

## Lead-Selective Electrode Based on the Misfit Compound $(\text{PbS})_{1.18}\text{TiS}_2^1$

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**Abstract**—A lead-selective solid-contact electrode was prepared on the basis of the misfit compound  $(\text{PbS})_{1.18}\text{TiS}_2$ . The electrode exhibits the slope of the electrode function is  $-(26 \pm 1)$  mV/pc and provides the determination of  $1 \times 10^{-5}$ – $5 \times 10^{-2}$  M lead in the pH range 2.75–5.0. High selectivity of the electrode for  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ , and  $\text{Sr}^{2+}$  ions was demonstrated. The addition of graphite to the active phase of the membrane impaired the selectivity of the electrode. The electrode was used for the potentiometric indication of the titration end point in the determination of lead in copper alloys.

Lead sulfide is used intensively by many manufacturers of ion-selective electrodes for as an electrode-active material. The main disadvantage of this material is its low conductivity; hence, powdered PbS is mixed with highly conductive components ( $\text{Ag}_2\text{S}$ , graphite, etc.). This impairs the selectivity of these electrodes and requires the absence of some ions in test solutions [1–3].

Recently synthesized composite compounds  $\text{PbS}(\text{TiS}_2)_n$  ( $n = 1$  and 2) are formed of alternating  $\text{TiS}_2$  and  $\text{PbS}$  layers in the order  $\text{PbS-TiS}_2\text{-PbS-TiS}_2\text{-...}$  with the formula  $(\text{PbS})_{1.18}\text{TiS}_2$  or  $\text{PbS-TiS}_2\text{-TiS}_2\text{-PbS-TiS}_2\text{-TiS}_2\text{-PbS-...}$  with the formula  $(\text{PbS})_{0.59}\text{TiS}_2$  [4]. These compounds are actually molecular homogeneous mixtures of  $\text{PbS}$  with highly conductive  $\text{TiS}_2$  because the electronic structure, chemical bonding, and electric properties of both structural fragments remain the same as in bulk materials. It was found [5] that  $(\text{PbS})_{1.18}\text{TiS}_2 = \text{PbTiS}_3$  does not dissolve  $\text{Ag}$ , which is a typical metal soluble in  $\text{TiS}_2$ , evidently because of the absence of free van der Waals gaps. This fact suggests that  $(\text{PbS})_{1.18}\text{TiS}_2$  can be used as the electrode-active compound in lead-selective electrodes. This work is devoted to the study of this possibility.

### EXPERIMENTAL

The material  $(\text{PbS})_{1.18}\text{TiS}_2$  for the preparation of the active element of the Pb-selective electrode was obtained by synthesis in fused-silica ampules evacuated to  $10^{-5}$  torr at  $800^\circ\text{C}$  for 10 days. As initial components, we used lead of analytical grade (99.9% purity),

sulfur of high-purity grade (OSCh 11–4, 99.99% purity), and previously synthesized  $\text{TiS}_2$ , which was obtained from titanium by iodide purification (99.95% purity). A standard procedure [6] was used for the synthesis and certification of  $\text{TiS}_2$ . Resulting  $(\text{PbS})_{1.18}\text{TiS}_2$  was certified by X-ray diffraction analysis (DRON 4-13 diffractometer,  $\text{CuK}_\alpha$  radiation, graphite monochromator). In this procedure, we checked that all phases other than  $(\text{PbS})_{1.18}\text{TiS}_2$  are absent and that the lattice parameters of the resulting material coincide with the data reported in the literature [7]. The procedure for the synthesis and certification of this material was described in detail in [8]. The conductivity of  $(\text{PbS})_{1.18}\text{TiS}_2$  was measured by the standard four-probe method for single-crystal and polycrystalline samples; it was  $\sim 40\,000$  S/cm for single-crystal samples and  $\sim 10\,000$  S/cm for polycrystalline pressed samples at room temperature. Details of the experiment were presented in [9].

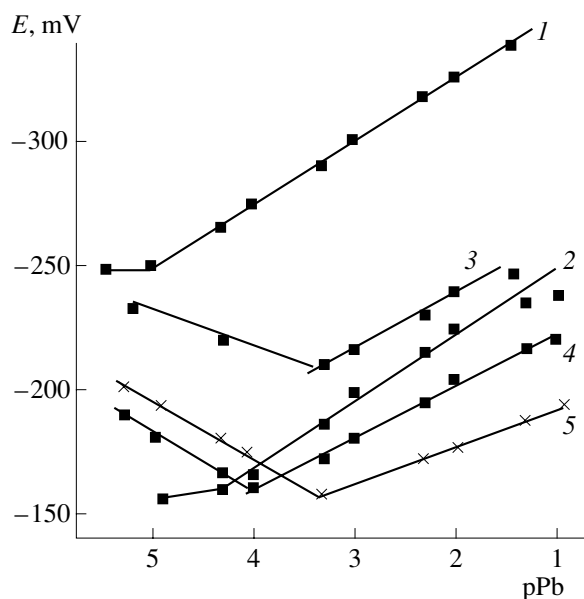
A molybdenum-glass tube (5 mm  $\times$  10–15 cm) was cleaned and degreased, and the working end of the tube was filed with Wood alloy thus preparing a site for applying the active element. A current lead was soldered to a Wood alloy film of the thickness 1–3 mm. The tightness of the contact between glass and metal was carefully checked. Powdered  $(\text{PbS})_{1.18}\text{TiS}_2$  was mixed with a solution of polystyrene in methyl ethyl ketone, applied to the prepared metal site, and dried for a day. The consumption of  $(\text{PbS})_{1.18}\text{TiS}_2$  was 50 mg per electrode. The volume fraction of  $(\text{PbS})_{1.18}\text{TiS}_2$  in the applied mixture was close to 80%, which is much larger than the critical value required for attaining good contact between particles; this provided stable characteristics of electrodes for small deviations in the  $(\text{PbS})_{1.18}\text{TiS}_2$ /polystyrene ratio.

<sup>1</sup>Presented at the V All-Russian Conference with the Participation of CIS Countries on Electrochemical Methods of Analysis (EMA-99), Moscow, December 6–8, 1999.

**Table 1.** Characteristics of lead-selective electrodes

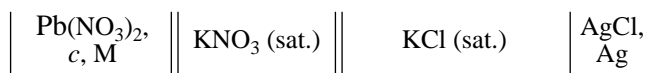
Nos. of electrodes	Electrode-active compound	Linearity range of the function $E = f(\text{p}c_{\text{Pb}})$ , M	Slope of the electrode function, mV/pc	Operating pH range
1	(PbS) <sub>1.18</sub> TiS <sub>2</sub>	$1 \times 10^{-5}$ – $5 \times 10^{-2}$	$-(26 \pm 1)$	3.5–5.0
2	(PbS) <sub>1.18</sub> TiS <sub>2</sub> + graphite	$5 \times 10^{-5}$ – $5 \times 10^{-2}$	$-(27 \pm 1)$	3.5–5.0
3	PbS	$5 \times 10^{-4}$ – $1 \times 10^{-2}$	$-(20 \pm 1)$	2.5–4.0
4	PbS + graphite	$1 \times 10^{-4}$ – $1 \times 10^{-1}$	$-(24 \pm 1)$	4.0–5.0
5	5/graphite	$5 \times 10^{-4}$ – $1 \times 10^{-2}$	$-(16 \pm 1)$	4.0–5.5

The characteristics of electrodes based on (PbS)<sub>1.18</sub>TiS<sub>2</sub> were compared with the characteristics of electrodes based on PbS. The material for preparing the latter electrodes was obtained and certified similarly to (PbS)<sub>1.18</sub>TiS<sub>2</sub> except for the addition of TiS<sub>2</sub>; the design of electrodes was analogous in all cases. We studied the electrode characteristics of Pb-selective electrodes with the following types of the active element: (PbS)<sub>1.18</sub>TiS<sub>2</sub> (electrode 1), (PbS)<sub>1.18</sub>TiS<sub>2</sub> in mixture with spectral-grade graphite powder (electrode 2), PbS (electrode 3), PbS in mixture with graphite (electrode 4), and graphite (electrode 5). The addition of graphite to the electrode based on PbS was required to impart conductivity to this material. In other solutions, graphite was added for studying its effect on electrode characteristics.



**Fig. 1.** Electrode functions of Pb-selective electrodes 1–5 with different membrane compositions at pH 4.5; points correspond to the experimental data; curve numbers (1–5) correspond to compositions of electrodes presented in Table 1.

The characteristics of Pb-selective electrodes were studied by the measurement of the electromotive force in the circuit



using EV-74 and I-115 instruments in the millivoltmeter mode; pH of solutions was monitored with a glass electrode using a pH-673 instrument. All measurements were performed at  $20 \pm 2^\circ\text{C}$ . Before putting into operation or after the deterioration of characteristics in the course of operation, electrodes were conditioned in  $10^{-3}$  M Pb(NO<sub>3</sub>)<sub>2</sub> for 30 min with a closed circuit, and with subsequent washing in distilled water for 20 min until constant potential was attained. Between measurements, electrodes were kept dry.

The dependence of the potential of Pb-selective electrodes on the concentration of Pb(II) was studied in Pb(NO<sub>3</sub>)<sub>2</sub> solutions in the concentration range  $1 \times 10^{-6}$ – $1 \times 10^{-1}$  M at constant pH in the range 2.5–5.5. The selectivity of electrodes was assessed by the mixed solution method ( $c_{\text{Me}} = 1 \times 10^{-2}$  M).

For the titrimetric determination of lead(II) by the precipitation method, we used 0.1 M K<sub>2</sub>CrO<sub>4</sub>; titration was performed at pH 5.0 (acetate buffer solution). The titration end point was determined graphically from the integral ( $E$  (mV) vs.  $V$  (mL)) and differential ( $dE/dV$  vs.  $V$  (mL)) titration curves. From the obtained data, a calibration plot was constructed on the coordinates amount of the titrant (mmol) vs. amount of lead (mmol).

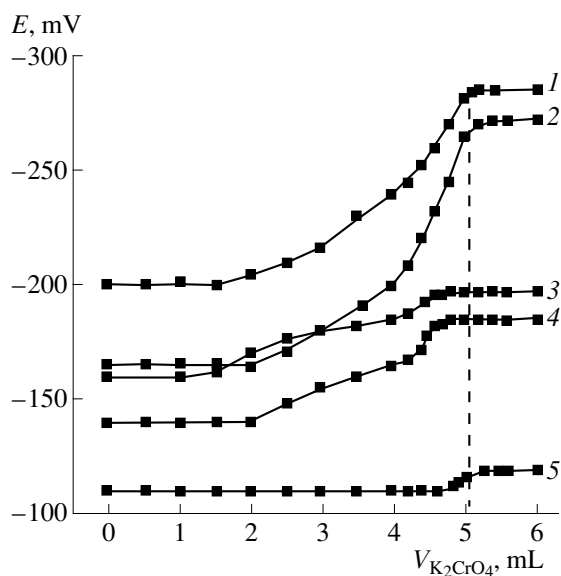
## RESULTS AND DISCUSSION

The electrode characteristics of Pb-selective electrodes with active elements of different composition (electrodes 1–5) are presented in Table 1, and the corresponding linear portions of electrode functions are shown in Fig. 1. From these data, it follows that electrode 1 based on (PbS)<sub>1.18</sub>TiS<sub>2</sub> exhibits the best electrode characteristics. The electrode function of this material is linear in the range of lead(II) concentration

**Table 2.** Potentiometric selectivity coefficients ( $-\log K_{\text{Pb}, M}^{\text{pot}}$ ) for lead-selective electrodes

Ion	Electrode 1	Electrode 2	Electrode 3	Electrode 4	Electrode 5
K <sup>+</sup>	3.2	2.4	2.2	1.4	1.2
Ni <sup>2+</sup>	2.5	2.4	0.3	0	1.2
Co <sup>2+</sup>	2.4	2.0	0	-0.2	1.2
Zn <sup>2+</sup>	2.3	1.7	-0.7	-0.8	1.0
Cu <sup>2+</sup>	2.1	1.5	-0.7	-0.8	1.0
Ag <sup>+</sup>	2.0	1.2	-0.7	-0.7	1.1
Ba <sup>2+</sup>	3.0	2.0	2.0	2.0	2.0
Sr <sup>2+</sup>	3.0	2.3	2.3	2.3	2.2

from  $1 \times 10^{-5}$  to  $5 \times 10^{-2}$  M. For this electrode, the detection limit of lead in pure solutions was  $5.6 \times 10^{-6}$  M. The membrane is reversible to lead(II) ions in the pH range 2.75–5.0. The slope of the electrode function is  $-(26 \pm 1)$  mV/pc in the pH range 3.5–5.0. The response time  $t_{90}$  on switching from water to lead(II)  $1 \times 10^{-6}$ – $1 \times 10^{-5}$  M solutions is 2.5–1.5 min and less than 1 min for concentrations above  $1 \times 10^{-4}$  M. The addition of acetate ions does not significantly affect the characteristics of the Pb-selective electrode. The potential drift was no larger than  $\pm 1$  mV in a day; the detection limit remained constant within this time. On prolonged operation, the



**Fig. 2.** Curves of the potentiometric titration of 0.5 mmol of Pb(II) with 0.1 M  $\text{K}_2\text{CrO}_4$  at pH 5.0; curve numbers (1–5) correspond to compositions of electrodes 1–5 presented in Table 1.

electrode potential is shifted to the negative region with a rate of about 12 mV per month. The service life of the electrode is at least 360 h of continuous operation. The Pb-selective electrode retains these characteristics, if kept dry, for a year.

Table 2 presents potentiometric selectivity coefficients determined by the mixed solution method. The determination of Pb(II) with electrode 1 based on  $(\text{PbS})_{1.18}\text{TiS}_2$  is not affected by the interference from 1000-fold amounts of Ba(II), Sr(II), and K(I); 300-fold amounts of Ni(II); 250-fold amounts of Co(II); 200-fold amounts of Zn(II); 120-fold amounts of Cu(II); and 100-fold amounts of Ag(I). In the case of electrodes based on PbS, the above ions interfere with the determination and, according to our data and in full agreement with the data reported in the literature [1–3], must be absent. The lower the solubility of the corresponding sulfide, the more pronounced the interference of the ion with the determination of lead(II).

The addition of graphite to the active element of the membrane (electrodes 2 and 4) shifts the potentials to the more positive region compared to electrodes 1 and 3 and impairs the selectivity of electrodes 2 and 4 with respect to lead(II) in the presence of Ba(II), Sr(II), K(I), Ni(II), Co(II), Zn(II), Cu(II), and Ag(I).

The use of Pb-selective electrodes 1–5 as indicator electrodes in the titrimetric precipitation titration of lead(II) demonstrated that the titration end point is most clearly indicated using electrode 1 (Fig. 2).

Electrode 1 was tested in the analysis of an OS-8-12 standard bronze sample containing 12.19% Pb, 8.36% Sn, 0.88% Zn, 1.5% Ni, and 77.2% Cu. The sample was dissolved in  $\text{HNO}_3$  (1 : 1), the precipitate of metastannic acid was separated, and lead(II) was titrated at pH 5.0 with 0.1 M  $\text{K}_2\text{CrO}_4$ . Found Pb ( $12.22 \pm 0.23$ )% at ( $n = 5$ ,  $P = 0.95$ ). The relative standard deviation was 1.5%.

Thus, the misfit compound  $(\text{PbS})_{1.18}\text{TiS}_2$  can be recommended as the electrode-active compound for Pb-selective electrodes; it provides the determination of lead(II) in different materials containing Ag(I), Cu(II), Zn(II), Co(II), and Ni(II).

#### ACKNOWLEDGMENTS

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