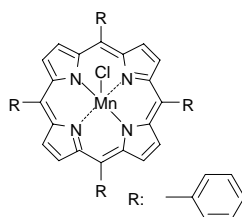


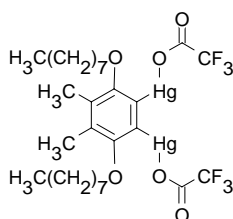
Chloride



Chloride ionophore I

(*meso*-Tetraphenylporphyrin manganese(III)-chloride complex; Mn(II)TPPCI)
 $C_{44}H_{28}ClMnN_4$ M_r 703.12 [32195-55-4]

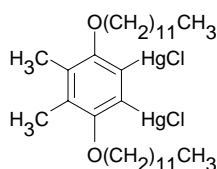
[24897](#) **Selectophore[®], function tested** 50 mg



Chloride ionophore II

(ETH 9009; 4,5-Dimethyl-3,6-dioctyloxy-*o*-phenylene-bis(mercurytrifluoroacetate))
 $C_{28}H_{40}F_6Hg_2O_6$ M_r 987.79 [1458889-57-2]

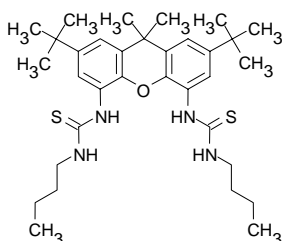
[24901](#) **Selectophore[®], function tested** 25 mg



Chloride ionophore III

(ETH 9033; 3,6-Didodecyloxy-4,5-dimethyl-*o*-phenylene-bis(mercury chloride))
 $C_{32}H_{56}Cl_2Hg_2O_2$ M_r 944.87 [178959-28-9]

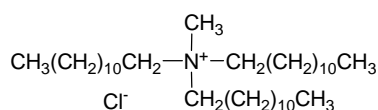
[24894](#) **Selectophore[®], function tested** 50 mg



Chloride ionophore IV

(4,5-Bis-[N'-(butyl)thioureido]-2,7-di-*tert*-butyl-9,9-dimethylxanthene)
 $C_{33}H_{50}N_4OS_2$ M_r 582.91 [187404-67-7]

[92332](#) **Selectophore[®], function tested** 25 mg, 100 mg



Tridodecylmethylammonium chloride

(Methyltridodecylammonium chloride)
 $[CH_3(CH_2)_{11}]_3N^+(Cl)CH_3$ M_r 572.47 [7173-54-8]

[91661](#) **Selectophore[®], function tested** 100 mg, 1 g

Chloride ionophore I-Cocktail A

Chloride-selective membrane solution for microelectrodes

[24902](#) **Selectophore**[®] package with 0.1 mL

Chloride-selective liquid ion-exchanger microelectrode-Cocktail A

Chloride-selective membrane solution for microelectrodes

[24899](#) **Selectophore**[®] package with 0.1 mL

Electrochemical Transduction

- Ion-Selective Electrodes
- Ion-selective Field Effect Transistors
- Fehler! Verweisquelle konnte nicht gefunden werden.

Optical Transduction

Electrochemical Transduction

Ion-Selective Electrodes

Application 1 and Sensor Type ^{1,2}

Assay of Cl⁻ activity with solvent polymeric membrane electrode based on Chloride ionophore II.

Recommended Membrane Composition

2.00	wt%	Chloride ionophore II (24901)
0.03	wt%	Tridodecylmethylammonium chloride (91661)
64.97	wt%	Bis(2-ethylhexyl) sebacate (84818)
33.00	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly

Reference || sample solution || liquid membrane | 0.01 M NaCl | AgCl, Ag

Electrode Characteristics and Function

Selectivity coefficients $\log K_{Cl, X}^{Pot}$ as obtained by the separate solution method (0.1 M solutions of the sodium salts, pH 7.4 TRIS/H₂SO₄).

	Found	Required ¹⁾
$\log K_{Cl, Br}^{Pot}$	0	< 0.7
$\log K_{Cl, SCN}^{Pot}$	-0.2	< 0.8
$\log K_{Cl, Salicylate}^{Pot}$	-0.4	< -0.3
$\log K_{Cl, CO_3}^{Pot}$	-5.5	< -1.4
$\log K_{Cl, HPO_4}^{Pot}$	-5.9	< -1.2
$\log K_{Cl, SO_4}^{Pot}$	-6.3	< -1.3
$\log K_{Cl, F}^{Pot}$	-5.4	
$\log K_{Cl, Acetate}^{Pot}$	-5.1	
$\log K_{Cl, NO_3}^{Pot}$	-3.2	
$\log K_{Cl, ClO_3}^{Pot}$	-1.8	

¹⁾ for measurement in whole blood, plasma and serum (1% interference, worst case)³

Slope of linear regression: -57.6±1.2 mV (10⁻⁵ to 10⁻¹ M NaCl)

Detection limit: 10⁻⁵ M NaCl

Stability: Standard deviation: 0.16 mV (0.01 M NaCl)

Drift: <1.5 mV/h

Response time: 90 % response time: 9.5 s

¹ M. Rothmaier, W. Simon, Chloride-selective electrodes based on mercury organic compounds as neutral carriers. **Anal. Chim. Acta** **271**, 135 (1993).

² H.J. Marsoner, Chr. Ritter, M. Ghahramani, Results with Chloride Selective Liquid Membrane Electrodes. TFCC Workshop, Helsinki 1985.

³ U. Oesch, D. Ammann, W. Simon, Design of anion-selective membranes for clinically relevant sensors. **J. Chem. Soc. Faraday Trans. 1**, **82**, 1179 (1986).

Application 2 and Sensor Type ⁴

Assay of Cl⁻ activity with solvent polymeric membrane electrode based on Tridodecylmethylammonium chloride with improved performance.

Recommended Membrane Composition

16.70	wt%	Tridodecylmethylammonium chloride (91661)
41.70	wt%	Dipentyl phthalate (80154)
8.30	wt%	Dodecylbenzenesulfonic acid (44199)
33.30	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly

Reference (e.g. Ag,AgCl,0.0033 M KCl) | 0.0001 M KNO₃ | | sample solution | | liquid membrane | 0.003 M KCl | AgCl, Ag

Electrode Characteristics and Function

Selectivity coefficients $\log K_{Cl, X}^{Pot}$

$\log K_{Cl, HCO_3}^{Pot}$	-1.7	$\log K_{Cl, SO_4}^{Pot}$	-1.62
$\log K_{Cl, HPO_4}^{Pot}$	-1.08	$\log K_{Cl, Acetate}^{Pot}$	< -1.35

Slope of linear regression: -52 mV (10⁻² to 5•10⁻⁴ M Cl⁻).

Application 3 and Sensor Type ^{5,6}

Assay of Cl⁻ activity with asymmetric cellulose acetate membrane electrode based on Chloride ionophore I. Asymmetric membranes are formed by hydrolyzing the surface of the homogeneous ion-selective membrane by base. This electrode shows decreased interference by salicylate and other hydrophobic anions.

Recommended Membrane Composition

1.00	wt%	Chloride ionophore I (24897)
66.00	wt%	2-Nitrophenyl octyl ether (73732)
33.00	wt%	Cellulose triacetate (22200)

Recommended Cell Assembly

Reference | | sample solution | | liquid membrane | 0.1 M NaH₂PO₄, 0.1 M Na₂HPO₄, 0.01 M NaCl | AgCl, Ag

Application 4 and Sensor Type ⁷

Assay of Cl⁻ activity with solvent polymeric membrane electrode based on Chloride ionophore III.

Recommended Membrane Composition

2.0	wt%	Chloride ionophore III (24894)
1.2	wt%	Tridodecylmethylammonium chloride (91661)
63.8	wt%	Bis(2-ethylhexyl) sebacate (84818)
33.0	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly

Reference | | sample solution | | liquid membrane | 0.01 M NaCl | AgCl, Ag

⁴ S. Nomura, Incorporation of dodecylbenzenesulfonic acid in a poly(vinyl chloride) matrix chloride ion-selective membrane based on tertiary ammonium. **Analyst** **120**, 503 (1995).

⁵ D.S. Oh, D.S. Shin, B. Kim, K.J. Paeng, M.J. Cha, G.S. Cha, Metalloporphyrin-Based Asymmetric Chloride Ion-Selective Membrane Electrodes with Decreased Salicylate Interference. **J. Kor. Chem. Soc.** **37**, 1080 (1993).

⁶ M.J. Cha, J.H. Shin, B.K. Oh, C.Y. Kim, G.S. Cha, D.S. Shin, B. Kim, Asymmetric cellulose acetate membrane-based carbonate- and chloride-selective electrodes. **Anal. Chim. Acta** **315**, 311 (1995).

⁷ M. Rothmaier, U. Schaller, W. Morf, E. Pretsch, Response mechanism of anion-selective electrodes based on mercury organic compounds as ionophores, **Anal. Chim. Acta** **327**, 17 (1996).

Electrode Characteristics and Function

Selectivity coefficients $\log K_{Cl, X}^{Pot}$ as obtained by the separate solution method (0.1 M solutions of the sodium salts at 22°C).

$\log K_{Cl, Br}^{Pot}$	-1.4	$\log K_{Cl, Acetate}^{Pot}$	-6.3
$\log K_{Cl, I}^{Pot}$	-1.7	$\log K_{Cl, F}^{Pot}$	-6.6
$\log K_{Cl, SCN}^{Pot}$	-0.3	$\log K_{Cl, HCO_3}^{Pot}$	-4.8
$\log K_{Cl, Salicylate}^{Pot}$	-0.1	$\log K_{Cl, HPO_4}^{Pot}$	-6.9
$\log K_{Cl, ClO_4}^{Pot}$	-4.5	$\log K_{Cl, SO_4}^{Pot}$	-6.4
$\log K_{Cl, NO_3}^{Pot}$	-6.7		

Slope of linear regression: -56.9 mV (10^{-5} to 10^{-1} M NaCl).

Response time: 90 % response time: 15.8s (10^{-3} to 10^{-2} M), 10.0s (10^{-2} to $2 \cdot 10^{-3}$ M)

Application 5 and Sensor Type ^{8,9}

Assay of Cl^- activity in biological samples with solvent polymeric membrane electrode based on Chloride ionophore IV.

Recommended Membrane Composition

1.0	wt%	Chloride ionophore IV (92332)
0.6	wt%	Tridodecylmethylammonium chloride (91661)
65.4	wt%	2-Nitrophenyl octyl ether (o-NPOE) (73732)
33.0	wt%	Poly(vinyl chloride) high molecular weight (81392)

Recommended Cell Assembly

Reference || sample solution || liquid membrane | 0.01 M NaCl | AgCl, Ag

⁸ K.P. Xiao, P. Bühlmann, S. Nishizawa, S. Amemiya, Y. Umezawa, A Chloride Ion-Selective Solvent Polymeric Membrane Electrode Based on a Hydrogen Bond Forming Ionophore. **Anal. Chem.** **69**, 1038 (1997).

⁹ P. Bühlmann, S. Nishizawa, K. P. Xiao and Y. Umezawa, Strong Hydrogen Bond-Mediated Complexation of $H_2PO_4^-$ by Neutral Bis-Thiourea Hosts. **Tetrahedron** **53(5)**, 1647 (1997).

Electrode Characteristics and Function

Selectivity coefficients $\log K_{Cl, X}^{Pot}$ as obtained by the matched potential method (0.1 M solutions of the sodium salts, pH 7.0

with 0.1 M HEPES-NaOH).

	Cl ⁻ conc. 10 ^{-5.00} to 10 ^{-4.70} M	Cl ⁻ conc. 10 ^{-2.34} to 10 ^{-2.04} M
$\log K_{Cl, Salicylate}^{Pot}$	0.7	1.8
$\log K_{Cl, SCN}^{Pot}$	1.0	1.6
$\log K_{Cl, NO_3}^{Pot}$	0.2	0.7
$\log K_{Cl, I}^{Pot}$	-0.2	0.5
$\log K_{Cl, Br}^{Pot}$	0.2	0.4
$\log K_{Cl, SO_4}^{Pot}$	-1.2	n.d.
$\log K_{Cl, HSO_3 / SO_3}^{Pot}$	-2.0	n.d.
$\log K_{Cl, Acetate}^{Pot}$	-2.3	n.d.
$\log K_{Cl, HCO_3}^{Pot}$	-2.6	n.d.
$\log K_{Cl, H_2 PO_4 / HPO_4}^{Pot}$	<-3.5	n.d.

Slope of linear regression: -54,0 mV (10⁻⁵ to 10⁻² M NaCl).
 Detection limit: $6.5 \pm 3.0 \cdot 10^{-6}$ M

Microelectrodes

Application 1 and Sensor Type^{general 10, application 11}

Assay of Cl⁻ in intracellular liquids with Cl⁻-selective microelectrodes based on Chloride ionophore I.

Chloride ionophore I-Cocktail A ([24902](#))

Cocktail Composition

5.00	wt%	Chloride ionophore I (24897)
4.00	wt%	1-Decanol (30608)
1.00	wt%	Tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) (87255)
90.00	wt%	2-Nitrophenyl octyl ether (73732)

Electrode Characteristics and Function

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

$\log K_{Cl, HCO_3}^{Pot}$	-1.5	$\log K_{Cl, SCN}^{Pot}$	3.4
$\log K_{Cl, Acetate}^{Pot}$	-1.3	$\log K_{Cl, Salicylate}^{Pot}$	3.0
$\log K_{Cl, SO_4}^{Pot}$	-2.6		

Slope of linear regression: 57.5 ± 0.5 mV (10^{-3} to $3 \cdot 10^{-1}$ M NaCl in 0.01 M TRIS/H₂SO₄, pH 7.4)
 Electrical resistance, tip diameter ~1 µm: ~70 MΩ

Application 2 and Sensor Type^{12, 13}

Intracellular measurements of Cl⁻ activity without interferences from alkali metal cations. This microelectrode based on Chloride-selective liquid ion-exchanger microelectrode-Cocktail A is also insensitive to changes of pH in the range 4-9.

Chloride-selective liquid ion-exchanger microelectrode-Cocktail A ([24899](#))

Cocktail Composition

10.00	wt%	Trioctylpropylammonium chloride
90.00	wt%	1,2-Dimethyl-3-nitrobenzene (40870)

Electrode Characteristics and Function

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

$\log K_{Cl, HCO_3}^{Pot}$	-1.4	$\log K_{Cl, Methylsulfonate}^{Pot}$	-0.7
$\log K_{Cl, HPO_4}^{Pot}$	-1.0	$\log K_{Cl, Propionate}^{Pot}$	-0.3
$\log K_{Cl, Acetate}^{Pot}$	-0.5		

Slope of linear regression: < 50 mV (10^{-3} to $2 \cdot 10^{-1}$ M KCl)
 Response time: <200ms
 Drift: <1mV/h

¹⁰ M. Huser, W.E. Morf, K. Fluri, K. Seiler, P. Schulthess, W. Simon, Transport Properties of Anion-Selective Membranes Based on Cobyrinates and Metalloporphyrin Complexes as Ionophores. *Helv. Chim. Acta* **73**, 1481 (1990).

¹¹ Y. Kondo, T. Bühner, K. Seiler, E. Frömter, W. Simon, A new double-barrelled, ionophore-based microelectrode for chloride ions. *Pflügers Arch.* **414**, 663 (1989).

¹² R.N. Khuri, S.K. Agulian, K. Bogharian, Electrochemical potentials of chloride in distal renal tubule of the rat. *Am. J. Physiol.* **227**, 1352 (1974).

¹³ C.M. Baumgarten, An improved liquid ion exchanger for chloride ion-selective microelectrodes. *Am. J. Physiol.* **241**, C258 (1981).

Ion-selective Field Effect Transistors

Application 1 and Sensor Type ^{14,15}

Determination of chloride with a chloride selective field-effect transistor (ISFET). The gate membrane is based on an "Urushi" matrix with good durability.

Recommended Membrane Composition

50.00 wt% Tridodecylmethylammonium chloride ([91661](#))
 50.00 wt% Urushi latex

Electrode Characteristics

Selectivity coefficients $\log K_{Cl, X}^{Pot}$

$\log K_{Cl, HCO_3}^{Pot}$	-1.6	$\log K_{Cl, Br}^{Pot}$	0.2
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$\log K_{Cl, HPO_4}^{Pot}$	-1.6	$\log K_{Cl, SCN}^{Pot}$	2.2
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$\log K_{Cl, SO_4}^{Pot}$	-1.2		
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Slope of linear regression: -51 mV (1M to 10⁻⁴ M Cl⁻)

¹⁴ S. Wakida, M. Yamane, K. Higashi, K., Hiroy, Y. Ujihira, Urushi matrix sodium, potassium, calcium and chloride-selective field-effect transistors. **Sensors and Actuators B1**, 412 (1990).

¹⁵ S. Wakida, M. Yamane, K. Hiroy, A novel Urushi matrix chloride ion-selective field effect transistor. **Talanta** **35**, 326 (1988).

Optical Transduction

Application and Sensor Type ^{16, 17}

Optical sensing membrane for the determination of chloride serum.

Recommended Membrane Composition

2.35	wt%	Chromoionophore VI (ETH 7075) (27095)
3.15	wt%	Fehler! Verweisquelle konnte nicht gefunden werden. (TOTCI)
63.00	wt%	Bis(1-butylpentyl) adipate (02150)
31.50	wt%	Poly(vinyl chloride) high molecular weight (81392)

Absorbance Maxima of Chromoionophore VI in polymeric optode membranes:

$$\lambda_{\text{deprot}}^{\text{max}} : 530 \text{ nm}$$

Optode Characteristics

Selectivity coefficients $\log K_{\text{Cl, X}}^{\text{Opt}}$ as obtained by the fixed interference method (pH-buffered solutions).

$\log K_{\text{Cl, SO}_4}^{\text{Opt}}$	-2.8	$\log K_{\text{Cl, I}}^{\text{Opt}}$	1.0
$\log K_{\text{Cl, Br}}^{\text{Opt}}$	0.3	$\log K_{\text{Cl, ClO}_4}^{\text{Opt}}$	-0.7
$\log K_{\text{Cl, NO}_3}^{\text{Opt}}$	-1.8	$\log K_{\text{Cl, SCN}}^{\text{Opt}}$	1.1

Measuring range: 10^{-5} to 10^{-1} M at pH 3.6 (0.1 M HCOOH/HCOOK)

¹⁶ .S.S. Tan, P.C. Hauser, K. Wang, K. Fluri, K. Seiler, B. Rusterholz, G. Suter, M. Krüttli, U.E. Spichiger, W. Simon, Reversible optical sensing membrane for the determination of chloride in serum . *Anal. Chim. Acta* **255**, 35 (1991).

¹⁷ U.E. Spichiger, D. Freiner, E. Bakker, T. Rosatzin, W. Simon, Optodes in clinical chemistry: potential and limitations. *Sens. Actuators B* **11**, 263 (1993).