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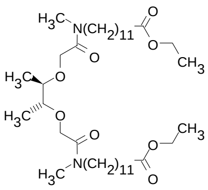
Calcium

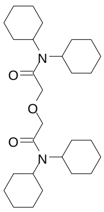


Calcium ionophore I

(ETH 1001; (−)-(*R*,*R*)-*N*,*N*′-Bis-[11-(ethoxycarbonyl)undecyl]-*N*,*N*′,4,5-tetramethyl-3,6-dioxaoctane-diamide; Diethyl *N*,*N*′-[(4*R*,5*R*)-4,5-dimethyl-1,8-dioxo-3,6-dioxaoctamethylene]bis(12-methylaminododecanoate))

$C_{38}H_{72}N_2O_8$ M_r 689.99 [58801-34-6]

21192 **Selectophore®, function tested** 50 mg, 250 mg

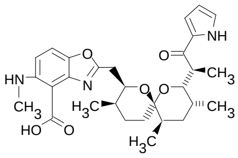


Calcium ionophore II

(ETH 129; N,N,N′,N′-Tetra[cyclohexyl]diglycolic acid diamide; N,N,N′,N′-Tetracyclohexyl-3-oxapentanediamide)

$C_{28}H_{48}N_2O_3$ M_r 460.69 [74267-27-9]

21193 **Selectophore®, function tested** 50 mg, 250 mg

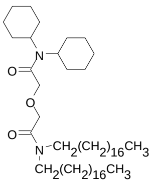


Calcium ionophore III

(A 23187; Calcimycin)

$C_{29}H_{37}N_3O_6$ M_r 523.62 [52665-69-7]

21186 **Selectophore®, function tested** 5 mg, 25 mg

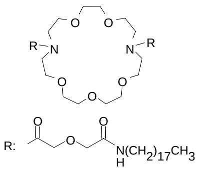


Calcium ionophore IV

(ETH 5234; *N,N*-Dicyclohexyl-*N′,N′*-dioctadecyl-diglycolic diamide; *N,N*-Dicyclohexyl-*N′,N′*-dioctadecyl-3-oxapentanediamide)

$C_{52}H_{100}N_2O_3$ M_r 801.36 [126572-74-5]

21198 **Selectophore®, function tested** 50 mg, 250 mg

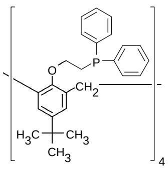


Calcium ionophore V

(K23E1; 10,19-Bis[(octadecylcarbamoyl)methoxyacetyl]-1,4,7,13,16-pentaoxa-10,19-diazacycloheneicosane)

$C_{58}H_{112}N_4O_{11}$ M_r 1041.53 [160563-01-9]

21203 **Selectophore®, function tested** 25 mg, 250 mg

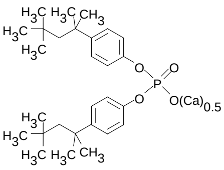


Calcium ionophore VI

(*tert*-Butyl-calix[4]arene tetrakis[2-(diphenylphosphoryl)ethyl ether])

$C_{100}H_{108}O_8P_4$ M_r 1561.82 [171979-66-1]

72385 **Selectophore®, function tested** 50 mg, 250 mg



Bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate Calcium salt

(hemi-Calcium bis[4-(1,1,3,3-tetramethylbutyl)phenyl] phosphate)

$C_{28}H_{42}Ca_{0.5}O_4P$ M_r 493.66 [40835-97-0]

15180 **Selectophore®, function tested** 1 g

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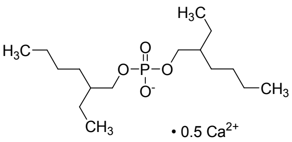

Bis(2-ethylhexyl) phosphate hemicalcium salt

(hemi-Calcium bis(2-ethylhexyl) phosphate)

$C_{32}H_{70}Ca_{0.5}O_8P_2$ M$_r$ 684.92 [10442-05-4]

08733	**Selectophore®**	1 g

Calcium ionophore I - Cocktail A

Calcium-selective membrane solution for microelectrodes

21048	**Selectophore®**	package with 0.1 mL

Calcium ionophore II - Cocktail A

Calcium-selective membrane solution for microelectrodes

21196	**Selectophore®**	package with 0.1 mL

Ion-Selective Electrodes

Microelectrodes

Ion-Selective Field Effect Transistors

Ion-Selective Conductometric Microsensors

Optical Transduction

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Electrochemical Transduction

Ion-Selective Electrodes

Application 1 and Sensor Type [1,2,3]

Assay of Ca^{2+} activity in whole blood, plasma, serum (ionized or total calcium) with solvent polymeric membrane electrodes based on Calcium ionophore I.

Recommended Membrane Composition

3.30	wt%	Calcium ionophore I (21192)
63.70	wt%	Bis(1-butylpentyl)decan-1,10-diyl diglutarate (30585)*
2.10	wt%	Potassium tetrakis(4-chlorophenyl)borate (60591)
30.90	wt%	Poly(vinyl chloride) high molecular weight (81392)

* The use of bis(l-butylpentyl)adipate (02150) or bis(2-ethylhexyl)sebacate (84818) leads to membrane electrodes of similar performance

Recommended Cell Assembly

Reference ⎮⎮ sample solution ⎮⎮ ion-selective membrane ⎮ 0.001 M $CaCl_2$ ⎮ AgCl, Ag

Electrode Characteristics and Function

Selectivity coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the separate solution method (0.1 M solutions of the chlorides)

	required[1)]	found
$\log K^{Pot}_{Ca,H}$	< -2.3	-2.9
$\log K^{Pot}_{Ca,Na}$	< -3.6	-3.7
$\log K^{Pot}_{Ca,K}$	< -0.6	-3.7
$\log K^{Pot}_{Ca,Mg}$	< -1.9	-4.7

Stability:	Drift 0.01 mV/h		
Standard deviation:	0.03 mV		
Reproducibility:	0.13 mV		
Lifetime:	log P_{TLC}[2)] ionophore	> 8.4	7.5
	plasticizer	> 12.8	10.8

1) for measurements in whole blood (1% interference, worst case)[4,5]
2) lipophilicity, determined by thin layer chromatography [6]

[1] D. Ammann, P. Anker, E. Metzger, U. Oesch, W. Simon, in: Ion Measurements in Physiology and Medicine, Eds. M. Kessler, D.K. Harrison, J. Höper, Springer-Verlag, Berlin, Heidelberg 102 (1985).
[2] P. Anker, E. Wieland, D. Ammann, R.E. Dohner, R. Asper, W. Simon, Neutral carrier based ion-selective electrode for the determination of total calcium in blood serum. **Anal. Chem. *53***, 1970 (1981).
[3] P. Anker, D. Ammann, P.C. Meier, W. Simon, Neutral carrier electrode for continuous measurement of blood Ca2+ in the extracorporeal circulation. **Clin. Chem. *30***, 454 (1984).
[4] A. Lewenstam, Ion selective electrodes in clinical chemistry. **Anal. Proc. *28***, 106 (1991).
[5] U. Oesch, P. Anker, D. Ammann, W. Simon, in: Ion-Selective Electrodes, Eds. E. Pungor, I. Buzás, Akadémiai Kiadó, Budapest 81 (1985).
[6] O. Dinten, U.E. Spichiger, N. Chaniotakis, P. Gehrig, B. Rusterholz, W.E. Morf, W. Simon, Lifetime of neutral-carrier-based liquid membranes in aqueous samples and blood and the lipophilicity of membrane components, **Anal. Chem. *63***, 596 (1991).

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Application 2 and Sensor Type [7,8]

Assay of Ca^{2+} activity with solvent polymeric membrane electrodes based on Calcium ionophore II, the detection limit lying in the sub-nanomolar range.

Recommended Membrane Composition

1.00	wt%	Calcium ionophore II (21193)
0.60	wt%	Potassium tetrakis(4-chlorophenyl)borate (60591)
65.60	wt%	2-Nitrophenyl octyl ether (73732)
32.80	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly

Reference ⏐⏐ sample solution ⏐⏐ ion-selective membrane⏐ 0.01 M $CaCl_2$ + 5 • 10^{-2} EDTA, pH 8.5⏐ Ag, AgCl

Electrode Characteristics and Function

Selectivity coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the fixed interference method (0.1 M buffered solutions of the chlorides).

$\log K^{Pot}_{Ca,K}$	- 10.1	$\log K^{Pot}_{Ca,Na}$	- 8.3
$\log K^{Pot}_{Ca,Mg}$	- 9.3		

Slope of linear regression: 33.4±0.1 mV/dec (membranes conditions in 0.01 M NaCl)

Detection limit (Ca^{2+} -buffered solutions containing 94 mM Na^+): log a_{Ca} ~ - 9.7
Detection limit (Ca^{2+} -buffered solutions containing 125 mM Na^+): log a_{Ca} ~ - 10.1
Lifetime: log P_{TLC} [1)] ionophore: 7.2
Response time: 90% response time 2.5 s

[1)] lipophility, determined by thin layer chromatography[6]

Application 3 and Sensor Type [9]

Assay of Ca^{2+} activity in blood serum with solvent polymeric membrane electrodes with good potential stability and reproducibility, based on Calcium ionophore II.

Recommended Membrane Composition

1.0	wt%	Calcium ionophore II (21193)
1.0	wt%	Potassium tetrakis(4-chlorophenyl)borate (60591)
65.0	wt%	Bis(2-ethylhexyl)phthalate (80030)
33.0	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly

Reference⏐⏐sample solution⏐⏐liquid membrane⏐0.001 M $CaCl_2$, 0.1 M NaCl⏐AgCl,Ag

Electrode Characteristics and Function

Selectivity coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the fixed interference method in Ca^{2+}-buffered solution (M: Na^+, K^+, Mg^{2+}, Cl^-)

$\log K^{Pot}_{Ca,Na}$	-2.9	$\log K^{Pot}_{Ca,NH_4}$	-2.9
$\log K^{Pot}_{Ca,K}$	-2.7	$\log K^{Pot}_{Ca,Mg}$	-3.2

Slope of linear regression: 28 mV/dec (2 • 10^{-7} to 10^{-1} M Ca^{2+})
Detection limit: 2 • 10^{-8} M Ca^{2+}
Practical pH measuring range: 3-8
Response time: 90% response time 4 s (10^{-5} to 10^{-4} M Ca^{2+})

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[7] E. Bakker, Determination of Unbiased Selectivity Coefficients of Neutral Carrier-Based Cation-Selective Electrodes. **Anal. Chem. *69***, 1061 (1997).
[8] Bedlechowicz-Sliwakowska I, Lingenfelter P, Sokalski T, Lewenstam A, Maj-Zurawska M., Ion-selective electrode for measuring low Ca2+ concentrations in the presence of high K+, Na+ and Mg2+ background. **Anal. Bioanal. Chem. *385(8)***, 1477 (2006).
[9] Y. Ma, X. Rao, S. Zhong, S. Ren, T. Yu, Q. Zhen, A study of calcium ion-selective PVC membrane electrode based on neutral carrier N,N,N',N'-tetracyclo-3-oxapentanediamide (correction of oxapetanediamide). **J. Tongji Med. Univ. *12***, 98 (1992).

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Application 4 and Sensor Type [10]

Assay of Ca^{2+} activity with solvent polymeric membrane electrodes based on the highly lipophilic Calcium ionophore IV.

Recommended Membrane Composition

1.00	wt%	Calcium ionophore IV (21198)
0.28	wt%	Potassium tetrakis(4-chlorophenyl)borate (60591)
65.82	wt%	2-Nitrophenyl octyl ether (73732)
32.90	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly

Reference ⎪⎪ sample solution ⎪⎪ ion-selective electrode ⎪ 0.01 M $CaCl_2$ ⎪ AgCl,Ag

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the separate solution method (0.1 M solutions of the chlorides).[10]

$\log K^{Pot}_{Ca,H}$	-3.1	$\log K^{Pot}_{Ca,K}$	-7.5
$\log K^{Pot}_{Ca,Li}$	-5.8	$\log K^{Pot}_{Ca,Mg}$	-4.4
$\log K^{Pot}_{Ca,Na}$	-5.9		

Slope of linear regression: 29.7±1.7 mV/dec (10^{-8} to 10^{-1} M $CaCl_2$)
Detection limit ($CaCl_2$ ion background of 125 mM KCl): log a_{ca} ~-9.7
Lifetime: log P_{TLC}[1)] ionophore: 22.6 ± 3.7
Response time: 90% response time 1.2 s (10^{-4} to 10^{-3}M $CaCl_2$)

[1)] lipophility, determined by thin layer chromatography[6]

Application 5 and Sensor Type [11]

Assay of Ca^{2+} activity with solvent polymeric membrane electrodes based on Calcium ionophore V.

Recommended Membrane Composition

2.0	wt%	Calcium ionophore V (21203)
0.9	wt%	Potassium tetrakis(4-chlorophenyl)borate (60591)
66.0	wt%	Nitrophenyl octyl ether (73732)
31.1	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly

Reference ⎪⎪ sample solution ⎪⎪ ion-selective electrode ⎪ 0.1 M $CaCl_2$ ⎪ AgCl,Ag

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the separate solution method (0.1 M of the chloride salts).

$\log K^{Pot}_{Ca,H}$	-3.6	$\log K^{Pot}_{Ca,Cs}$	-4.0
$\log K^{Pot}_{Ca,Li}$	-4.1	$\log K^{Pot}_{Ca,NH_4}$	-4.2
$\log K^{Pot}_{Ca,Na}$	-4.1	$\log K^{Pot}_{Ca,Mg}$	-5.0
$\log K^{Pot}_{Ca,K}$	-4.4	$\log K^{Pot}_{Ca,Sr}$	-1.0
$\log K^{Pot}_{Ca,Rb}$	-4.2	$\log K^{Pot}_{Ca,Ba}$	-2.1

Lifetime: log P_{TLC}[1)] ionophore: 14.6

[1)] lipophility, determined by thin layer chromatography[6]

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Application 6 and Sensor Type [12]
Assay of Ca^{2+} activity with solvent polymeric membrane electrodes based on Calcium ionophore VI.

Recommended Membrane Composition

0.66	wt%	Calcium ionophore VI (72385)
0.07	wt%	Potassium tetrakis(4-chlorophenyl)borate (60591)
66.18	wt%	2-Nitrophenyl octyl ether (73732)
33.09	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly
Reference | | sample solution | | ion-selective electrode | 0.1 M $CaCl_2$ | AgCl,Ag

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the separate solution method (0.1 M of the chloride salts).

$\log K^{Pot}_{Ca,Na}$	-2.2	$\log K^{Pot}_{Ca,Li}$	-1.6
$\log K^{Pot}_{Ca,K}$	-2.7	$\log K^{Pot}_{Ca,Mg}$	-2.6
$\log K^{Pot}_{Ca,NH_4}$	-2.0		

Slope of linear regression: 26.35 mV (10^{-4} to 10^{-1} $CaCl_2$)

Application 7 and Sensor Type [13]
Assay of Ca^{2+} activity with solvent polymeric membrane electrodes based on the liquid ion-exchanger Bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate Calcium salt.

Recommended Membrane Composition

7.00	wt%	Bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate Calcium salt (15180)
29.86	wt%	Poly(vinyl chloride) high molecular weight (81392)
63.14	wt%	Di-n-octylphenylphosphonate (12584)

Recommended Cell Assembly
Reference | | sample solution | | ion-selective electrode | 0.1 M $CaCl_2$ | AgCl,Ag

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the separate solution method (0.1 M of the chloride salts).

$\log K^{Pot}_{Ca,Na}$	-4.4	$\log K^{Pot}_{Ca,Mg}$	-4.9
$\log K^{Pot}_{Ca,K}$	-4.5		

Slope of linear regression: 30.5 at 25°C (10^{-5} to 10^{-0} Ca^{2+})
Detection limit: $3.2 \cdot 10^{-6}$ M Ca^{2+}
pH range for 10^{-3} M $CaCl_2$: 4.8 to 8.8
Response time: <10 s
Operational lifetime: 3 months
Membrane resistance: 3 MΩ

[12] T. McKittrick, D. Diamond, D.J. Marrs, P. O'Hagan, M. Anthony McKervey. Calcium-selective electrode based on a calix[4]arene tetraphosphine oxide, **Talanta *43***, 1145 (1996).
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Application 8 and Sensor Type [14]

Assay of Ca^{2+} activity with solvent polymeric membrane electrodes based on the liquid ion-exchanger Bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate Calcium salt.

Recommended Membrane Composition

0.10	wt%	Bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate Calcium salt (15180)
33.43	wt%	Poly(vinyl chloride) high molecular weight (81392)
66.43	wt%	Bis(2-ethylhexyl)sebacate (84818)

Recommended Cell Assembly

Reference ‖ sample solution ‖ ion-selective electrode | 0.1 M $CaCl_2$ | AgCl,Ag

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the separate solution method (0.1 M of the chloride salts).

$\log K^{Pot}_{Ca,NH_4}$	-3.3	$\log K^{Pot}_{Ca,H}$	-2.4
$\log K^{Pot}_{Ca,Li}$	-4.1	$\log K^{Pot}_{Ca,Mg}$	-6.2
$\log K^{Pot}_{Ca,Na}$	-4.0	$\log K^{Pot}_{Ca,Ba}$	-3.0
$\log K^{Pot}_{Ca,K}$	-3.0		

Slope of linear regression: 31.9 ± 2.3 mV (10^{-4} to 10^{-1} $CaCl_2$)
Membrane resistance: 9.9 ± 1.0 MΩ

[14] U. Schaller, E. Bakker, E. Pretsch, Carrier mechanism of acidic ionophores in solvent polymeric membrane ion-selective electrodes. **Anal. Chem. *67***, 3123 (1995).

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Microelectrodes

Application 1 and Sensor Type *general 15,16,17, application 18,19,20,21,22,23,24,25,26,27,28,29,30,31*
Assay of Ca^{2+} activity in extra- and intracellular (single-cell) liquids with Ca^{2+} microelectrodes of tip diameter > 1µm based on Calcium ionophore I.

Calcium ionophore I - Cocktail A (21048)

Cocktail Composition:

10.0	wt%	Calcium ionophore I (21192)
89.0	wt%	2-Nitrophenyl octyl ether (73732)
1.0	wt%	Sodium tetraphenylborate (72018)

Recommended Cell Assembly
Reference ││ sample solution ││ cocktail│ 0.001 M $CaCl_2$ + 0.011 M NTA + 0.047 M $Na_2B_4O_7$│ AgCl,Ag

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the fixed interference method in Ca^{2+} buffered solutions (for M: Na^+, K^+) or Ca^{2+}-unbuffered solutions (for M: Mg^{2+}).[15]

$\log K^{Pot}_{Ca,Na}$	-5.5	$\log K^{Pot}_{Ca,Mg}$	<-4.9
$\log K^{Pot}_{Ca,K}$	-5.4		

Slope of linear regression: 28.1 $\pm$ 1.8 mV (10^{-7} to 10^{-2} M $CaCl_2$)
Detection limit (Ca2+-buffered solutions, constant ion background of 125 mM K^+): log a_{Ca} ~-7.4
Electrical resistance tip diameter 1 to 2 µm: ~$2 \cdot 10^{10}$ Ω
Response time 90% response time: $\leq$ 5 s[15]
Time constant: τ = 7 ms

[15] F. Lanter, R.A. Steiner, D. Ammann, W. Simon, Critical evaluation of the applicability of neutral carrier-based calcium selective microelectrodes. **Anal. Chim. Acta *135***, 51 (1982).
[16] R.Y. Tsien, T.J. Rink, Ca^{2+}-selective electrodes: a novel PVC-gelled neutral carrier mixture compared with other currently available sensors. **J. Neurosci. Methods *4***, 73 (1981).
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[19] D.M. Bers, D. Ellis, Changes of intracellular calcium and sodium activities in sheep heart Purkinje fibres measured with ion-selective micro-electrodes. **J. Physiol. *310***, 73P (1981).
[20] R. Pumain, I. Kurcewicz, J. Louvel, Fast extracellular calcium transients: involvement in epileptic processes. **Science *222***, 177 (1983).
[21] R. Weingart, P. Hess, Free calcium in sheep cardiac tissue and frog skeletal muscle measured with Ca^{2+}-selective microelectrodes. **Pflügers Arch. *402***, 1 (1984).
[22] C. Nicholson, Modulation of extracellular calcium and its functional implications. **Fed. Proc. *39***, 1519 (1980).
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[27] S. Levy, A. Fein, Relationship between light sensitivity and intracellular free Ca concentration in Limulus ventral photoreceptors. A quantitative study using Ca-selective microelectrodes. **J. Gen. Physiol. *85***, 805 (1985).
[28] A. Picard, M. Dorée, Is calcium the second messenger of 1-methyladenine in meiosis reinitiation of starfish oocytes? **Exp. Cell. Res. *145***, 325 (1983).
[29] K.P. Dresdner, R.P. Kline, Extracellular calcium ion depletion in frog cardiac ventricular muscle. **Biophys. J. *48***, 33 (1985).
[30] H. Yamaguchi, Recording of intracellular Ca^{2+} from smooth muscle cells by sub-micron tip, double-barrelled Ca^{2+}-selective microelectrodes. **Cell Calcium 7**, 203 (1986).
[31] E. Kelepouris, Z.S. Agus, M.M. Civan, Intracellular calcium activity in split frog skin epithelium: effect of cAMP. **J. Membr. Biol. *88***, 113 (1985).

Application 2 and Sensor Type [32,33,34]
Assay of Ca^{2+} activity in extra- and intracellular (single cell) liquids with Ca^{2+} microelectrodes based on Calcium ionophore II.

Calcium ionophore II - Cocktail A

Cocktail Composition

5.0	wt%	Calcium ionophore II (21193)
94.0	wt%	2-Nitrophenyl octyl ether (o-NPOE) (73732)
31.	wt%	Sodium tetraphenylborate (72018)

Recommended Cell Assembly
Reference | sample solution || cocktail | 10^{-7} M $CaCl_2$ | AgCl, Ag

Use
Before use, mix cocktail A with 14 wt% poly(vinyl chloride) (81392) to obtain a stable and reproducable response[32].

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the fixed interference method in Ca^{2+}-buffered solutions (M: Na^+, K^+) or Ca^{2+}-unbuffered solutions M: Mg^{2+}).

$\log K^{Pot}_{Ca,Na}$	-5.6	$\log K^{Pot}_{Ca,Mg}$	-6.7
$\log K^{Pot}_{Ca,K}$	-7.2		

Slope of linear regression: 29.9 mV (10^{-8} to 10^{-3} M Ca^{2+})
Detection limit (Ca^{2+}-buffered solutions, constant ion background of 125 mM K^+): $\log a_{Ca}$ ~-9.2
Electrical resistance, tip diameter 1 to 1.5 µm, filling height 78 to 100 µm: ~$4 \cdot 10^{10}$ Ω
Response Time 90% response time: ≤ 5 s

Application 3 and Sensor Type [32,33,34]
Assay of Ca^{2+} activity in intra- and extracellular (single cell) liquids with Ca^{2+}-microelectrodes of tip diameter <1 µm based on Calcium ionophore II.

Cocktail Composition for electrode tip diameter <1 µm

21.50	wt%	Calcium ionophore II (21193)
3.50	wt%	Poly(vinyl chloride) high molecular weight (81392)
75.00	wt%	Tetrahydrofuran (87396)

Recommended Cell Assembly
Reference | sample solution || cocktail | 0.01 M $CaCl_2$ | AgCl,Ag

Electrode Characteristics and Function
See Calcium ionophore II - Cocktail A (21196)

[32] D. Ammann, T. Bührer, U. Schefer, M. Müller, W. Simon, Intracellular neutral carrier-based Ca^{2+} microelectrode with subnanomolar detection limit. **Pflügers Arch. *409***, 223 (1987).
[33] H.M. Brown, S.K. Marron, Fabrication method to enhance stability of N,N,N',N'-tetracyclohexyl-3-oxapentanediamide calcium microelectrodes. **Anal. Chem. *62***, 2153 (1990).
[34] D. Ammann, P. Caroni, Preparation and use of micro- and macroelectrodes for measurement of transmembrane potentials and ion activities. **Methods in Enzymol. *172***, 136 (1989).

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Ion-Selective Field Effect Transistors

Application 1 and Sensor Type [35]
Assay of Ca^{2+} activity with Urushi matrix ion-selective field effect transistors of good durability based on Calcium ionophore I.

Recommended Membrane Composition:

5.0	wt%	Calcium ionophore I (21192)
44.0	wt%	2-Nitrophenyl octyl ether (73732)
50.0	wt%	Urushi latex
1.0	wt%	Sodium tetraphenylborate (72018)

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$ as obtained by the fixed interference method in Ca^{2+} buffered solutions (for M: Na^{+}, K^{+}) or Ca^{2+}-unbuffered solutions (for M: Mg^{2+}).[15]

$\log K^{Pot}_{Ca,Na}$	-4.8	$\log K^{Pot}_{Ca,NH_4}$	-4.4
$\log K^{Pot}_{Ca,K}$	-5.8	$\log K^{Pot}_{Ca,Mg}$	-4.6

Slope of linear regression: 25 mV ($10^{-5.5}$ to $10^{-1.5}$ M Ca^{2+})

Application 2 and Sensor Type [36]
Determination of Ca^{2+} with an ion-selective field effect transistor based on a photo-curable polysiloxane membrane containing Calcium ionophore IV.

Recommended Membrane Composition:

0.99	wt%	Calcium ionophore IV (21198)
0.55	wt%	Potassium tetrakis[3.5-bis(trifluoromethyl)phenyl]borate (60588)
0.88	wt%	2,2-Dimethoxy-2-phenylacetophenone (38781)
0.88	wt%	Dibutyltin dilaurate (34930)
8.79	wt%	3-(Trimethoxysilyl)propyl methacrylate (64210)
87.91	wt%	10-12%(3-cyanopropyl)methyl/88-90% (dimethylsiloxane) copolymer

Electrode Characteristics and Function

Selectivity Coefficients $\log K^{Pot}_{Ca,M}$

$\log K^{Pot}_{Ca,Na}$	< -3.5	$\log K^{Pot}_{Ca,Mg}$	< -4.0
$\log K^{Pot}_{Ca,K}$	< -3.5		

Slope of linear regression: Nernstian behaviour (10^{-5} to 10^{-1} M $CaCl_2$)

[35] S.I. Wakida, M. Yamane, K. Higashi, K. Hiro, Y. Ujihara, Urushi matrix sodium, potassium, calcium and chloride-selective field-effect transistors. **Sens. Actuators *B1***, 412 (1990).
[36] P.D. Van der Wal, A. Van den Berg, N.A. de Rooij, Universal approach for the fabrication of Ca^{2+}-, K^{+}- and NO_3^{-}-sensitive membrane ISFETs. **Sens. Actuators *B* 18-19**, 200 (1994).

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Ion-Selective Conductometric Microsensors

Application and Sensor Type [37]
Assay of Ca^{2+} activity with ion-selective conductometric microsensors (ISCOM). Detection is accomplished by measurement of the bulk conductance of the solvent polymeric membrane based on Calcium ionophore IV.

Recommended Membrane Composition:

5.0	wt%	Calcium ionophore IV (21198)
30.0	w%	Poly(vinyl chloride) high molecular weight (81392)
65.0	wt%	2-Nitrophenyl octyl ether (73732)

Electrode Characteristics and Function
Detection limit: ~10^{-7} M Ca^{2+} (measurements in 1 M $NaNO_3$)
Response time: ~2 s

[37] A.A. Shul′′ga, B. Ahlers, K. Cammann, Ion-selective conductometric microsensors based on the phenomenon of specific salt extraction. **J. Electroanal. Chem. *395***, 305 (1995).

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Optical Transduction

Application 1 and Sensor Type [38,39]
Assay of Ca^{2+} activity in aqueous pH-buffered solutions with polymeric optode membranes based on Chromoionophore I (ETH 5294) and Calcium ionophore I.

Recommended Membrane Composition

2.20	wt%	Chromoionophore I (27086)
8.01	wt%	Calcium ionophore I (21192)
4.49	wt%	Bis(2-ethylhexyl)sebacate (84818)
57.27	wt%	Poly(vinyl chloride) high molecular weight (81392)
28.03	wt%	Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (72017)

Recommended pH Buffer
0.16 M sodium acetate, adjusted with acetic acid to pH 5.3 for recording the calibration curve.[40]

Optode Characteristics and Function

Selectivity Coefficients $\log K^{Opt}_{Ca, M}$ as obtained by the separate solution method in pH-buffered solutions.

$\log K^{Opt}_{Ca, Na}$	-3.6	$\log K^{Opt}_{Ca, Mg}$	-4.1
$\log K^{Opt}_{Ca, K}$	-3.8		

Application 2 and Sensor Type [41]
Assay of Ca^{2+} activity in aqueous pH-buffered solutions with solvent polymeric optode membranes based on Chromoionophore III (ETH 5350) and Calcium ionophore II.

Recommended Membrane Composition

9.20	wt%	Calcium ionophore II (21193)
2.20	wt%	Chromoionophore III (27088)
4.50	wt%	Sodium tetrakis[3.5-bis(trifluoromethyl)phenyl]borate (72017)
56.40	wt%	Bis(2-ethylhexyl)sebacate (84818)
27.80	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended pH Buffer
0.1 M sodium acetate adjusted to pH 5.4 with 3 M acetic acid.

Optode Characteristics and Function

Selectivity Coefficients $\log K^{Opt}_{Ca, Na}$ -6.1 as obtained by the fixed interference method.[38]

Response time: ~1 min

[38] Fluka 58166: K. Seiler, Ion-selective Optode Membranes, monograph, describing theory, preparation and application of ion-selective optode membranes as well as recent developments in this field. With 237 references. published by Fluka Chemie GmbH, Buchs, Switzerland (1993).
Fluka 58165: K. Seiler, Ionenselektive Optodenmembranen, dt. Monographie, herausgegeben von Fluka Chemie GmbH, Buchs, Switzerland (1993).
[39] W.E. Morf, K. Seiler, B. Rusterholz, W. Simon, Design of a novel calcium-selective optode membrane based on neutral ionophores. **Anal. Chem.** ***62***, 738 (1990).
[40] D.D. Perrin, B. Dempsey, Buffers for pH and Metal Ion Control. Chapman & Hall, London, New York (1983).
[41] T. Rosatzin, P. Holy, K. Seiler, B. Rusterholz, W. Simon, Immobilization of components in polymer membrane-based calcium-selective bulk optodes. **Anal. Chem.** ***64***, 2029 (1992).

Application 3 and Sensor Type [38,42]
Assay of Ca^{2+} activity in aqueous pH-buffered solutions and in diluted blood plasma with solvent polymeric optode membranes based on Chromoionophore II (ETH 2439) and Calcium ionophore I.

Recommended Membrane Composition

1.47	wt%	Chromoionophore II (27087)
5.98	wt%	Calcium ionophore I (21192)
2.56	wt%	Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (72017)
60.90	wt%	Bis(2-ethylhexyl)sebacate (84818)
29.09	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended pH Buffer
0.02 M sodium hydroxide adjusted to pH 3.3 with acetic acid.

Application 4 and Sensor Type [43]
Assay of Ca^{2+} activity in diluted human plasma with solvent polymeric optode membranes based on Chromoionophore I (ETH 5294) and Calcium ionophore I.

Recommended Membrane Composition

2.20	wt%	Chromoionophore I (27086)
8.01	wt%	Calcium ionophore I (21192)
4.49	wt%	Bis(2-ethylhexyl)sebacate (84818)
57.27	wt%	Poly(vinyl chloride) high molecular weight (81392)
28.03	wt%	Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (72017)

Recommended pH Buffer
Sodium acetate type at pH 3.52

Optode Characteristics and Function

Selectivity Coefficients $\log K^{Opt}_{Ca,M}$ as obtained by the fixed interference method.[38]

$\log K^{Opt}_{Ca,Li}$	-3.1	$\log K^{Opt}_{Ca,K}$	-3.8
$\log K^{Opt}_{Ca,Na}$	-3.6	$\log K^{Opt}_{Ca,Mg}$	-4.1

Application 5 and Sensor Type [44]
Flow-through type Ca^{2+} ion selective optodes for determination of Ca2+ in biological samples such as human serum based on Calcium ionophore V.

Recommended Membrane Composition

1.0	wt%	Calcium ionophore V (21203)
1.2	wt%	Chromophore (LAD-3)*
31.0	wt%	o-trifluoromethylphenyl dodecyl ether (TFPDE)*
66.8	wt%	ODS beads*

*not available from Sigma-Aldrich

Recommended pH Buffer
0.05 M Tris-HCl, pH 7.0

[42] K. Seiler, R. Eugster, W.E. Morf, K. Wang, M. Czösz, B. Rusterholz, W. Simon, U.E. Spichiger, Application of calcium optode in human plasma. **Fresenius J. Anal. Chem.** ***337***, 109 (1990).
[43] U.E. Spichiger, K. Seiler, K. Wang, G. Suter, W.E. Morf, W. Simon, Optical quantification of sodium, potassium, and calcium ions in diluted human plasma based on ion-selective liquid membranes. **Proc. SPIE-Int. Soc. Opt. Eng.** ***1510***, 118 (1991).
[44] H. Hisamoto, K. Watanabe, E. Nakagawa, D. Siswanta, Y. Shichi, K. Suzuki, Flow-through type calcium ion selective optodes based on novel neutral ionophores and a lipophilic anionic dye. **Anal. Chim. Acta** ***299***, 179 (1994).

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Optode Characteristics and Function

Selectivity Coefficients $\log K^{Opt}_{Ca,M}$ as obtained by the separate solution method in pH buffered solutions at 516 nm.

$\log K^{Opt}_{Ca,Li}$	-4.0	$\log K^{Opt}_{Ca,NH_4}$	-4.4
$\log K^{Opt}_{Ca,Na}$	-4.8	$\log K^{Opt}_{Ca,Mg}$	-4.0
$\log K^{Opt}_{Ca,K}$	-4.1	$\log K^{Opt}_{Ca,Ba}$	-1.7

Concentration range: 10^{-7} M to 10^{-1} M.