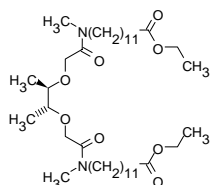


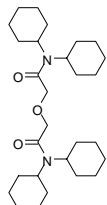
Calcium



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'-[(4R,5R)-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]

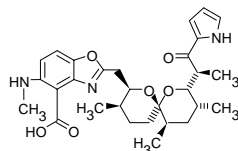
[21192](#) **Selectophore[®], function tested** 50 mg, 250 mg



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]

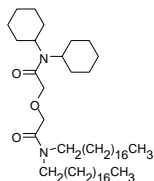
[21193](#) **Selectophore[®], function tested** 50 mg, 250 mg



Calcium ionophore III

(A 23187; Calcimycin)
 $C_{29}H_{37}N_3O_6$ M_r 523.62 [52665-69-7]

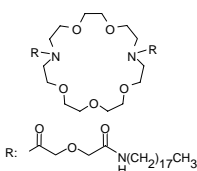
[21186](#) **Selectophore[®], function tested** 5 mg, 25 mg



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]

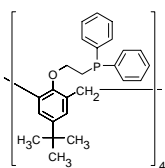
[21198](#) **Selectophore[®], function tested** 50 mg, 250 mg



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]

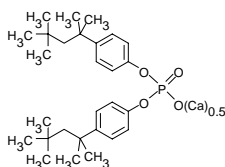
[21203](#) **Selectophore[®], function tested** 25 mg, 250 mg



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]

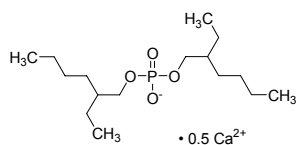
[72385](#) **Selectophore[®], function tested** 50 mg, 250 mg



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

**Bis(2-ethylhexyl) phosphate hemicalcium salt**

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

C₃₂H₇₀Ca_{0.5}O₈P₂ 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**

Electrochemical Transduction

Ion-Selective Electrodes

Application 1 and Sensor Type ^{1,2,3}

Assay of Ca²⁺ 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(1-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 CaCl₂ | AgCl, Ag

Electrode Characteristics and Function

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

	required ¹⁾	found
$\log K_{Ca, H}^{Pot}$	< -2.3	-2.9
$\log K_{Ca, Na}^{Pot}$	< -3.6	-3.7
$\log K_{Ca, K}^{Pot}$	< -0.6	-3.7
$\log K_{Ca, Mg}^{Pot}$	< -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 chromatography⁶

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).

Application 2 and Sensor Type ⁷

Assay of Ca²⁺ activity with solvent polymeric membrane electrodes based on Calcium ionophore II, the detection limit lying in the sub-nanomolar range.

Recommended Cell Assembly

Reference || sample solution || ion-selective membrane | 0.01 M MgCl₂ | Ag, AgCl

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)

Electrode Characteristics and Function

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

$\log K_{Ca, H}^{Pot}$	-1.6	$\log K_{Ca, K}^{Pot}$	-4.0
$\log K_{Ca, Li}^{Pot}$	-3.3	$\log K_{Ca, Mg}^{Pot}$	-4.9
$\log K_{Ca, Na}^{Pot}$	-3.7		

Detection limit (Ca²⁺-buffered solutions containing 94 mM Na⁺): $\log a_{Ca} \sim -9.7$

Detection limit (Ca²⁺-buffered solutions containing 125 mM Na⁺): $\log a_{Ca} \sim -10.1$

Lifetime: $\log P_{TLC}^{(1)}$ ionophore: 7.2

Response time: 90% response time 2.5 s

¹⁾ lipophilicity, determined by thin layer chromatography⁶

Application 3 and Sensor Type ⁸

Assay of Ca²⁺ 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 (63088)
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 CaCl₂, 0.1 M NaCl | AgCl, Ag

Electrode Characteristics and Function

Selectivity coefficients $\log K_{Ca, M}^{Pot}$ as obtained by the fixed interference method in Ca²⁺-buffered solution

(M: Na⁺, K⁺, Mg²⁺, Cl⁻)

$\log K_{Ca, Na}^{Pot}$	-2.85	$\log K_{Ca, NH_4}^{Pot}$	-2.88
$\log K_{Ca, K}^{Pot}$	-2.69	$\log K_{Ca, Mg}^{Pot}$	-3.15

Slope of linear regression: 28 mV (2 · 10⁻⁷ to 10⁻¹ Ca²⁺)

Detection limit: 2 · 10⁻⁸ M Ca²⁺

Practical pH measuring range: 3-8

Response time: 90% response time 4 s (10⁻⁵ to 10⁻⁴ Ca²⁺)

⁷ U. Schefer, D. Ammann, E. Pretsch, U. Oesch, W. Simon, Neutral carrier based calcium(2+)-selective electrode with detection limit in the sub-nanomolar range. **Anal. Chem.** **58**, 2282 (1986).

⁸ 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 oxapentanediamide). **J. Tongji Med. Univ.** **12**, 98 (1992)

Application 4 and Sensor Type ⁹

Assay of Ca²⁺ 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 CaCl₂ | AgCl,Ag

Electrode Characteristics and Function

Selectivity Coefficients $\log K_{Ca, M}^{Pot}$ as obtained by the separate solution method (0.1 M solutions of the chlorides).⁹

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

Slope of linear regression: 29.7 ± 1.7 mV (10⁻⁸ to 10⁻¹ CaCl₂)

Detection limit (CaCl₂ 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 CaCl₂)

¹⁾ lipophilicity, determined by thin layer chromatography⁶

Application 5 and Sensor Type ¹⁰

Assay of Ca²⁺ 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 CaCl₂ | AgCl,Ag

Electrode Characteristics and Function

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

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

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

¹⁾ lipophilicity, determined by thin layer chromatography⁶

⁹ P. Gehrig, B. Rusterholz, W. Simon, Very lipophilic calcium. ion-selective ionophore for chemical sensors of high life-time. *Chimia* **43**, 377 (1989).

¹⁰ K. Suzuki, K. Watanabe, Y. Matsumoto, M. Kobayashi, S. Sato, D. Siswanta, H. Hisamoto, Design and Synthesis of Calcium and Magnesium Ionophores Based on Double-Armed Diazacrown Ether Compounds and Their Application to an Ion Sensing Component for an Ion-Selective Electrode. *Anal. Chem.* **67**, 324 (1995).

Application 6 and Sensor Type ¹¹

Assay of Ca²⁺ 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 CaCl₂ | AgCl,Ag

Electrode Characteristics and Function

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

$\log K_{Ca, Na}^{Pot}$ -2.2 $\log K_{Ca, Li}^{Pot}$ -1.6

$\log K_{Ca, K}^{Pot}$ -2.7 $\log K_{Ca, Mg}^{Pot}$ -2.6

$\log K_{Ca, NH_4}^{Pot}$ -2.0

Slope of linear regression: 26.35 mV (10⁻⁴ to 10⁻¹ CaCl₂)

Application 7 and Sensor Type ¹²

Assay of Ca²⁺ 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 CaCl₂ | AgCl,Ag

Electrode Characteristics and Function

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

$\log K_{Ca, Na}^{Pot}$ -4.4 $\log K_{Ca, Mg}^{Pot}$ -4.9

$\log K_{Ca, K}^{Pot}$ -4.5

Slope of linear regression: 30.5 at 25°C (10⁻⁵ to 10⁻⁰ Ca²⁺)

Detection limit: 3.2 · 10⁻⁶ M Ca²⁺

pH range for 10⁻³ M CaCl₂: 4.8 to 8.8

Response time: <10 s

Operational lifetime: 3 months

Membrane resistance: 3 MΩ

¹¹ 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).

¹² G.J. Moody, The role of polymeric materials in the fabrication of ion-selective electrodes and biosensors. **Polym. Mat. Sci. Eng.** **64**, 362, (1991) and ref. cited therein.

Application 8 and Sensor Type ¹³

Assay of Ca²⁺ 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 CaCl₂ | AgCl,Ag

Electrode Characteristics and Function

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

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

Slope of linear regression: 31.9 ± 2.3 mV (10⁻⁴ to 10⁻¹ CaCl₂)

Membrane resistance: 9.9 ± 1.0 MΩ

¹³ U. Schaller, E. Bakker, E. Pretsch, Carrier mechanism of acidic ionophores in solvent polymeric membrane ion-selective electrodes. *Anal. Chem.* **67**, 3123 (1995).

Microelectrodes

Application 1 and Sensor Type general 14, 15, 16, application 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30

Assay of Ca^{2+} activity in extra- and intracellular (single-cell) liquids with Ca^{2+} microelectrodes of tip diameter > $1\mu\text{m}$ 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 $\text{Na}_2\text{B}_4\text{O}_7$ | AgCl,Ag

Electrode Characteristics and Function

Selectivity Coefficients $\log K_{\text{Ca, M}}^{\text{Pot}}$ 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+}).¹⁴

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

Slope of linear regression: 28.1 ± 1.8 mV (10^{-7} to 10^{-2} M CaCl_2)

Detection limit (Ca^{2+} -buffered solutions, constant ion background of 125 mM K^+): $\log a_{\text{Ca}} \sim -7.4$

Electrical resistance tip diameter 1 to 2 μm : $\sim 2 \cdot 10^{10} \Omega$

Response time 90% response time: ≤ 5 s¹⁴

Time constant: $\tau = 7$ ms

¹⁴ 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).

¹⁵ 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).

¹⁶ E. Ujec, E.E.O. Keller, N. Kõiz, V. Pavlik, J. Machek, Low-impedance, coaxial, ion-selective, double-barrel microelectrodes and their use in biological measurements. **Bioelectrochem. Bioenerg.** **7**, 363 (1980).

¹⁷ E. Marban, T.J. Rink, R.W. Tsien, R.Y. Tsien, Free calcium in heart muscle at rest and during contraction measured with Ca^{2+} -sensitive microelectrodes. **Nature** **286**, 845 (1980).

¹⁸ 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).

¹⁹ R. Pumain, I. Kurcewicz, J. Louvel, Fast extracellular calcium transients: involvement in epileptic processes. **Science** **222**, 177 (1983).

²⁰ 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).

²¹ C. Nicholson, Modulation of extracellular calcium and its functional implications. **Fed. Proc.** **39**, 1519 (1980).

²² A.L.F. Gorman, S. Levy, E. Nasi, D. Tillotson, Intracellular calcium measured with calcium-sensitive micro-electrodes and Arsenazo III in voltage-clamped Aplysia neurones. **J. Physiol.** **353**, 127 (1984).

²³ R. DiPolo, H. Rojas, J. Vergara, R. Lopez, C. Caputo, Measurements of intracellular ionized calcium in squid giant axons using calcium-selective electrodes. **Biochim. Biophys. Acta** **728**, 311 (1983).

²⁴ F.J. Alvarez-Leefmans, T.J. Rink, R.Y. Tsien, Free calcium ions in neurones of Helix aspersa measured with ion-selective micro-electrodes. **J. Physiol.** **315**, 531 (1981).

²⁵ M.J. Berridge, Preliminary measurements of intracellular calcium in an insect salivary gland using a calcium-sensitive microelectrode. **Cell Calcium** **1**, 217 (1980).

²⁶ 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).

²⁷ A. Picard, M. Dorée, Is calcium the second messenger of 1-methyladenine in meiosis reinitiation of starfish oocytes? **Exp. Cell. Res.** **145**, 325 (1983).

²⁸ K.P. Dresdner, R.P. Kline, Extracellular calcium ion depletion in frog cardiac ventricular muscle. **Biophys. J.** **48**, 33 (1985).

²⁹ 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).

³⁰ 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 ^{31,32,33}

 Assay of Ca²⁺ activity in extra- and intracellular (single cell) liquids with Ca²⁺ 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 CaCl₂ | AgCl, Ag

Use

 Before use, mix cocktail A with 14 wt% poly(vinyl chloride) ([81392](#)) to obtain a stable and reproducible response³¹.

Electrode Characteristics and Function

 Selectivity Coefficients $\log K_{Ca, M}^{Pot}$ as obtained by the fixed interference method in Ca²⁺-buffered solutions (M: Na⁺, K⁺) or Ca²⁺-unbuffered solutions M: Mg²⁺).

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

 Slope of linear regression: 29.9 mV (10⁻⁸ to 10⁻³ M Ca²⁺)

 Detection limit (Ca²⁺-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 · 10¹⁰ Ω

Response Time 90% response time: ≤ 5 s

Application 3 and Sensor Type ^{31,32,33}

 Assay of Ca²⁺ activity in intra- and extracellular (single cell) liquids with Ca²⁺-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 CaCl₂ | AgCl, Ag

Electrode Characteristics and Function

 See Calcium ionophore II - Cocktail A ([21196](#))

³¹ D. Ammann, T. Bührer, U. Schefer, M. Müller, W. Simon, Intracellular neutral carrier-based Ca²⁺ microelectrode with subnanomolar detection limit. *Pflügers Arch.* **409**, 223 (1987).

³² 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).

³³ 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).

Ion-Selective Field Effect Transistors

Application 1 and Sensor Type ³⁴

Assay of Ca²⁺ 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 $\log K_{Ca, M}^{Pot}$ as obtained by the fixed interference method in Ca²⁺ buffered solutions (for M: Na⁺, K⁺) or Ca²⁺-unbuffered solutions (for M: Mg²⁺).¹⁴

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

Slope of linear regression: 25 mV (10^{-5.5} to 10^{-1.5} M Ca²⁺)

Application 2 and Sensor Type ³⁵

Determination of Ca²⁺ 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 $\log K_{Ca, M}^{Pot}$

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

Slope of linear regression: Nernstian behaviour (10⁻⁵ to 10⁻¹ M CaCl₂)

³⁴ 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).

³⁵ P.D. Van der Wal, A. Van den Berg, N.A. de Rooij, Universal approach for the fabrication of Ca²⁺-, K⁺- and NO₃⁻-sensitive membrane ISFETs. **Sens. Actuators B 18-19**, 200 (1994).

Ion-Selective Conductometric Microsensors

Application and Sensor Type ³⁶

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: $\sim 10^{-7}$ M Ca^{2+} (measurements in 1 M NaNO_3)

Response time: ~ 2 s

³⁶ 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).

Optical Transduction

Application 1 and Sensor Type ^{37,38}

Assay of Ca²⁺ 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. ³⁹

Optode Characteristics and Function

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

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

Application 2 and Sensor Type ⁴⁰

Assay of Ca²⁺ 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 $\log K_{Ca, Na}^{Opt}$ -6.1 as obtained by the fixed interference method. ³⁷

Response time: ~1 min

³⁷ 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).

³⁸ 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).

³⁹ D.D. Perrin, B. Dempsey, Buffers for pH and Metal Ion Control. Chapman & Hall, London, New York (1983).

⁴⁰ 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^{37,41}

Assay of Ca²⁺ 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 Type⁴²

Assay of Ca²⁺ 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	$\log K_{Ca, M}^{Opt}$	as obtained by the fixed interference method. ³⁷
	-3.1	-3.8
	-3.6	-4.1

Application 5 and Sensor Type⁴³

Flow-through type Ca²⁺ 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

⁴¹ 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).

⁴² 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).

⁴³ 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).

Optode Characteristics and Function

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

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

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