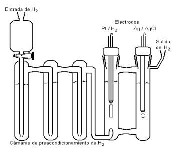
Uncertainty
in pH MEASUREMENT

Celda de vidrio tipo Harned



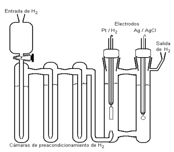
1

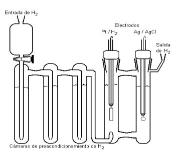
2

3

9 cells
HCl 0,01 m
T, P, mV

$\boldsymbol{m}$ 0.005





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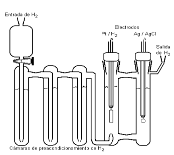
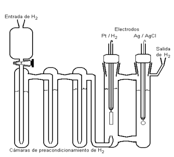


4, 5, 6 $\boldsymbol{m}$ 0.010

....



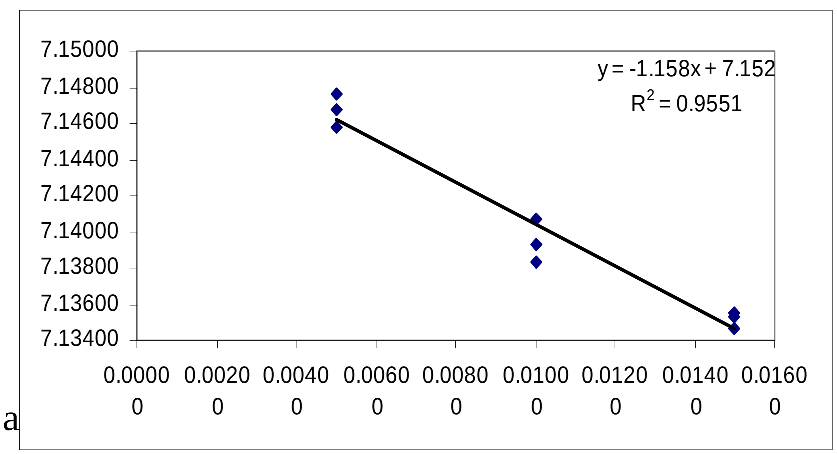
7, 8, 9 $\boldsymbol{m}$ 0.015

$$E°_{Ag/AgCl} = \frac{E}{1000} + \left(\frac{2 \cdot R \cdot T}{F}\right) \cdot \ln(m_{HCl}) + \left[\left(\frac{2 \cdot R \cdot T}{F}\right) \cdot \ln(\gamma_{HCl})\right] \cdot 1000$$

$$p(a_H \gamma_{Cl}) = -\log(m_H \cdot \gamma_H \cdot \gamma_{Cl}) = \left[\frac{F(E - E°_{Ag/AgCl})}{R \cdot T \cdot \ln(10)}\right] + \log(m_{Cl})$$

m_{Cl}	$P(a_H, \gamma_{Cl}) = -\log(m_H, \gamma_H, \gamma_{Cl})$
0,005	---
0,010	---
0,015	---

$$-\log(a_H \gamma_{Cl})_{m \to 0} = -\log a_H - \log(\gamma_{Cl})_{m_{Cl} \to 0} = pH - \log(\gamma_{Cl})_{m_{Cl} \to 0}$$



SIM pH measurement

- **GOAL:** To measure the pH of an unknown sample

- **Step 1. Measure E° for Ag/AgCl electrode in the harned cell using HCl. The value of the HCl concentration was determined by gravimetric-potenciometric titration using Tris(hydroxymethyl)aminomethane.**

$$E^\circ = E_{cell} + 2k\log(m_{HCl}\gamma_{\pm} / m^\circ)$$

$$E^\circ_{Ag/AgCl} = \frac{E}{1000} + \left(\frac{2\cdot R\cdot T}{F}\right)\cdot \ln(m_{HCl}) + \left[\left(\frac{2\cdot R\cdot T}{F}\right)\cdot \ln(\gamma_{HCl})\right]\cdot 1000$$

- **Step 2. Measure E_{cell} for the harner cell for the buffer solution with unknown pH, using 0,005, 0,010 y 0,015 m added NaCl.**

- **Step 3. Extrapolation of the acidity function to m_{NaCl}=0 to obtain $p(a_H\gamma_{Cl})^\circ$**

- $$p(a_H\gamma_{Cl}) = (E_{cell} - E^\circ)/k + \log(m_{NaCl} / m^\circ$$

$$p(a_H\gamma_{Cl}) = -\log(m_H \cdot \gamma_H \cdot \gamma_{Cl}) = \left[\frac{F(E - E^\circ_{Ag/AgCl})}{R\cdot T\cdot \ln(10)}\right] + \log(m_{Cl})$$

SIM pH measurement

- **Step 4. Use of the Bates-Guggenheim convention:**

$$\log \gamma_{Cl(I)} = -AI^{1/2} / (1 + 1{,}5 I^{1/2})$$

A=	0.5108
I=	0.1000

- **Step 5. Obtain p*a*$_H$ *from the steps 3 and 4*:**

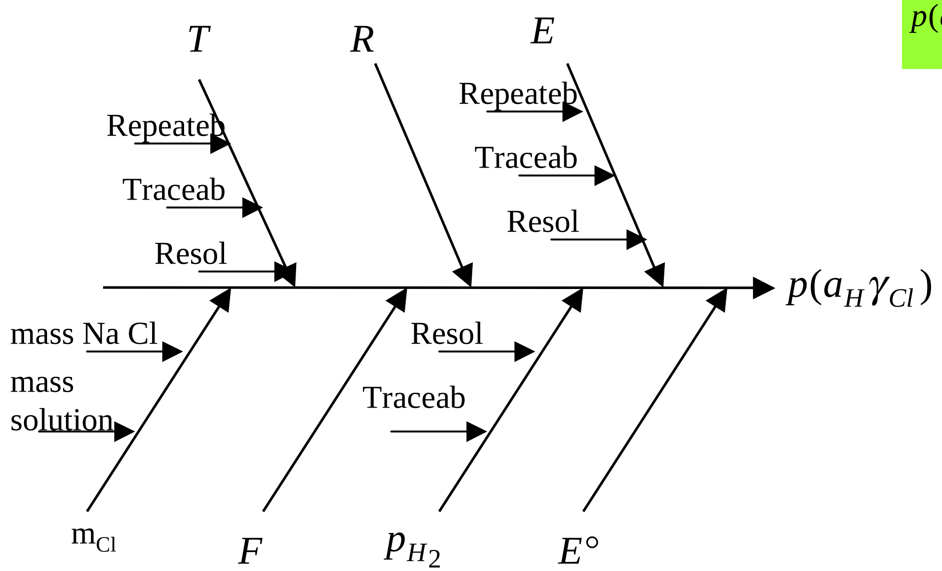
$$pa_H = p(a_H \gamma_{Cl})^{\circ} + \log \gamma_{Cl(I)}$$

$$-log(a_H \gamma_{Cl})_{m \to 0} = log\ a_H - log(\gamma_{Cl})_{m_{Cl \to 0}} = pH - log(\gamma_{Cl})_{m_{Cl \to 0}}$$

Uncertainty contribution in *pH*

Quantity		***u_{st}***	***Sens. Coeff.***	***Contribution***
$p(a_H\gamma Cl)$		0,000220	1	0,000219948
$p(a_H\gamma Cl)°$		0,001025	1	0,001025091
			u_{comb}	0,0010484
		k=2	U	0,002

Uncertainty evaluation in $p(a_H\gamma_{Cl})$



$$p(a_H\gamma_{Cl}) = -\log\left(m_H \cdot \gamma_H \cdot \gamma_{Cl}\right) = \left[\frac{F(E - E°_{Ag/AgCl})}{R \cdot T \cdot \ln(10)}\right] + \log(m_{Cl})$$

$$\frac{\partial p}{\partial E} = \frac{F}{R \cdot T} \cdot \ln(10)$$

$$\frac{\partial p}{\partial E°} = -\frac{F}{R \cdot T} \cdot \ln(10)$$

$$\frac{\partial p}{\partial T} = -\frac{F(E - E°)}{R \cdot T^2 \cdot \ln(10)}$$

$$E = E_{Experimental} + \Delta E$$

$$E = E_{Experimental} + \frac{RT}{2F} \cdot \ln\left[\frac{p°}{p_{H_2}}\right]$$

$$\frac{\partial p}{\partial p_{H_2}} = -\frac{1/2}{p_{H_2}}$$

$$\frac{\partial p}{\partial R} = \frac{2 \cdot T \cdot \ln(10)}{F}\left[\log(m_{HCl}) - 0.25 \cdot \ln(\gamma_{HCl})\right]$$

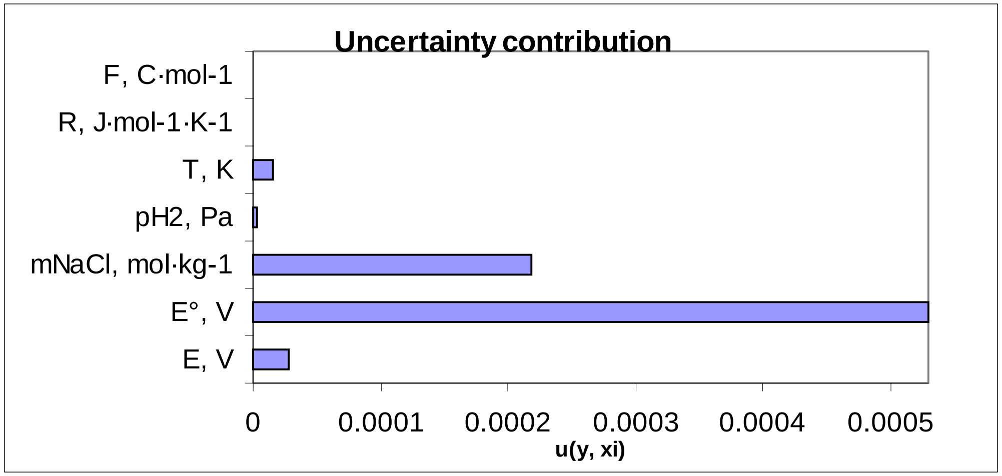
$$\frac{\partial p}{\partial F} = -\frac{2 \cdot R \cdot T \cdot \ln(10)}{F^2}\left[\log(m_{HCl}) - 0.25 \cdot \ln(\gamma_{HCl})\right]$$

$$\frac{\partial p}{\partial m_{NaCl}} = \frac{1}{m_{NaCl} \cdot \ln(10)}$$

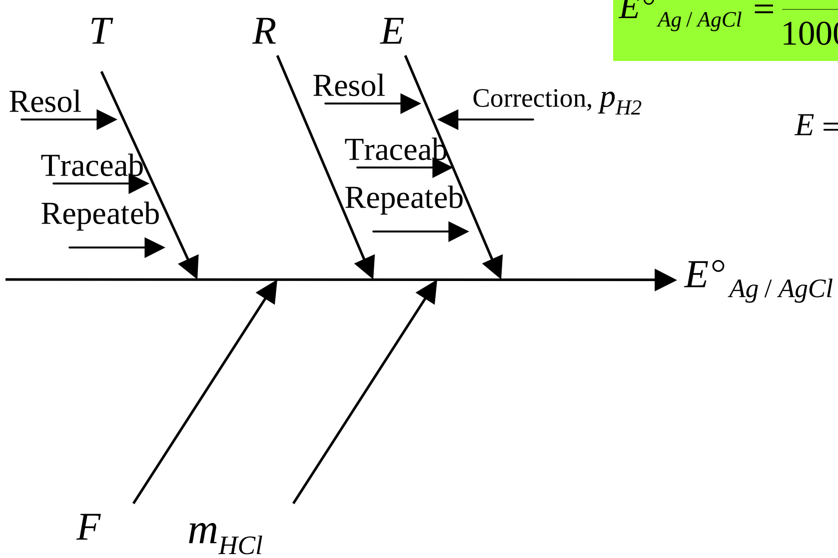
$$u[p(a_H\gamma_{Cl})] = \sqrt{\left[\frac{\partial p}{\partial E}\right]^2 \cdot u^2(E) + \left[\frac{\partial p}{\partial E°}\right]^2 \cdot u^2(E°) + \left[\frac{\partial p}{\partial T}\right]^2 \cdot u^2(T) + \left[\frac{\partial p}{\partial p_{H_2}}\right]^2 \cdot u^2(p_{H_2}) + \left[\frac{\partial p}{\partial R}\right]^2 \cdot u^2(R) + \left[\frac{\partial p}{\partial F}\right]^2 \cdot u^2(F) + \left[\frac{\partial p}{\partial m_{NaCl}}\right]^2 \cdot u^2(m_{NaCl})}$$

Uncertainty contribution in $p(a_H \gamma_{Cl})$

	SUMARY TABLE for ACIDITY FUNCTION at NaCl 0.005*m*							
Quantity	***Description***	***V***	***Units***	***Source of the informat ion***	***u_i***	***Type of distributi on***	***Sensitivity Coefficient***	***Contributi on***
E, V	cell potential	0.7812824	V	Experiment	1.6035E-06	A, normal	16.90381107	2.71051E-05
E°, V	standard poten	0.2223139	V	Experiment	3.135E-05	A, normal	-16.90381107	-5.29935E-04
m_{NaCl}, mol·k	molality of NaC	0.0050348	mol/kg	Exzperimer	2.52348E-06	A, normal	86.25850477	0.000217672
p_{H2}, Pa	hidrogen press	78146.503	Pa	Estimate	0.94648472	B,normal	-2.77872E-06	-2.63002E-06
T, K	Temperature	298.14419	K	Experiment	0.00050332	A, normal	-0.031691708	-1.59511E-05
R, J·mol-1·K-1	Gas constant	8.314472	J/molK	CODATA	1.50E-05	B,normal	-0.02866685	-4.30003E-07
F, C·mol-1	Faraday consta	96485.342	C/mol	CODATA	3.90E-03	B,normal	2.47032E-06	9.63425E-09
							u_{comb}	2.199E-04
							U	4.399E-04



Uncertainty evaluation in $E°_{Ag/AgCl}$



$$E°_{Ag/AgCl} = \frac{E}{1000} + \left(\frac{2\cdot R\cdot T}{F}\right)\cdot \ln(m_{HCl}) + \left[\left(\frac{2\cdot R\cdot T}{F}\right)\cdot \ln(\gamma_{HCl})\right]\cdot 1000$$

$$E = \frac{emf_{i+1} - emf_i}{2} + \frac{R\cdot T}{2F}\cdot \ln\left[\frac{p°}{p_{H_2}}\right]$$

$$\frac{\partial E°}{\partial T} = \frac{R}{F}\left[\frac{1}{2}\cdot \ln\frac{p°}{p_{H_2}} + 2\cdot \ln 10\cdot(\log\gamma_{HCl} + \log m_{HCl})\right]$$

$$\frac{\partial E°}{\partial R} = \frac{T}{F}\left[\frac{1}{2}\cdot \ln\frac{p°}{p_{H_2}} + 2\cdot \ln 10\cdot(\log\gamma_{HCl} + \log m_{HCl})\right]$$

$$\frac{\partial E°}{\partial F} = -\frac{R\cdot T}{F^2}\cdot\left[\frac{1}{2}\cdot \ln\frac{p°}{p_{H_2}} + 2\cdot \ln 10\cdot(\log\gamma_{HCl} + \log m_{HCl})\right]$$

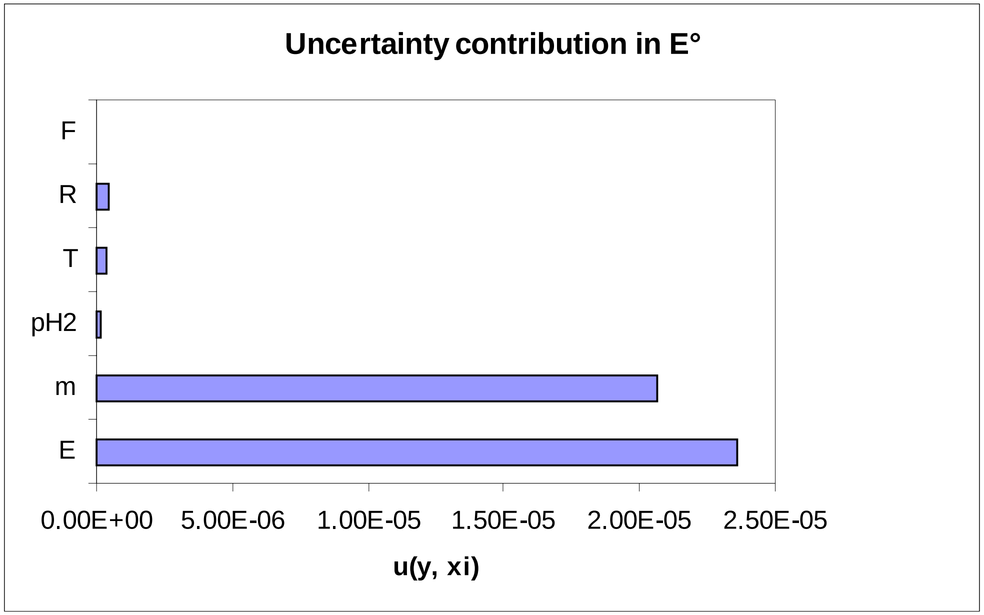
$$\frac{\partial E°}{\partial p_{H_2}} = \frac{R\cdot T}{F^2}\cdot\frac{1}{p_{H_2}}$$

$$\frac{\partial E°}{\partial m_{HCl}} = \frac{2\cdot R\cdot T\cdot}{F}\cdot\frac{\ln 10}{m_{HCl}}$$

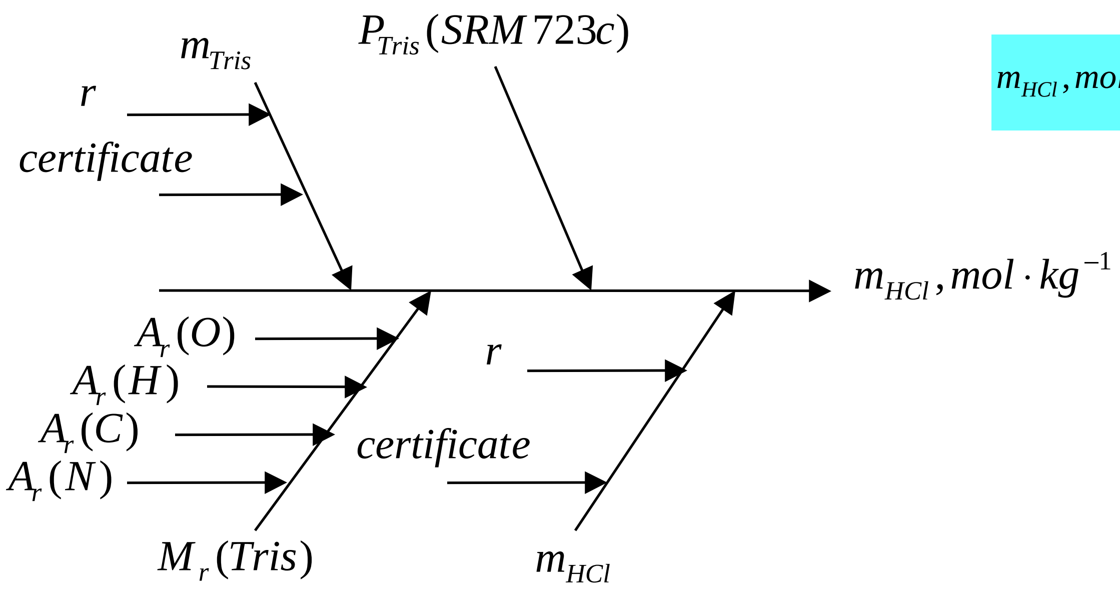
$$u_C(E°) = \sqrt{\left[\frac{\partial E°}{\partial E}\right]^2\cdot u^2(E) + \left[\frac{\partial E°}{\partial R}\right]^2\cdot u^2(R) + \left[\frac{\partial E°}{\partial T}\right]^2\cdot u^2(T) + \left[\frac{\partial E°}{\partial F}\right]^2\cdot u^2(F) + \left[\frac{\partial E°}{\partial m_{HCl}}\right]^2\cdot u^2(m_{HCl})}$$

Uncertainty contribution inE°$_{Ag/AgCl}$

	SUMARY TABLE for E°							
Quantity	***Description***	***V***	***Units***	***Source of the information***	***u_i***	***Type of distribution***	***Sensitivity coefficient***	***Contribution***
E	cell potencial	0.4640653	V	Experiment	2.36E-05	A, normal	1	2.36005E-05
m	molality	0.0100112	mol/kg	Experiment	4.01873E-06	A, normal	5.132696993	2.06269E-05
p_{H2}	hidrogen press	77753.646	Pa	Estimate	0.94648472	B, normal	-1.65216E-07	-1.56374E-07
T	temperature	298.14548	K	Experiment	0.00050332	A,normal	-0.000799441	-4.02376E-07
R	Gas constant	8.314472	J/molK	CODATA	1.50E-05	B, normal	-0.02866685	-4.30003E-07
F	Faraday consta	96485.342	C/mol	CODATA	3.90E-03	B, normal	2.47032E-06	9.63425E-09
							u_i	3.135E-05
							U	6.27E-05



Uncertainty evaluation in m_{HCl}



$$m_{HCl}, mol \cdot kg^{-1} = \frac{m_{Tris} \cdot P_{Tris}}{M_r(Tris) \cdot m_{HCl}} \cdot 1000$$

$$u_1(m) = \sqrt{\left[\frac{u(m_{HCl})}{m_{HCl}}\right]^2 + \left[\frac{u(m_{TRIS})}{m_{TRIS}}\right]^2 + \left[\frac{u(M_{r,TRIS})}{M_{r,TRIS}}\right]^2 + \left[\frac{u(P_{TRIS})}{P_{TRIS}}\right]^2}$$

$$u_C(m) = \sqrt{u_1(m)^2 + \left(\frac{s_m}{\sqrt{15}}\right)^2}$$

Uncertainty contribution in m_{HCl}

	Description	V	Units	Source of the information	u_i	Type of distribution	u_i/V	$(u_i/V)^2$
m	molality	1.00112E-05	mol/kg	experimental measurement	3.2100E-06	A, , normal	3.2064E-01	1.0281E-01
m_{HCl}	Mass of HCl	8.275950667	gr	certificate	7.4330E-05	B, normal	8.9815E-06	8.06671E-11
m_{TRIS}	Mass of TRIS	0.010032333	gr	certificate	2.23607E-06	B, normal	0.000222886	4.96782E-08
P_{TRIS}	Purity of TRIS	0.99901	%	certificate	9.10668E-05	B, normal	9.1157E-05	8.3096E-09
M_r	Molar mass of TRIS	121.13508	g/mol	IUPAC	0.001970431	B, rectangular	1.62664E-05	2.64596E-10
m =	1.0011E-05							
u_C =	3.20996E-06