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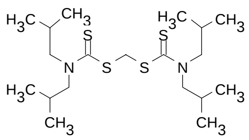
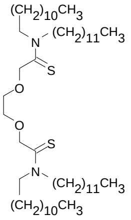
Lead



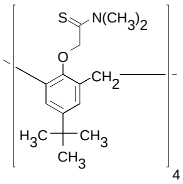
Lead ionophore II
(MBDiBDTC; *S,S'*-Methylenebis(*N,N*-diisobutyldithiocarbamate)
$C_{19}H_{38}N_2S_4$ M_r = 422.77 [90276-58-7]

15336 **Selectophore®, function tested** 50 mg



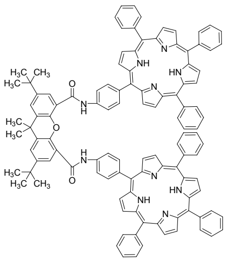
Lead ionophore III
(ETH 5435; *N,N,N',N'*-Tetradodecyl-3,6-dioxaoctanedithioamide)
$C_{54}H_{108}N_2O_2S_4$ M_r = 881.35 [141754-61-2]

98108 **Selectophore®, function tested** 50 mg



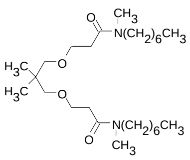
Lead ionophore IV
(*tert*-Butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide))
$C_{60}H_{84}N_2O_4S_4$ M_r = 1054.59 [145237-46-3]

15343 **Selectophore®, function tested** 50 mg



Lead ionophore VII
(ADPX)
$C_{113}H_{88}N_{10}O_3$ M_r = 1633.97

61796 **Selectophore®, function tested** 50 mg



Uranyl ionophore I
(ETH 295; *N,N'*-Diheptyl-*N,N'*,6,6-tetramethyl-4,8-dioxaundecanediamide)
$C_{27}H_{54}N_2O_4$ M_r 470.73 [69844-41-3]

94265 **Selectophore®, function tested** 50 mg

Electrochemical Transduction
- Ion-Selective Electrodes
- Chemically modified Electrodes

Optical Transduction

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Electrochemical Transduction

Ion-Selective Electrodes

Application 1 and Sensor Type [1, 2]
Lead-selective solvent polymeric membrane electrode based on Lead ionophore II.

Recommended Membrane Composition

11.20	wt%	Lead ionophore II (15336)
2.00	wt%	Potassium tetrakis(*p*-chlorophenyl)borate (KT*p*ClPB) (60591)
49.60	wt%	2-Nitrophenyl octyl ether (73732)
37.20	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly
Reference | | sample solution | | liquid membrane | 0.001 M $PbiCl_2$ | AgCl,Ag

Electrode Characteristics and Function

Selectivity coefficients $\log K^{Pot}_{Pb,M}$ .as obtained by the mixed solution method (concentration of the interfering ions are 0.1 M except for Cu (10^{-5} M), Fe and Zn (10^{-3} M). Measured in $Pb(NO_3)_2$ solution of 10^{-1} to 10^{-8} M).

$\log K^{Pot}_{Pb,Na}$	-2.14	$\log K^{Pot}_{Pb,Mn}$	-5.21
$\log K^{Pot}_{Pb,K}$	-2.20	$\log K^{Pot}_{Pb,Ca}$	-5.45
$\log K^{Pot}_{Pb,Fe}$	-2.54	$\log K^{Pot}_{Pb,Mg}$	-5.26
$\log K^{Pot}_{Pb,Zn}$	-3.50	$\log K^{Pot}_{Pb,Sr}$	-5.25
$\log K^{Pot}_{Pb,Cd}$	-3.57	$\log K^{Pot}_{Pb,Cr}$	-4.6
$\log K^{Pot}_{Pb,Ni}$	-5.0	$\log K^{Pot}_{Pb,Cu}$	0.7
$\log K^{Pot}_{Pb,Co}$	-5.2		

Slope of linear regression: 28 mV (10^{-6} – 10^{-2} M $Pb(NO_3)_2$).
Detection limit: $3.5 \cdot 10^{-7}$ M
Response time: 95% response time 16s (10^{-3} to $1^{0\text{-}2}$ M $Pb(NO_3)_2$).
pH range: 3.1-5.4 (measured in 10-^{3} M $Pb(NO_3)_2$ solution.

Application 2 and Sensor Type [3]
Lead-selective solvent polymeric membrane electrode based on Lead ionophore III.

Recommended Membrane Composition

1.31	wt%	Lead ionophore III (ETH 5435) (98108)
0.82	wt	Potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTpClPB) (60588)
62.57	wt%	Bis(2-ethylhexyl) sebacate (84818)
35.30	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly
Reference | | sample solution | | liquid membrane | 0.0005 M $PbCl_2$ and 0.05M $MgCl_2$ | AgCl,Ag

[1] S. Kamata, K. Onoyama, Lead-selective membrane electrode using methylene bis(diisobutyldithiocarbamate) neutral carrier. **Anal. Chem. *63***, 1295 (1991).
[2] S. Kamata, K. Onoyama, Methylene Bis(diisobutyldithiocarbamate) Neutral Carrier as Lead Sensing Material. **Chem. Lett. *653*** (1991).
[3] T. Sokalski, A. Ceresa, T. Zwicki, E Pretsch, Large Improvement of Lower Detection Limit of Ion-Selective Polymer Membrane Electrodes. **J. Am. Chem. Soc. *119***, 11347 (1997).

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Electrode Characteristics and Function

Selectivity coefficients $\log K^{Pot}_{Pb, M}$. as obtained by the separate solution method in 0.01M nitrate solutions of Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} buffered to pH 4.7 with a magnesium acetate buffer ($2.5 \cdot 10^{-4}$ M Mg^{2+}, 10^{-3}M total Ac^-)

$\log K^{Pot}_{Pb, H}$	-2.2	$\log K^{Pot}_{Pb, Sr}$	-4.2
$\log K^{Pot}_{Pb, Li}$	-2.7	$\log K^{Pot}_{Pb, Ba}$	-4.1
$\log K^{Pot}_{Pb, Na}$	-2.2	$\log K^{Pot}_{Pb, Mn}$	-4.1
$\log K^{Pot}_{Pb, K}$	-2.2	$\log K^{Pot}_{Pb, Co}$	-4.3
$\log K^{Pot}_{Pb, NH_4}$	-2.5	$\log K^{Pot}_{Pb, Ni}$	-4.2
$\log K^{Pot}_{Pb, Mg}$	-3.6	$\log K^{Pot}_{Pb, Cu}$	-0.5
$\log K^{Pot}_{Pb, Ca}$	-4.0	$\log K^{Pot}_{Pb, Zn}$	-3.7
$\log K^{Pot}_{Pb, Cd}$	0.9		

Application 3 and Sensor Type [4,5]
Lead-selective solvent polymeric membrane electrode based on Lead ionophore V with very good selectivity over Cu, Zn and Cd.

Recommended Membrane Composition

1.00	wt%	Lead ionophore V (15343)
0.35	wt%	Potassium tetrakis(4-chloropheny)borate (60591)
65.65	wt%	2-Nitrophenyl octyl ether (73732)
33.00	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly
Reference (e.g. Ag, AgCl, 0.1 M KCl | 0.1M KNO_3) | | sample solution | | liquid membrane | 0.005 M $PbCl_2$ | AgCl,Ag

Electrode Characteristics and Function

Selectivity coefficients $\log K^{Pot}_{Pb, M}$ as obtained by the fixed interference method. For Ag and Hg the separate solution method is used (0.01 M solution, pH 4 for Pb and Ag, pH 2 for Hg)

$\log K^{Pot}_{Pb, Hg}$	0.6	$\log K^{Pot}_{Pb, K}$	-4.3
$\log K^{Pot}_{Pb, Ag}$	1.5	$\log K^{Pot}_{Pb, Ba}$	-4.8
$\log K^{Pot}_{Pb, Cu}$	-3.3	$\log K^{Pot}_{Pb, Ca}$	-4.8
$\log K^{Pot}_{Pb, Na}$	-3.5	$\log K^{Pot}_{Pb, Zn}$	-4.8
$\log K^{Pot}_{Pb, Li}$	-3.5	$\log K^{Pot}_{Pb, Mg}$	-5.0

[4] E. Malinowska, Z. Brzozka, K. Kasiura, R.J.M. Egberink, D.N. Reinhoudt, Lead selective electrodes based on thioamide functionalized calix[4]arenes as ionophores. **Anal. Chim. Acta *298***, 253 (1994).
[5] C. McGraw, T. Radu, A. Radu, D. Diamond, Evaluation of Liquid- and Solid-Contact, Pb2+-Selective Polymer-Membrane Electrodes for Soil Analysis, **Electroanalysis *20***, 340 (2008).

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$\log K^{Pot}_{Pb,Cd}$	-3.7	$\log K^{Pot}_{Pb,Ni}$	-5.0
$\log K^{Pot}_{Pb,NH_4}$	-4.0	$\log K^{Pot}_{Pb,Co}$	-5.0

Slope of linear regression: 28.7 mV/dec ($1\cdot10^{-6} – 2\cdot10^{-2}$ M Pb^{2+})
Response time: 95% response time: <10 s
Detection limit: $3\cdot10^{-7}$ Pb^{2+}
pH range: 3-6
Drift (0.01 M Pb, t = 25 min): <0.01 mV/min

Application 4 and Sensor Type [6]
Lead-selective solvent polymeric membrane electrode based on Lead ionophore VII at pH 4.5-7.5.

Recommended Membrane Composition

3.0	wt%	Lead ionophore VII (61796)
2.8	wt%	Sodium tetraphenylborate (NaTPB) (72018)
63.2	wt%	2-Nitrophenyl octyl ether (*o*-NPOE) (73732)
31.0	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly
Reference (e.g. Ag, AgCl, KCl (sat) │ sat. NH_4NO_3)││ sample solution ││ liquid membrane │ 0.001 M $Pb(NO_3)_2$ │ AgCl,Ag

Electrode Characteristics and Function

Selectivity coefficients $\log K^{Pot}_{Pb,M}$ as obtained by the separate solution method. (0.01M solutions in 0.001 M Tris-HNO_3 buffer, pH 6.0)

$\log K^{Pot}_{Pb,Na}$	-1.0	$\log K^{Pot}_{Pb,Mg}$	-3.3
$\log K^{Pot}_{Pb,K}$	-0.6	$\log K^{Pot}_{Pb,Zn}$	-2.8
$\log K^{Pot}_{Pb,Ca}$	-3.2	$\log K^{Pot}_{Pb,Cu}$	-14.5

Slope of linear regression: 28.4 mV/dec ($4\cdot10^{-5} – 5\cdot10^{-2}$ M Pb^{2+})
Detection limit: $1\cdot10^{-5}$ Pb^{2+}

Application 5 and Sensor Type [7]
Lead-selective solvent polymeric membrane electrode based on Uranyl ionophore I.

Recommended Membrane Composition

1.00	wt%	Uranyl ionophore I (94265)
0.42	wt%	Potassium tetrakis(4-chlorophenyl)borate (60591)
68.58	wt%	2-Nitrophenyl octyl ether (73732)
30.00	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Membrane Composition
Reference (e.g. Ag, AgCl, 1 M KCl│0.1 M KNO_3)│sample solution││liquid membrane│0.005 M $PbCl_2$│AgCl,Ag

[6] W.J. Zhang, C.Y. Li, Y.B. Zhang, J. Jin, Synthesis of an Amide-Linked Diporphyrin Xanthene as a Neutral Carrier for a Lead(II)-Sensitive Electrode. **Anal. Lett.** ***40***, 1023 (2007).
[7] E. Malinowska, Lead-selective membrane electrodes based on neutral carriers. Part I. Acyclic amides and oxamides. **Analyst** ***115***, 1085 (1990).

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Electrode Characteristics and Function

Selectivity coefficients $\log K^{Pot}_{Pb,M}$ as obtained by the separate solution method (pH 4).

$\log K^{Pot}_{Pb,Ag}$	0.16	$\log K^{Pot}_{Pb,Ca}$	-2.3
$\log K^{Pot}_{Pb,H}$	-0.16	$\log K^{Pot}_{Pb,Cu}$	-3.9
$\log K^{Pot}_{Pb,Na}$	-3.6	$\log K^{Pot}_{Pb,Cd}$	-4.1
$\log K^{Pot}_{Pb,Li}$	-2.9	$\log K^{Pot}_{Pb,Zn}$	-4.3
$\log K^{Pot}_{Pb,NH_4}$	-3.5	$\log K^{Pot}_{Pb,Mg}$	-4.6
$\log K^{Pot}_{Pb,K}$	-3.9	$\log K^{Pot}_{Pb,Co}$	-4.1
$\log K^{Pot}_{Pb,Sr}$	-1.7	$\log K^{Pot}_{Pb,Ni}$	-4.6
$\log K^{Pot}_{Pb,Ba}$	-2.4		

Slope of linear regression: 35.3 mV ($6•10^{-6}$ - $1•10^{-1}$ M Pb^{2+})
Detection limit: $3•10^{-6}$ M $Pb(NO_3)_2$
Response time: 95% response time: <15 s (10^{-3} to 10^{-2} M Pb^{2+})
pH range: 2-6
Drift: <0.01 mV/min (10^{-2} M Pb^{2+})

Chemically modified Electrodes

Application and Sensor Type [8]
Lead-selective glassy carbon electrodes for accumulation voltametry based on Lead ionophore II. With this chemically modified electrode (CME) mmol concentration of lead(II) can be detected.

Recommended Membrane Composition
Solution A: $5•10^{-3}$ M Lead ionophore II (15336) in 2-propanol (34863)
Solution B: Nafion (5% solution in lower aliphatic alcohols and water) (70160) diluted to 1% with methanol (42105)

Coating solutions:

2 µL	Solution A
2 µL	Solution B
10 µL	Methanol (42105)

A glassy carbon electrode is polished on Al_2O_3 slurry, sonicated in methanol, air-dried and coated with the solution at an area of 0.38 cm^3. This corresponds to a coating with 10 mmol Lead ionophore II and 20 µg Nafion with a calculated film thickness of 0.39 µm.

Electrode Characteristics and Function
Accumulation of lead(II) from 0.1 M acetate buffer (pH 4) followed by voltametry gave a quasi-reversible reduction peak at –0.85 V.
Half-wave potential: $E_{1/2}$: -0.57 V
Peak to peak separation: ΔE_P = 0.51 V
Linear response range: $5•10^{-7}$ M to $6•10^{-6}$ M Pb^{2+} (120 s accumulation)
Detection limit: 10^{-7} M Pb^{2+} (with 600s accumulation)
Interference: Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Ag^{+} and Hg^{2+} are the most highly interfering species.

[8] M. Lerchi, E. Bakker, B. Rusterholz, W. Simon, Lead-selective bulk optodes based on neutral ionophores with subnanomolar detection limits. **Anal. Chem. *64***,1534 (1992).

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Optical Transduction

Application and Sensor Type[9,10]

Lead-selective bulk optode membrane with subnanomolar detection limit based on Lead ionophore III.

Recommended Membrane Composition

2.40	wt%	Lead ionophore III (98108)
0.72	wt%	Chromoionophore VII (ETH 5418) (27095)
64.00	wt%	Bis(2-ethylhexyl) sebacate (84818)
0.88	wt%	Potassium tetrakis[3.5-bis(trifluoromethyl)phenyl] borate (60588)
32.00	wt%	Poly(vinyl chloride) high molecular weight (81392)

Optode Characteristics and Function

Selectivity coefficients $\log K^{Opt}_{Pb,M}$. as obtained by the separate solution method (pH 4.7).

$\log K^{Opt}_{Pb,Na}$	-5.6	$\log K^{Opt}_{Pb,Co}$	-6.5
$\log K^{Opt}_{Pb,K}$	-5.3	$\log K^{Opt}_{Pb,Ni}$	-4.8
$\log K^{Opt}_{Pb,Mg}$	-10.9	$\log K^{Opt}_{Pb,Cu}$	0.7
$\log K^{Opt}_{Pb,Ca}$	-10.8	$\log K^{Opt}_{Pb,Zn}$	-4.6
$\log K^{Opt}_{Pb,Mn}$	-3.0	$\log K^{Opt}_{Pb,Cd}$	1.2

Measuring range: $5 \cdot 10^{-9}$ to $5 \cdot 10^{-3}$ M Pb^{2+} (pH 5.68)
Detection limit: $3.2 \cdot 10^{-12}$ M Pb^{2+}

[9] M. Lerchi, W. Simon, Optodes for environmental chemical monitoring of lead. **Proc. SPIE Int. Soc. Opt. Eng. *1716***, 336 (1993).
[10] E. Bakker, M. Willer, E. Pretsch, Detection limit of ion-selective bulk optodes and corresponding electrodes. **Anal. Chim. Acta *282***, 265 (1993).