集在汞电极上,吸附在汞电极上的 Se(0) 被还原成 Se(-II) 产生电流。实际上 Se-I_2 络合物 1951 年就有作者把它用来测定海水中硒(光度法),但用在溶出伏安法测定微量硒的确是一种创新。

其他生成硒络合物的溶出伏安法见文献[38-40]。

文献[41]用铋膜石墨电极测定硒时,产生一催化氢波,电位为 1150 mV(vs. Ag/AgCl),并被实验证明的确为一催化氢波;作者用同样的催化氢波体系测定了另一元素^[42]。

还有方法把阴极溶出伏安与催化极谱联用,

使测定灵敏度大为提高。它的原理是在一定的电位下富集,然后把电极放入有催化体系的溶液中,电极反应如下:



生成的 H_2SeO_3 又在电极上还原,产生很大的催化电流,灵敏度达到 $7.0 \times 10^{-10} \text{ mol/L}$ 。

为了提高灵敏度,有方法先把硒富集在一个载体上^[43-44],然后进行收集,再用伏安法测定。实践证明,用伏安法测定硒是一简单可行的方法,特别在研究其反应机理方面更有特色。

3 结 语

由于溶出伏安法可以有效地提高灵敏度,降低检测限,溶出伏安仪价廉,它是目前乃至今后相当长时间内测定微量硒的主要方法之一。但任何一种分析方法都有不足,溶出伏安法存在最大的难题是工作电极的表面(特别是固体电极)的污染,影响了电极的稳定性。随着使用方便的电化学敏感电极深入研发,前处理样品方法联用、清洗和再生电极表面的技术不断改进,测定硒体系不断的更新以及电极反应机理的深入研究,必将使伏安法技术得到新的发展。

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Present status of voltammetric behavior of selenium

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Abstract: The electrochemistry of selenium and various selenium compounds were investigated by a variety of techniques including pulse and cyclic voltammetry, coulometry, and the rotating-disk electrode since 1990. The mechanism for the electrochemical reaction processes, type of the electrode and supporting electrolyte were also investigated extensively. Furthermore, the detection limits of various methods were compared. The investigation indicatese the further study on the electrochemical property of the selenium and various selenium compounds, and it has great reference value to developing new system of the determination of selenium.

Key words: selenium; anodic; stripping voltammetry; cathodic stripping voltammetry

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