

# Catalytic Adsorptive Stripping Voltammetric Determination of Germanium

Subjects: Chemistry, Analytical

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In organic free aqueous solutions, germanium is present in the form of  $\text{Ge(OH)}_4$  tetrahydroxide ( $\text{pH} < 7$ ) or as  $\text{H}_3\text{GeO}_4^-$ , which dominates in alkaline media ( $\text{pH} > 9$ ). In the presence of many ligands containing carboxylic, di-orthophenolic, and polyalcoholic functional groups,  $\text{Ge(IV)}$  forms stable five-membered ring chelate complexes displaying coordination number 6.

Keywords: vanadium ; germanium ; aminopolycarboxylic complexes ; catalytic adsorptive stripping voltammetry ; HEDTA

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## 1. Adsorptive Stripping Voltammetric Determination of Germanium

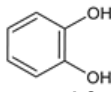
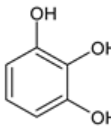
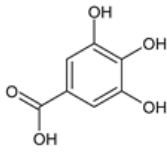
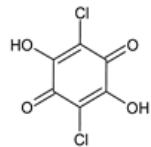
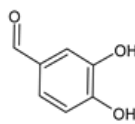
When only two organic ligands coordinate  $\text{Ge(IV)}$ , the remaining coordination sites are occupied by water molecules <sup>[1]</sup>. The water molecules can be easily replaced by other ligands and mixed complexes can be formed. Germanium complexes of different 1,2-diphenol derivatives have been used since the 1990s to determine  $\text{Ge(IV)}$  traces by means of adsorptive stripping voltammetry (AdSV) because of their ability to accumulate on the surface of the working electrode. The AdSV procedures mainly use catechol <sup>[2][3][4][5][6][7]</sup>, but there are also articles describing how other complexes can also be used to determine trace levels of germanium <sup>[8][9][10][11][12][13]</sup>. Various electrode reaction schemes have been suggested, but there is no general consensus on the composition and stoichiometry of electroactive complexes <sup>[5][6][14]</sup> and the nature of products produced by electroreduction processes <sup>[5][6][15][16][17][18]</sup>.

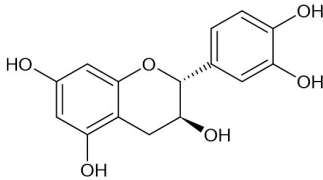
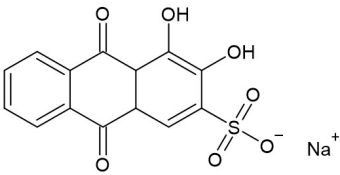
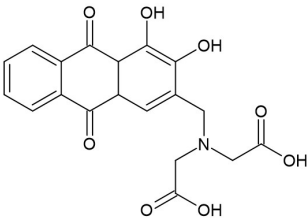
When it comes to practical applications, AdSV procedures for the determination of germanium(IV) allow  $\text{Ge(IV)}$  to be determined at levels of several nanomol per liter <sup>[3][5][12]</sup>. However, because of the extremely low germanium content in certain samples, a catalytic approach, namely catalytic adsorptive stripping voltammetry (CAdSV) that would provide considerably greater sensitivity would be desirable.

## 2. Catalytic Amplification of Germanium Voltammetric Signals in the Presence of Oxoacid Anions

Anions such as  $\text{BrO}_3^-$  are among the catalytic agents most widely used for the amplification of voltammetric signals of  $\text{Ge(IV)}$ -catechol and  $\text{Ge(IV)}$ -pyrogallol complexes (**Table 1**). As in the case of AdSV procedures for  $\text{Ge(IV)}$  determination, several schemes were proposed to describe the catalytic reactions induced by some germanium complexes with ligands containing the  $-\text{C}(\text{OH})-\text{C}(\text{OH})$  group (e.g., catechol, gallic acid, pyrogallol) in the presence of various oxidants <sup>[15][16][17][19][20]</sup>. These schemes were based on the assumption that the catalytic reaction involves a simple regeneration of the product of electroreduction, namely the  $\text{Ge(IV)}$ -catechol complex.

**Table 1.** Catalytic systems involving germanium and their properties.

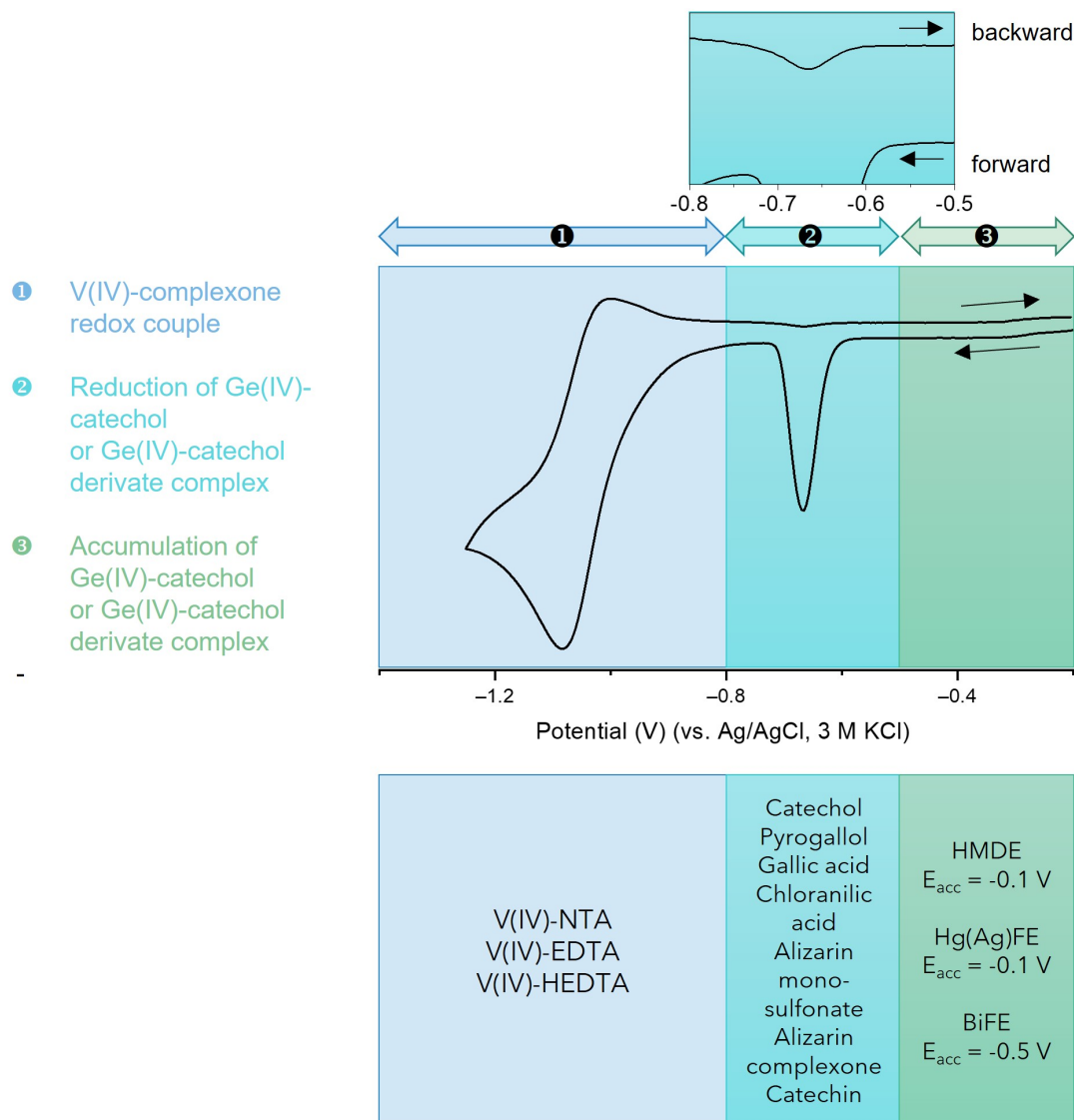
Ligand	Catalytic Agent	Supporting Electrolyte	Electrode	P <sub>2</sub> /P <sub>1</sub>	Linear Range nM	LOD nM	References
 Benzene-1,2-diol catechol	BrO <sub>3</sub> <sup>−</sup>	Acetate buffer	DME	2.2	1–7000	1	[15]
	VO <sup>2+</sup>	HClO <sub>4</sub> , NaClO <sub>4</sub>	HMDE	11	n.a.	n.a.	[19]
	BrO <sub>3</sub> <sup>−</sup>	Acetate buffer	HMDE	24	n.a.	n.a.	[20]
	V(IV)-EDTA	Acetate buffer	HMDE	3.5	n.a.	n.a.	[20]
	V(IV)-HEDTA	Acetate buffer	HMDE	26	0.05–20	0.01	[20]
	V(IV)-HEDTA	Acetate buffer	Hg(Ag)FE	n. a.	0.01	0.15	[20]
	V(IV)-HEDTA	Acetate buffer	BiFE/GC	n. a.	1.5–24	1.0	[21]
	V(IV)-HEDTA	Acetate buffer	BiFE/SPE	n. a.	1.5–19.5	1.0	[21]
	V(IV)-HEDTA	Acetate buffer	BiFE/SPE <sub>meso</sub>	n. a.	5.0–70	1.2	[21]
 Benzene-1,2,3-triol Pyrogallol	BrO <sub>3</sub> <sup>−</sup>	Acetate buffer, trisodium citrate	BiFE/GC	1.5	7–230	0.8	[16]
	V(IV)-HEDTA	Acetate buffer	HMDE	100	0.25–25	0.02	[22]
	V(IV)-EDTA	Acetate buffer	HMDE	10	n.a.	n.a.	[22]
	V(IV)-NTA	Acetate buffer	HMDE	1.5	n.a.	n.a.	[22]
 3,4,5-Trihydroxybenzoic acid, gallic acid	V(IV)-EDTA	HClO <sub>4</sub>	HMDE	n.a.	0.03–10	0.02	[17]
	V(IV)-EDTA	H <sub>2</sub> SO <sub>4</sub>	DME	10	0.55–275	0.05	[18]
 2,5-Dichloro-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione, chloranilic acid	V(IV)-HEDTA	Acetic acid	HMDE	21	0.75–50	0.085	[23]
	V(IV)-HEDTA	Acetic acid	Hg(Ag)FE	12	1–25	0.7	[23]
 3,4-Dihydroxybenzaldehyde (DHB)	V(IV)-EDTA	KCl	HMDE	17	0.1–10	0.05	[24]

Ligand	Catalytic Agent	Supporting Electrolyte	Electrode	P <sub>2</sub> /P <sub>1</sub>	Linear Range nM	LOD nM	References
 <b>Catechin</b>	V(IV)-HEDTA	Acetate buffer	HMDE	n.a.	40-480	n.a.	[25]
 <b>Alizarin sodium monosulfonate</b>	V(IV)-HEDTA	Acetate buffer	HMDE	n.a.	40-440	n.a.	[25]
 <b>Alizarin complexone</b>	V(IV)-HEDTA	Acetate buffer	HMDE	n.a.	40-1200	n.a.	[25]

### 3. Catalytic Amplification of Germanium Voltammetric Signals by Aminopolycarboxylic Acid Complexes with V(IV)

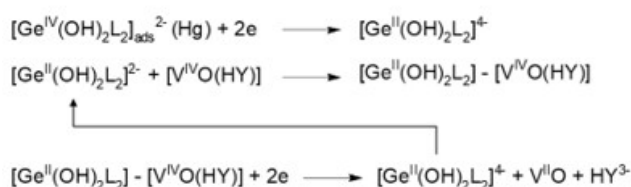
The Ge(IV) can be also efficiently amplified by complexes of V(IV) with aminopolycarboxylic acids such as EDTA, HEDTA and NTA. The ratio of the peak current obtained when the catalytic systems are used to the peak current obtained for the AdSV system in the absence of any oxidant ranges from several to several dozens. The amplification factor (PCAdSV/PAdSV) depends on many parameters, primarily on the type of V(IV) complex and the ligand that form complexes with Ge(IV), but also on the type of the working electrode, the supporting electrolyte composition, and, finally the instrumental parameters.

The characteristic features of the cyclic voltammograms obtained for the catalytic systems of Ge(IV) employing aminopolycarboxylic acid complexes of V(IV) are highlighted in **Figure 1**.



**Figure 1.** CV voltammogram of the Ge(IV) catalytic system and its characteristic features.

Part 1 of the CV voltammogram represents the region of the reduction-oxidation of the V(IV) complex. A vanadium complex that undergoes a more electrochemically reversible reduction can amplify the germanium signal to a greater extent than one that is reduced irreversibly. The catalytic activity of the three reported ligands can be ranked as follows: HEDTA > EDTA > NTA. The region labeled 2 represents the catalytically amplified signal of germanium. The peak potential of the Ge(IV) signal depends on the ligand type and the material of the working electrode. It is localized between -0.55 V and -0.65 V for the HMDE and Hg(Ag)FE electrodes. When BiFE electrodes are used, the Ge(IV) peak appears at slightly more negative potentials namely, between -0.7 V and -0.8 V. Additionally, both the negative-going and positive-going branches of CV runs show cathodic signals, which confirms the catalytic nature of the electrode process. The cathodic peak observed at backward running is clearly visible on the magnified part of section 2. Such a CV curve implies that the investigated catalytic systems may be attributed to catalytic systems of the second kind [26]. Under this assumption, the electroreduction of adsorbed Ge(IV)-catechol produces a very active Ge(II)-catechol complex  $[\text{Ge}^{\text{II}}(\text{OH})_2\text{L}_2]^{4-}$  (Scheme 1), which forms a composite complex with V(IV)-HEDTA denoted as  $[\text{Ge}^{\text{II}}(\text{OH})_2\text{L}_2] \cdot [\text{V}^{\text{IV}}\text{O}(\text{HY})]$  (Scheme 1). In this composite complex, vanadium(IV) undergoes reduction to vanadium(II), which results in the breakdown of the multi-component complex. The regenerated germanium catecholate complex  $[\text{Ge}^{\text{II}}(\text{OH})_2\text{L}_2]^{4-}$  retains its activity and combines with additional V(IV)-HEDTA ion. In this way, the catalytic cycle forms, indicated by an arrow in Scheme 1. The number of electrons per germanium ion exchanged during electroreduction increases significantly, which contributes to a substantial rise in the current of the recorded germanium peaks, and thus to an increase in the sensitivity of the analytical procedure.



**Scheme 1.** Catalytic reactions responsible for the

amplification of the Ge(IV) voltammetric signal.

The section labeled 3 presents the range of potentials that can be applied for the adsorptive accumulation of the Ge(IV) complex. On the positive side of potentials, this range is limited by the oxidation process of the electrode material. In the case of the bismuth electrode, this range is narrower than that for the mercury electrode, because the bismuth oxidation process is already noticeable at potentials more positive than -0.4 V.

To apply the catalytic system for the determination of Ge(IV), an extensive optimization study should be undertaken on the influence of chemical and instrumental variables.

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