

Table 1 : Electrochemical sensors based on ion transfer at the ITIES

| Target Analyte | Ionophore | Aqueous electrolyte solution | Organic electrolyte solution | Interface type | Detection method | Sensitivity | Limit of detection | Ref. |
|---|-----------------------|--|--|---|------------------|--------------------------|--|------|
| Propranolol | No | Artificial serum | 10 mM BTPPA ⁺ TPBCL ⁻ in PVC-gel (1,6-DCH) | μITIES array 8 pores (∅ 52 μm, S = 500 μm) silicon membrane | DPSV | 0.09 nA μM ⁻¹ | 0.05 μM | 1 |
| Myoglobin | Anionic surfactants | 0.1 M KCl 3.0 < pH < 7.1 | 20 mM TPnA ⁺ TPB ⁻ in 1,2-DCE + ionophore | Single ITIES (∅ 0.2 mm) | DPV | xx | 3 μM | 2 |
| K ⁺ , Na ⁺ , Ca ²⁺ | Commercial ionophores | 0.1 M NaCl or 0.1 M KCl or 0.1 M CaCl ₂ . | Gel containing TBA ⁺ TPB ⁻ , PVC, ionophore, TCNQ | Single ITIES formed at a 1.5 or 3 mm ∅ GC electrode | CV | xx | xx | 3 |
| Cd ²⁺ | 1,10-phenanthroline | Li ₂ SO ₄ | TDA ⁺ TPBCL ⁻ in 1,2-DCE + ionophore | Single μITIES (∅ 25 μm) | CV | xx | xx | 4 |
| Dopamine, noradrenaline | DB18C6 | 1 mM HCl | 10 mM BTPPA ⁺ TPBCL ⁻ in 1,2-DCE + ionophore | μITIES array 66 pores (∅ 10 μm, S = 100 μm) PET membrane | CV | xx | xx | 5 |
| Protein digest | No | 10 mM HCl | 10 mM BTPPA ⁺ TPBCL ⁻ in PVC-gel (1,6-DCH) | μITIES array 8 pores (∅ 52 μm, S = 500 μm) silicon membrane | DPSV | xx | 3 μM (concentration of proteins before digest) | 6 |
| Ca ²⁺ | Calcium ionophore IV | 10 mM KCl | Dodecyl 2-nitrophenylether, TDA ⁺ TPBCL ⁻ , ionophore + K ⁺ TPFB ⁻ + THF | Thin layer ion selective coulometric system | Coulometry | 0.868 C / M | 10 μM | 7 |
| Ca ²⁺ | Calcium ionophore IV | 10 mM KCl | Dodecyl 2-nitrophenylether, TDA ⁺ TPBCL ⁻ , | Hollow fiber cell | Coulometry | 29.3 C / M | 10 μM | 8 |

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|--|---|---|--|---|------------------|-------------------------------|--------------------|------|
| | | | ionophore + K ⁺ TPFB ⁻ + THF | | | | | |
| H ⁺ | Hydrogen ionophore IV | 10 mM NaCl | 3 % PVC NPOE + ionophore + TBA ⁺ TPBCL ⁻ | Single μ ITIES (elliptic hole 20.2 μm by 110 μm) | DPSV | XX | XX | 9 |
| Sr ²⁺ | CMPO | 2 mM TMA(NO ₃) | P ₆₆₆₁₄ TPBCL ⁻ (RTIL) | Single μITIES (∅ 25 μm) | CV | XX | XX | 10 |
| Parathion, methyl parathion | Hydrogen ionophore IV | 10 mM LiCl + organophosphorus hydrolase | 3 % PVC NPOE + ionophore + TBA ⁺ TPBCL ⁻ | Single μ ITIES (elliptic hole 20.2 μm by 110 μm) | DPSV | XX | 0.5 μM | 11 |
| Ca ²⁺ | Calcium ionophore IV | 10 mM KCl | Dodecyl 2-nitrophenylether, TDA ⁺ TPBCL ⁻ , ionophore + K ⁺ TPFB ⁻ + THF | Hollow fiber cell | Coulometry | XX Selectivity improvement | XX | 12 |
| Ag ⁺ , K ⁺ , Ca ²⁺ , Ba ²⁺ | Calixarenes, vanilomycin, + another one | Chloride and sulfate salts | (a) 0.1 M TDA ⁺ TFAB ⁻ (NPOE-PVC) + ionophore (b) 0.1 M TDA ⁺ TFAB ⁻ (DCE) + ionophore | (a) Au or GC electrode (5 mm) – PEDOT-C14 (b) single ITIES (∅ 5 μm pipette) | CV | XX | XX | 13 |
| Paraoxon | Hydrogen ionophore IV | 10 mM NaCl | 3 % PVC NPOE + ionophore + TBA ⁺ TPBCL ⁻ | Single μ ITIES (elliptic hole 20.2 μm by 110 μm) | DPSV | XX | 0.5 μM | 14 |
| Lysozyme | No | 10 mM HCl | 10 mM BTPPA ⁺ TPBCL ⁻ in PVC-gel (1,6-DCH) | μITIES array 30 pores (∅ 22 μm, S = 200 μm) silicon membrane | AdDPSV | 4.31 nA μM ⁻¹ | 0.03 μM | 15 |
| Propranolol | α ₁ -acid- | 10 mM LiCl + x | 10 mM BTPPA ⁺ | Single μITIES (∅ 10 μm) | DPV, CV | XX | XX | 16 |

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|-------------------------------|--------------|--|--|---|------------------|---|---------------------------|------|
| | glycoprotein | μM Phosphate buffer | TPBCl ⁻ in 1,2-DCE | pipette) | | | | |
| Poly-L-Lysine dendrigrafts | No | 10 mM HCl | 10 mM BTPPA ⁺ TPBCl ⁻ in 1,2-DCE | Single ITIES (\varnothing 1 cm) | CV | 1.84 – 25.8 $\mu\text{A } \mu\text{M}^{-1}$ | 0.65– 11.10 μM | 17 |
| Myoglobin | No | 10 mM HCl or 1-100 mM LiCl | 10 mM BTPPA ⁺ TPBCl ⁻ in PVC-gel (1,6-DCH) | μITIES array 8 pores (\varnothing 12.8 μm , S = 400 μm) silicon membrane | CV | XX | 1 μM | 18 |
| Heparin | No | 10 mM LiCl or NaCl | TDMA ⁺ TFPB ⁻ (RTIL) | PVDF microporous filter (A = 0.07 cm ²) | CV | XX | 0.1 U mL ⁻¹ | 19 |
| Er(III) | HDB | 0.1 M MgCl ₂ | Graphite powder, 5 % MWCNT, [OMIM] ⁺ BF ₄ ⁻ , ionophore, TCNQ | Composite carbon electrode | DPV | 19.9 mV per decade | 0.5 μM | 20 |
| Cr(VI) | Aliquat 336 | 10 mM K ₂ SO ₄ | 3 % PVC NPOE + ionophore + 10 mM TOA ⁺ TFAB ⁻ | μITIES array 66 pores (\varnothing 10 μm , S = 100 μm) PET membrane | DPSV | 1.37 nA μM^{-1} | 0.5 μM | 21 |
| Rb ⁺ | CMPO | 5 mM Rb(NO ₃) | P ₆₆₆₁₄ TPBCl ⁻ (RTIL) | Single μITIES (\varnothing 25 μm) | CV | XX | XX | 22 |
| Albumin | DNNS | 0.1 M KCl (pH 3.4) | 20 mM TPnA ⁺ TPB ⁻ in 1,2-DCE + ionophore | Porous membrane supported interface | CA (FIA) | 1.8 C M ⁻¹ | 1.2 μM | 23 |
| Creatinine | No | 0.05 M MgCl ₂ + H ₂ SO ₄ (pH 2.2) | 20 mM TPnA ⁺ TPB ⁻ in NB | Dialysis membrane supported interface | CA (FIA) | 0.648 $\mu\text{A } \text{mM}^{-1}$ | 210 μM | 24 |
| NH ₄ ⁺ | Cyclodextrin | 1 mM HCl | 1 mM BTPPA ⁺ TPBCl ⁻ in 1,6-DCH | μITIES array 66 pores (\varnothing 10 μm , S = 100 μm) PET membrane | dSWV | 1.01 nA μM^{-1} | 0.12 μM | 25 |
| ClO ₄ ⁻ | No | 10 mM NaCl | 3 % PVC NPOE + 10 mM TOA ⁺ TFAB ⁻ | μITIES array 66 pores (\varnothing 10 μm , S = 100 μm) PET membrane | DPSV | 1.32 nA μM^{-1} | 0.1 μM | 26 |

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| NO ₃ ⁻ | TDMA ⁺ | 1 mM NaCl | TDA ⁺ TPBCL ⁻ , ionophore + THF + DOS | Thin layer ion selective coulometric system | Coulometry | 3.6 C M ⁻¹ | 1.1 μM | 27 |
| K ⁺ | Valinomycin | 0.1 mM NaI | Dodecyl 2-nitrophenylether, TDA ⁺ TPBCL ⁻ , ionophore + KTPBCL + THF + PVC | Thin layer ion selective coulometric system | Coulometry | 1.18 C M ⁻¹ | 0.1 μM | 28 |
| K ⁺ , NH ₄ ⁺ | Valinomycin | K ₂ SO ₄ , 0.5 mM H ₂ SO ₄ , 0.1 mM HCl | 0.1 M TDA ⁺ TFAB ⁻ (NPOE-PVC) + ionophore | Rotating Au electrode (5 mm) – PEDOT-C14 | DPSV | 21.2 nA nM ⁻¹ (K ⁺) | 0.6 nM (K ⁺) | 29 |
| Amylin | No | 10 mM HCl or 1 mM PBS | 10 mM BTPPA ⁺ TPBCL ⁻ in PVC-gel (1,6-DCH) | μITIES array 30 pores (∅ 22 μm, S = 200 μm) silicon membrane | CV | 0.13 nA μM ⁻¹ | 2 μM | 30 |
| Insulin | No | 10 mM HCl | 10 mM BTPPA ⁺ TPBCL ⁻ in PVC-gel (1,6-DCH) | μITIES array 30 pores (∅ 22 μm, S = 200 μm) silicon membrane | AdSV | XX | 1 μM | 31 |
| Haemoglobin | No | 10 mM HCl | 10 mM BTPPA ⁺ TPBCL ⁻ in PVC-gel (1,6-DCH) | μITIES array 30 pores (∅ 22 μm, S = 200 μm) silicon membrane | AdSV | 7.46 nA μM ⁻¹ | 48 nM | 32 |
| K ⁺ , Na ⁺ , Ca ²⁺ | Commercial ionophores | Sea water and drink sample, plasma and whole blood | Gel containing TBA ⁺ TPB ⁻ , PVC, ionophore, TCNQ | Screen-printed electrode modified with a gel | CV | xx | xx | 33 |
| Daunorubicin | No | Buffered solution (2 < pH < 12) | 1 mM BTPPA ⁺ TPBCL ⁻ in 1,6-DCH | μITIES array 66 pores (∅ 10 μm, S = 100 μm) PET membrane | DPV | 0.019 nA μM ⁻¹ | 0.8 μM | 34 |
| Dopamine, | DB18C6 | 1 mM HCl (pH 3) | 1 mM BTPPA ⁺ | μITIES array 66 pores | SWV | 0.199 nA μM ⁻¹ | 0.35 μM | 35 |

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|--|--|--|--|--|------------------|--|--|------|
| Noradrenaline | | | TPBCl ⁻ , 10 mM DB18C6 in 1,6-DCH | (\varnothing 10 μ m, S = 100 μ m) PET membrane | | (Dopamine) 0.04 nA μ M ⁻¹ (Noradrenaline) | (Dopamine) 1.7 μ M (Noradrenaline) | |
| K ⁺ , Na ⁺ | DB18C6 derivative (K ⁺), B15C5 derivative (Na ⁺) | KCl and NaCl solutions | 2 mM BTPPA ⁺ TPBCl ⁻ , ionophore in 1,2-DCE | Single μ TIES (\varnothing 28-34 μ m) | CV | XX | XX | 36 |
| ClO ₄ ⁻ | Ni(DBM) ₂ | 10 mM NaCl + River water | 3 % PVC NPOE + 10 mM TOA ⁺ TFAB ⁻ | μ TIES array 66 pores (\varnothing 10 μ m, S = 100 μ m) PET membrane | DPSV | 0.21 nA ppm ⁻¹ | 10 ppb | 37 |
| Myoglobin, haemoglobin | AOT ⁻ | 10 mM HCl | 10 mM BTPPA ⁺ TPBCl ⁻ or 10 mM Na ⁺ AOT ⁻ in PVC-gel (1,6-DCH) | μ TIES array 8 pores (\varnothing 12.8 μ m, S = 400 μ m) silicon membrane | CV | XX | XX | 38 |
| Cs ⁺ | CMPO | 5 mM CsNO ₃ | CPMO + P ₆₆₆₁₄ TPBCl ⁻ (RTIL) | Single μ TIES (\varnothing 25 μ m) | CV | XX | XX | 39 |
| Cd ²⁺ | 8-HQ | 10 mM LiCl | 5 mM THA ⁺ TPBCl ⁻ 50 mM 8-HQ in 1,2-DCE | μ TIES array (1-256 pores, \varnothing 50 μ m, S = 500 μ m) | SWV | 0.046 nA ppb ⁻¹ | 11 ppb | 40 |
| Cd ²⁺ , Zn ²⁺ , Pb ²⁺ | 8-HQ | 10 mM LiCl | 5 mM THA ⁺ TPBCl ⁻ 50 mM 8-HQ in 1,2-DCE | μ TIES array (1-256 pores, \varnothing 50 μ m, S = 500 μ m) | SWV | XX | 0.2 ppm (Pb ²⁺) | 41 |
| Perfluoroalkanesulfonate, Perfluoroalkane carbonate, | No | 1 M Li ₂ SO ₄ , 0.1 mM KCl | 0.1 M TDA ⁺ TFAB ⁻ , NPOE-PVC | Au electrode (5 mm) – POT | LSSV | XX | 50 pM | 42 |
| Heparin | DNNS-TDA ⁺ | Human blood | Ionophore + | Thin layer ion selective | Coulometry | XX | XX | 43 |

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|--------------------------------------|----------------------|------------------------------------|--|--|------------------|---|--|------|
| | | | NPOE | coulometric system | | | | |
| Ca ²⁺ | Calcium ionophore II | 10 mM CH ₃ COOK | 0.1 M TDA ⁺ TFAB ⁻ , NPOE-PVC | Rotating Au electrode (5 mm) – PEDOT | LSSV | 430 A M ⁻¹ | 0.1 nM | 44 |
| Propranolol | No | Artificial biological fluid | 10 mM BTPPA ⁺ TPBCl ⁻ in PVC-gel (1,6-DCH) | μITIES array (52 pores, Ø 55 μm, S = 1000 μm) | DPSV | 43 nA μM ⁻¹ | 50 nM | 45 |
| Ractopamine | No | 10 mM LiCl | 10 mM BTPPA ⁺ TPBCl ⁻ in PVC-gel (1,6-DCH) | μITIES array 8 pores (Ø 22.2 μm, S = 200 μm) silicon membrane | LSSV | 0.272 nA μM ⁻¹ | 0.1 μM | 46 |
| Propranolol | No | 10 mM LiCl | 10 mM BTPPA ⁺ TPBCl ⁻ in 1,6-DCH | nanolITIES array 400 pores (Ø 100 nm or 34 nm, S = 10 times the diameter) silicon nitride membrane | CV | 0.0018 nA μM ⁻¹ (Ø 34 nm) 0.0011 nA μM ⁻¹ (Ø 100 nm) | 0.8 nM | 47 |
| Acetylcholine, tryptamine, serotonin | No | Artificial seawater | 5 mM TDA ⁺ TFAB ⁻ in 1,2DCE | Single nanolITIES (Ø 19-35 nm)) | CV | XX | 205 μM (Acetylcholine), 86 μM Tryptamine | 48 |
| Topotecan | No | 10 mM Tris acetic acid buffer pH 4 | 10 mM TOA ⁺ TFAB ⁻ in PVC-NPOE | Single μITIES (Elliptical microhole 38 × 23 μm) | DPSV | 0.012 nA μM ⁻¹ | 0.1 μM | 49 |

List of abbreviations.

Ionophore: DB18C6: dibenzo-18-crown-6; Calcium ionophore IV: *N,N*-Dicyclohexyl-*N',N'*-dioctadecyl-3-oxapentanediamide; Hydrogen ionophore IV: Octadecyl isonicotinate; CMPO: octyl-(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine; HDB: *N'*-(2-hydroxy-1,2-diphenylethylidene); Aliquat 336: tricaprylmethylammonium chloride; DNNS: dinonylnaphthalenesulfonate; TDMA⁺: tridodecylmethylammonium; B15C5: benzo-15-crown-5; Ni(DBM)₂: bis(dibenzoylmethanato)Ni(II); AOT⁻: 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate; 8-HQ: 8-hydroxyquinolinol; TDA⁺: tetradodecylammonium; Calcium ionophore II: *N,N,N',N'*-Tetra[cyclohexyl]diglycolic acid diamide. **Aqueous electrolyte solution:** PBS: Phosphate buffer saline. **Organic electrolyte solution:** BTPPA⁺: Bis(triphenylphosphoranylidene)ammonium; TPBCl⁻: tetrakis(4-chlorophenyl)borate; PVC: poly(vinyl chloride); 1,6-DCH: 1,6-dichlorohexane; TPnA⁺: tetrapentylammonium; TPB⁻: tetrphenylborate; 1,2-DCE: 1,2-dichloroethane; TBA⁺: tetrabutylammonium; TCNQ: 7,7,8,8-tetracyanoquinodimethane; TPFB⁻: tetrakis[3,4-bis(trifluoromethyl)phenyl]borate; THF: tetrahydrofuran; NPOE: *o*-nitrophenyloctylether; P₆₆₆₁₄: trihexyltetradecylphosphonium; TFAB⁻: tetrakis(pentafluorophenyl)borate; MWCNT:

multiwalled carbon nanotubes; [OMIM]⁺: 1-octyl-3-methylimidazolium; TOA⁺: tetraoctylammonium; DOS: [bis(3-ethyl-hexyl)sebacate]; THA⁺: tetrahexylammonium; Interface type: μ TIES: micro-interface between two immiscible electrolyte solutions; S: spacing; GC: glassy carbon; PET: polyethylene terephthalate; PEDOT: poly(2-*n*-tetradecyl-2,3-dihydro-thieno[3,4-*b*][1,4]dioxin); PVDF: polyvinylidene fluoride; POT: poly(octylthiophene); **Detection method:** DPSV: Differential pulse stripping voltammetry; DPV: Differential pulse voltammetry; CV: cyclic voltammetry; AdDPSV: Adsorptive differential pulse stripping voltammetry; CA: Chronoamperometry; FIA: Flow injection analysis; dSWV: numerical derivative square wave voltammetry; AdSV: Adsorptive stripping voltammetry; SWV: Square wave voltammetry; LSSV: Linear sweep stripping voltammetry.

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