

Prepared silver(I) sulfide electrode for GLDTC²⁻ potentiometric study with mercury (II)

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A prepared silver(I) sulfide electrode, constructed at Faculty of science in Skopje, was found to be responsive to carboxy-dithiocarbamat anions. This paper offers possibilities to titrate GLDTC²⁻ (glycindithiocarbamat anion) with Hg(II) within pH range of 5-7. The described method is highly sensitive and allows determination down to 10⁻⁵ mol/dm³ GLDTC²⁻. The prepared electrode could change the commercial electrodes in this kind of GLDTC²⁻ study.

INTRODUCTION

This paper deals with a rapid and accurate potentiometric method described for determining GLDTC²⁻ (glycindithiocarbamat anion) by titrating with mercury(II) nitrate using a prepared silver(I) sulfide electrode.

EXPERIMENTAL

Reagents: All used reagents were of "pro analysi" grade (Merck, Sigma, BDH, Alkaloid). A GLDTC²⁻ stock solution was prepared by dissolving an appropriate amount of synthesized ammonium-glycindithiocarbamat in water (1). That has been standardized with the standard iodine (2). A mercury(II) nitrate stock solution, standardized with EDTA and Xylenol orange as an indicator, has been used for preparing series standards with the pH range of 10⁻¹-10⁷ mol/dm³ Hg(II). Preparation of the various buffer solution has been done according to the classical analytical handbooks. As a supporting electrolyte has been applied potassium nitrate.

Instruments and used electrodes: Specific Ion Meter Model 407A (ORION), pH-Meter (ISKRA) MA 5705; DHF prepared silver(I) sulfide electrode (made in Faculty of science in Skopje), two ion-sensitive electrodes ORION (N^o 94-29 & N^o 94-16); Double Junction Reference Electrode ORION (N^o 90-02) with the following outer chamber filling solution (10% KNO₃), combined glass electrode (ISKRA) Model 0101.

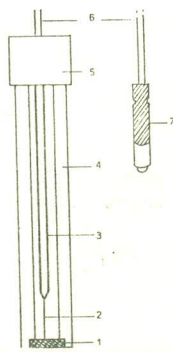


Fig 1.

1. ion-selective membrane
2. silver wire
3. copper wire
4. electrode body
5. cap
6. coaxial cable
7. connector

Prepared silver(I) sulfide electrode is homogenous all solid state electrode. The electrode body is a PVC tube with an ion-sensitive membrane fixed at its end in special way. The membrane is a pressed polycrystalline Ag_2S as a tablet.

The internal reference solution is left out and the junction between the membrane (an inorganic compound with ion conductivity) and a silver wire (a conductor of the first kind) is realised directly. The silver wire is welded on a copper one which ends through a coaxial cable with connector. The absence of the internal reference solution makes this electrode simpler for maintenance and manipulation (Fig 1).

Procedure: The GLDTC^{2-} activity has been measured potentiometrically by all three used sulfide indicator electrodes parallelly. The ionic strength has been kept on a constant value ($\mu=0.1$) with potassium nitrate. The direct potentiometry has been used for obtaining the calibration curves and the optimal pH range (3,4). The potentiometric titrations have served for determining the GLDTC^{2-} concentration interval, within that it has been possible to perform the GLDTC^{2-} analysis. Series GLDTC^{2-} solutions have been titrated with series Hg^{2+} solutions. During the titration it could give attention to the concentration proportion between reactants. The titrant had to be always one concentration decade stronger than the titrand to avoid the delution effect.

RESULTS AND DISCUSSIONS

The calibration curves obtained for GLDTC^{2-} with all three used electrodes have had slopes which have not been Nernstian (Fig. 2). Therefore any GLDTC^{2-} direct potentiometric determination or S -titrimetric investigation have been eliminated. It has been let only T -titrations. The IUPAC detection limits of the used electrodes were:

DHF	$1,41 \cdot 10^{-5}$	mol/dm^3	GLDTC^{2-}
ORION 94-29	$5,62 \cdot 10^{-6}$	mol/dm^3	GLDTC^{2-}
ORION 94-16	$1,89 \cdot 10^{-5}$	mol/dm^3	GLDTC^{2-}

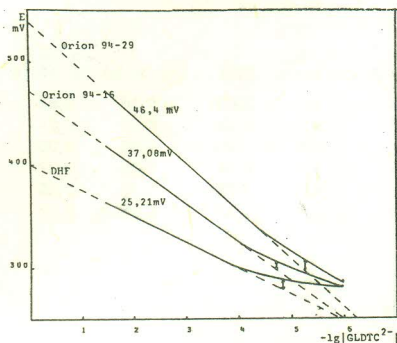


Fig. 2.
GLDTC²⁻ calibration curves
with sulfide electrodes

The optimal pH range of a given species using a given ion-selective electrode is such pH interval where the electrode potential is independent of the medium pH value. In that pH range the electrode potential depends on the investigated ion concentration only. For GLDTC²⁻ the optimal pH range has been over 4. (See Fig. 3.).

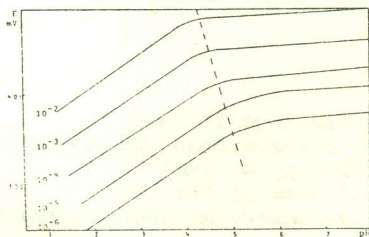


Fig. 3.
GLDTC²⁻ optimal pH range

Detection limits of mol/dm³ GLDTC²⁻ obtained T-titrametrically have been one concentration decade more narrow than graphically found IUPAC limits. T-titrametrical determination of GLDTC²⁻ with Hg(II) has been performed within a pH range of 4.82–7.05. The compound given by titrating has been a yellow precipitate distroing at higher pH than 7. The stoichiometric ratio metal:ligand has been 1:2 (Table 1.). The relative errors have been similar for all three electrodes. The differential curves have shown that sharp titrametrical jumps have been decreased with growing of the medium pH value (Fig. 4).

Comparing the results come by ORION electrodes and those by the constructed electrode at our Institute, we may conclude that this prepared membrane electrode could change the comercial electrodes in studing GLDTC²⁻ with Hg²⁺

Table 1 : GLDTC²⁻ determination with Hg²⁺ using sulfide electrodes

pH	given GLDTC ²⁻ -mg in 10 cm ³ solution	found GLDTC ²⁻ -mg in 10 cm ³ solution			relative errors (%)		
		DHF	OR. 94-29	OR. 94-16	DHF	OR. 94-29	OR. 94-16
4,91	21,09	21,08	21,06	21,22	0,05	0,14	0,62
6,94	21,09	20,98	21,17	20,96	0,52	0,37	0,61
5,03	2,109	2,126	2,213	2,109	0,80	4,93	0,00
6,96	2,109	2,123	2,134	2,142	0,64	1,85	0,07
4,93	0,210	0,215	0,206	0,216	2,38	1,90	2,86
7,01	0,210	0,206	0,217	0,202	1,90	3,33	3,80

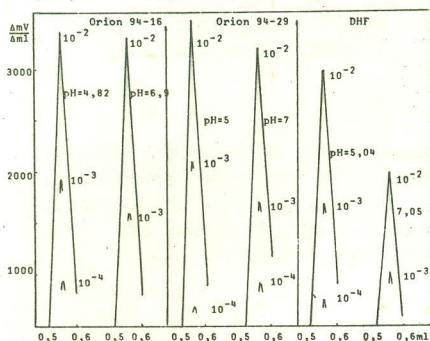


Fig. 4.
Differential diagrams for
GLDTC²⁻ titrations with Hg²⁺
using sulfide electrodes
at pH range of 5 and 7

References:

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ИЗВОД

ПРИГОТВЕНА СРЕБРО(I) СУЛФИДНА ЕЛЕКТРОДА ЗА ПОТЕНЦИОМЕТРИСКО
ИСПИТУВАЊЕ НА GLDTC²⁻ СО ЖИВА(II)

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Во презентираниот труд опишана е брза и точна потенциометриска метода за определување GLDTC²⁻ (глициндитиокарбамат) при титрација со жива(II) и употреба на приготвена потполно цврсто фазна сребро(I) сулфидна електрода. Електродата е направена во Институтот за хемија при ПМФ Скопје и таа со успех може да ги замени куповните електроди за испитување GLDTC²⁻ со жива(II).