# Simulation of standard addition method for Ca$^{2+}$ determination by ion-selective electrode

including effect of interferences, perturbation of activity coefficient by standard addition, and voltage reading error

**Boldface numbers are user-changable inputs**

|  | type value here |  | variable name |
|---|---|---|---|
| Reference potential | **1.00** volts | | Eo |
| Actual Nernst factor | **0.0591** volts | | nf |
| Assumed Nernst factor | **0.0591** volts | | nfa |
| Ion charge (n) | **2** | | n |
| [Ca$^{2+}$] in standard | **0.020** Moles/Liter | | Cs |
| vol. standard added | **2.00** mL | | Vs |
| [Ca$^{2+}$] in unknown | **0.00010** Moles/Liter | | Cx |
| Sample volume | **25.00** mL | | Vx |
| NaCl TISB conc | **0.040** Moles/Liter | | Cse |
| voltage reading error | **0.0005** volts | | ve |

| mL standard added | mmoles Ca$^{2+}$ | volume (mL) | total [Ca$^{2+}$] | Activity of Ca$^{2+}$ |
|---|---|---|---|---|
| 0.00 | =Cx*Vx+Cs*A17 | =Vx+A17 | =B17/C17 | =F27*D17 |
| =A17+Vs | =Cx*Vx+Cs*A18 | =Vx+A18 | =B18/C18 | =F28*D18 |

| [Ca$^{2+}$] by standard addition | ionic strength error (%) | measurement error (%) |
|---|---|---|
| =Cs*Vs/((Vx+Vs)*10^((-n)*deltaE/nfa)-Vx) | =100*(A22-Cx)/Cx | =100*(B22-A22)/A22 |

**Debye-Huckel calculation of activity coefficient of Ca$^{2+}$, in water at 25 C**

| A | B | bm for Ca$^{2+}$ | Ionic strength (I) | log (f) |
|---|---|---|---|---|
| 0.5085 | 32810000.00 | 6.00E-08 | =Cse+3*D17 | =((-A)*n*n*SQRT(I))/(1+B*bm*SQRT(I)) |
| | | after addition= | =Cse+3*D18 | =((-A)*n*n*SQRT(D28))/(1+B*bm*SQRT(D28)) |

Effect of ion interferences from impurities in commercial NaCl ionic strength buffer solution

| Ion | Atomic weight | selectivity constant * | charge | ug/mL in solution ** |
|---|---|---|---|---|
| $H^+$ | 1.008 | 10000000.00 | 1 | |
| $Zn^{2+}$ | 65.39 | 3.20 | 2 | 0.00E+00 |
| $Fe^{2+}$ | 55.85 | 0.80 | 2 | 0.00E+00 |
| $Pb^{2+}$ | 207.20 | 0.60 | 2 | 0.00E+00 |
| $Cu^{2+}$ | 63.55 | 0.30 | 2 | 2.00E-02 |
| $Ni^{2+}$ | 58.70 | 0.08 | 2 | 0.00E+00 |
| $Sr^{2+}$ | 87.62 | 0.02 | 2 | 0.00E+00 |
| $Mg^{2+}$ | 24.30 | 0.01 | 2 | 2.00E+01 |
| $Ba^{2+}$ | 137.30 | 0.01 | 2 | 0.00E+00 |
| $Na^+$ | 22.99 | 0.00 | 1 | 1.00E+02 |

* from the electrode's spec sheet

** from the reagent label

| voltage | deltaE | reading error |
|---|---|---|
| =Eo+(nf/n)*LOG10(E17+$H$50) | | |
| =Eo+(nf/n)*LOG10(E18+$H$50) | =(-F18)+$F$17 | =deltaE+ve |

**% total error**
###

| | f |
|---|---|
| | =10^E27 |
| | =10^E28 |

| M in solution | activity in solution | aa=activity equivalence |
|---|---|---|
| 1.00E-07 | =$F$27*F40 | =C40*G40^(n/D40) |
| =E41*0.001/B40 | =$F$27*F41 | =C41*G41^(n/D41) |
| =E42*0.001/B41 | =$F$27*F42 | =C42*G42^(n/D42) |
| =E43*0.001/B42 | =$F$27*F43 | =C43*G43^(n/D43) |
| =E44*0.001/B43 | =$F$27*F44 | =C44*G44^(n/D44) |
| =E45*0.001/B44 | =$F$27*F45 | =C45*G45^(n/D45) |
| =E46*0.001/B45 | =$F$27*F46 | =C46*G46^(n/D46) |
| =E47*0.001/B46 | =$F$27*F47 | =C47*G47^(n/D47) |
| =E48*0.001/B47 | =$F$27*F48 | =C48*G48^(n/D48) |
| =Cse+E49*0.001/B48 | =$F$27*F49 | =C49*G49^(n/D49) |
| | | =SUM(H40:H49) sum |