Chapter 1: Basics

1.1 Concentration Expressions

Normality: Equivalent grams of solute in 1 L of solution.

Its usefulness is limited to the volumetric analysis, since solutions of the same normality react volume to volume.

In order to establish the normality of a solution, it is necessary to know the gram equivalent weight of the dissolved substance, which is - by definition - the weight of the substance that, when reacted, is combined or replaced with 8.000 g of oxygen or 1.008 g of hydrogen.

For substances that react by exchanging ions, the gram equivalent weight of the substance is equal to the formula weight divided by the number of atoms or ions that have been substituted.

In contrast, for oxidizing and reducing compounds, the gram equivalent weight is equal to the formula weight divided by the number of electrons exchanged in their semi-reaction.

1. A 40% by weight H_2SO_4 solution has a density of 1.30 g/mL. Express its concentration in: a) mg/mL; b) molarity; c) normality; d) molality; e) molar fraction, and f) ppm. What volume of this solution will be necessary to prepare 500 mL of a 0.2N solution in sulfuric acid?

a) $$\frac{40\,\text{g } H_2SO_4}{100\,\text{g soln.}} \cdot \frac{1.30\,\text{g soln.}}{1\text{ mL}} \cdot \frac{10^3\,\text{mg} H_2SO_4}{1\,\text{g} H_2SO_4} = 520\text{ mg } H_2SO_4/\text{mL}$$

b) $$\frac{40\,\text{g } H_2SO_4}{100\text{ g soln.}} \frac{1.30\,\text{g soln.}}{1\text{mL soln.}} \frac{10^3\text{mL}}{\text{L}} \frac{1\text{mol } H_2SO_4}{98.09\,\text{g} H_2SO_4} = 5.30\text{ M}$$

c) $$\frac{5.30\text{ mol } H_2SO_4}{\text{L soln.}} \frac{2\,\text{eq}}{1\text{mol } H_2SO_4} = 10.60\,\text{N}$$

d) $$\frac{40\text{ g} H_2SO_4}{60\text{ g solvent}} \frac{10^3\text{ g solvent}}{1\text{Kg solvent}} \frac{1\text{mol } H_2SO_4}{98.09\,\text{g } H_2SO_4} = 6.80\text{ molal}$$

e) $$x = \frac{\dfrac{40}{98.09}\text{mol } H_2SO_4}{\left(\dfrac{40}{98.09} + \dfrac{60}{18.02}\right)\text{mol}_{\text{total}}} = 0.109$$

f) $$\frac{520\text{ mg } H_2SO_4}{\text{mL soln.}} \frac{10^3\text{ µg } H_2SO_4}{1\text{mg } H_2SO_4} \frac{\text{mL soln.}}{1.3\,\text{g soln.}} = 400000\text{ ppm}$$

g) 500mL·0.2N = x mL·10.60N $\Rightarrow$ x = 9.4 mL

2. A 2.70-g sample of metallic aluminum is attacked with 75.0 mL of a 24.7wt% H_2SO_4 solution of 1.18 g/mL density, according to the reaction: $2\ Al + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2$. The resulting solution is diluted to a total volume of 400 mL. Calculate: a) the sulfuric acid normality of this solution; b) the normality of this solution with respect to the aluminum salt it contains; c) the volume of 6.00 N ammonia necessary to neutralize the sulfuric acid present and precipitate the Al^{3+} as $Al(OH)_3$ in 50 mL of the solution.

a) $$75.0\ \text{mL soln.}\frac{1.18\text{g soln.}}{\text{mL soln.}}\frac{24.7\text{g } H_2SO_4}{100\text{g soln.}}\frac{1\text{ mol } H_2SO_4}{98.09\text{ g } H_2SO_4}=0.19\text{ mol } H_2SO_4$$

$$2.7\text{g Al}\cdot\frac{1\text{ mol Al}}{26.98\text{g Al}}\frac{3\text{mol } H_2SO_4}{2\text{mol Al}}=0.15\text{ mol } H_2SO_4\ \text{ consumed}$$

0.19 - 0.15 = 0.04 mol H_2SO_4 remaining free in 0.4 L soln.:

0.04 mol H_2SO_4/ 0.4 L soln. = 0.1 M = 0.2 N H_2SO_4

b) $$\frac{2.7\text{g Al}}{0.4\text{L soln.}}\cdot\frac{1\text{ mol Al}}{26.98\text{ g Al}}\frac{1\text{ mol } Al_2(SO_4)_3}{2\text{ mol Al}}\frac{6\text{eq } Al_2(SO_4)_3}{1\text{mol } Al_2(SO_4)_3}=0.75\text{N } Al_2(SO_4)_3$$

c) 50 mL·0.2 N = x mL·6.0 N $\Rightarrow$ x = 1.66 mL ammonia necessary to neutralize the sulfuric acid present. Besides, the ammonia necessary to precipitate Al^{3+} will be:

50mL · 0.75 N = y mL · 6.0 N $\Rightarrow$ y= 6.25 mL

1.66 mL + 6.25 mL = 7.91 mL_{total} NH_3

3. a) What mass of $KMnO_4$ must be weighed to prepare 500 mL of 0.100 N solution to be used as an oxidant in acidic medium? b) What volume of this solution would be needed to oxidize, in acidic medium, the Fe contained in 10.0 mL of a 0.50wt% solution in Fe^{2+}? c) What would be the normality of that solution if is used as oxidant in basic pH?

a) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$$500\text{mL}\frac{0.\text{meq}}{\text{mL}}\frac{1\text{mmol}}{5\text{ meq}}\frac{158.04\text{ mg } KMnO_4}{1\text{mmol } KMnO_4}=1580.4\text{ mg } KMnO_4 \cong 1.58\text{g } KMnO_4$$

b) $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

$$10\text{ mLsoln.}\frac{0.50\text{ g } Fe^{2+}}{100\text{ mL soln.}}\frac{1\text{eq } Fe^{2+}}{55.85\text{ g } Fe^{2+}}\frac{10^3\text{meq}}{1\text{eq}}=0.895\text{meq } Fe^{2+}$$

meq Fe^{2+} = $MnO_4^{-;}$ 0.895 meq = x mL · 0.1 N $\Rightarrow$ x = 8.95 mL

c) $MnO_4^- + 2H_2 0 + 3e^- \rightarrow \downarrow MnO_2 + 4OH^-$

$$\frac{0.1\,\text{eq KMnO}_4}{\text{L soln.}}\,\frac{3(\text{OH}^-)}{5(\text{H}^+)}=0.060\,\text{N}\,\text{KMnO}_4\text{ when used in alkaline medium}$$

4. When titrating a solution of NaOH with 2N HCl, 25 mL of NaOH consume 31.25 mL of HCl. Calculate the concentration of NaOH in normality and in g/L.

$$31.25\,\text{mL HCl}\frac{2\,\text{meq-g HCl}}{1\,\text{mL HCl}}\,\frac{1\,\text{meq-g NaOH}}{1\,\text{meq-g HCl}}\,\frac{1}{25\,\text{mL NaOH}}=\frac{2.5\,\text{meq-g NaOH}}{\text{mL NaOH}}=\frac{2.5\,\text{eq}-\text{g NaOH}}{\text{L NaOH}}=2.5\,\text{N}$$

Or, if you prefer: $V_{NaOH}\cdot N_{NaOH} = V_{HCl}\cdot N_{HCl}$

$$25\,\text{mL NaOH}\cdot N_{NaOH}=31.25\,\text{mL HCl}\cdot 2\,\text{N}\Rightarrow N_{NaOH}=2.5\,\text{N}$$

$$\frac{2.5\,\text{eq}-\text{g NaOH}}{\text{L}}\,\frac{40\,\text{g NaOH}}{1\,\text{eq}-\text{g NaOH}}=\frac{100\,\text{g NaOH}}{\text{L NaOH}}$$

The determination of the concentration of the NaOH solution is independent of the acid used. Whatever this is (HCl, H_2SO_4, HNO_3, H_3PO_4, CH_3COOH), if it is exactly 2 N in each case, 31.25 mL will also be consumed, and the concentration found for the NaOH will also be 2.5 N.

$$31.25\,\text{mL H}_2\text{SO}_4\,\frac{2\,\text{meq-g H}_2\text{SO}_4}{1\,\text{mL H}_2\text{SO}_4}\,\frac{1\,\text{meq-g NaOH}}{1\,\text{meq-g H}_2\text{SO}_4}\,\frac{1}{25\,\text{mL NaOH}}=\frac{2.5\,\text{meq-g NaOH}}{\text{mL NaOH}}=2.5\,\text{N}$$

What is the M of $H_2SO_4$2N?

$$\frac{2\,\text{eq-g H}_2\text{SO}_4}{1\text{L H}_2\text{SO}_4}\,\frac{\frac{98}{2}\text{g H}_2\text{SO}_4}{1\,\text{eq-g H}_2\text{SO}_4}\,\frac{1\,\text{mol H}_2\text{SO}_4}{98\,\text{g H}_2\text{SO}_4}=\frac{1\,\text{mol H}_2\text{SO}_4}{1\text{L H}_2\text{SO}_4}=1\text{M}$$

What is the M of H_3PO_4 2N?

$$\frac{2\,\text{eq-gH}_3\text{PO}_4}{1\text{L H}_3\text{PO}_4}\,\frac{\frac{98}{3}\text{gH}_3\text{PO}_4}{1\,\text{eq-gH}_3\text{PO}_4}\,\frac{1\,\text{molH}_3\text{PO}_4}{98\,\text{gH}_3\text{PO}_4}=\frac{0.66\,\text{molH}_3\text{PO}_4}{1\text{L H}_3\text{PO}_4}=0.66\text{M}$$

Had we used molarities to solve this exercise:

$$2\text{ NaOH} + \text{H}_2\text{SO}_4 \leftrightarrows \text{Na}_2\text{SO}_4 + 2\text{ H}_2\text{O}$$

$$31.25\,\text{mL H}_2\text{SO}_4\,\frac{1\,\text{mmol H}_2\text{SO}_4}{1\,\text{mL H}_2\text{SO}_4}\,\frac{2\,\text{mmol NaOH}}{1\,\text{mmol H}_2\text{SO}_4}\,\frac{1}{25\,\text{mL NaOH}}=\frac{2.5\,\text{mmol NaOH}}{1\,\text{mL NaOH}}=2.5\text{M}=2.5\text{N}$$

$$3\text{ NaOH} + \text{H}_3\text{PO}_4 \leftrightarrows \text{Na}_3\text{PO}_4 + 3\text{ H}_2\text{O}$$

$$31.25\,\text{mL H}_3\text{PO}_4\,\frac{0.66\,\text{mmol H}_3\text{PO}_4}{1\,\text{mL H}_3\text{PO}_4}\,\frac{3\,\text{mmol NaOH}}{1\,\text{mmol H}_3\text{PO}_4}\,\frac{1}{25\,\text{mL NaOH}}=\frac{2.5\,\text{mmol NaOH}}{1\,\text{mL NaOH}}=2.5\text{M}=2.5\text{N}$$

5. An impurified sample of Na_2CO_3 weighing 1.5000 g is dissolved in water and titrated with 0.5 N HCl, requiring 9.80 mL of the acid to decolorize phenolphthalein (violet in basic medium, colorless below pH 8) . Calculate the purity of carbonate.

$Na_2CO_3 + HCl \leftrightarrows NaHCO_3 + NaCl$ basic pH (phenolphthalein)

$NaHCO_3 + HCl \leftrightarrows H_2CO_3 + NaCl$ acid pH (methyl orange)

$V_{Na_2CO_3} \cdot N_{Na_2CO_3} = V_{HCl} \cdot N_{HCl}$

When using phenolphthalein as an indicator, the end point will indicate only the first protonation of the carbonate, that is, it only accepts one proton of the acid and the equivalent weight of the carbonate will be its formula weight divided by 1.

$$eq\text{-}g_{Na_2CO_3} = eq\text{-}g_{HCl}$$

$$9.8\,mL\,HCl - \frac{0.5\,meq\text{-}g\,HCl}{1\,mL\ HCl}\,\frac{1\,meq - g_{Na_2CO_3}}{1\,meq - g_{HCl}} = 4.9\,meq\text{-}g_{Na_2CO_3}$$

$$4.9\,meq\text{-}g_{Na_2CO_3} = \frac{mg\,Na_2CO_3}{\dfrac{106\,mg_{Na_2CO_3}}{1\ meq - g_{Na_2CO3}}} \Rightarrow 519.4\,mg_{Na_2CO_3} = 0.5194\,g_{Na_2CO_3}$$

$$\frac{0.5194\,g_{Na_2CO_3}}{1.5000\,g\,sample}\,\frac{100}{100} = 34.63\%\ Na_2CO_3$$

6. What would be the purity of the compound in the previous exercise if the indicator used was Methyl Orange that changes color around pH 3?

When using methyl orange as an indicator, the end point will indicate the total protonation of the carbonate, that is, it accepts two protons of the acid and the equivalent weight of the carbonate will be its formula weight divided by 2.

$$eq\text{-}g_{Na_2CO_3} = eq\text{-}g_{HCl}$$

$$9.8\,mL\,HCl - \frac{0.5\,meq\text{-}g\,HCl}{1\,mL\ HCl}\,\frac{1\,meq - g_{Na_2CO_3}}{1\,meq - g_{HCl}} = 4.9\,meq\text{-}g_{Na_2CO_3}$$

$$4.9\,meq\text{-}g_{Na_2CO_3} = \frac{mg\,Na_2CO_3}{\dfrac{106\,mg_{Na_2CO_3}}{2\ meq - g_{Na_2CO3}}} \Rightarrow 259.7\,mg_{Na_2CO_3} = 0.2597\,g_{Na_2CO_3}$$

$$\frac{0.2597\,g_{Na_2CO_3}}{1.5000\,g\,sample}\,\frac{100}{100} = 17.31\%\ Na_2CO_3$$

7. Iron contained in a 2.6475 g sample of a ferric ore, once attacked and reduced to Fe (II), is titrated with 2 N potassium permanganate in an acid medium where Mn (VII) is reduced to Mn (II) consuming 23.5 mL of the potassium salt. Calculate the weight percentage of iron in the ore. DATA: $E^0_{Fe(III)/Fe(II)} = 0.771\,V$; $E^0_{Mn(VII)/Mn(II)} = 1.510\,V$.

$$MnO_4^- + 8H^+ + 5e^- \leftrightarrows Mn^{2+} + 4H_2O \qquad\qquad Fe^{3+} + 1e^- \leftrightarrows Fe^{2+}$$

$$\text{Balanced equation:} \qquad 5\,Fe^{2+} + MnO_4^- + 8H^+ \leftrightarrows 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$$

$$eq\text{-}g_{Fe} = eq\text{-}g_{KMnO_4}$$

$$23.5\,mL\,KMnO_4\,\frac{2\,meq\text{-}g\,KMnO_4}{1\,mL\;KMnO_4}\,\frac{1\,meq-g_{Fe}}{1\,meq-g_{KMnO_4}} = 47\,meq\text{-}g_{Fe}$$

$$47\,meq\text{-}g_{Fe} = \frac{mg\,Fe}{\frac{55.85\,mgFe}{1\;meq-g_{Fe}}} \Rightarrow 2624.95\,mg\,Fe = 2.625\,g\,Fe$$

$$\frac{2.625\,g\,Fe}{2.6475\,g\,sample}\,\frac{100}{100} = 99.15\%\;Fe$$

Had we try to solve it by molarities:

$$\frac{2\,eg-g\,KMnO_4}{L\,KMnO_4}\,\frac{158.08\,g\,KMnO_4}{5\,eg-g\,KMnO_4}\,\frac{1\,mol\,KMnO_4}{158.08\,g\,KMnO_4} = 0.4\,\frac{mol\,KMnO_4}{L} = 0.4\,M\;KMnO_4$$

$$23.5\,mL\,KMnO_4\,\frac{0.4\,mmol\,KMnO_4}{1\,mL\;KMnO_4}\,\frac{5\,mmol\,Fe}{1\,mmol\,KMnO_4}\,\frac{55.85\,mg}{1\,mmol\,Fe} = 2624.95\,mg\,Fe$$

The result is obviously the same.

8. When analyzing a blood serum sample, it is found to contain 102.5 µg Ca^{2+} / mL of serum. If the serum density is 1.053 g/mL and the atomic weight of calcium is 40.08, what is the concentration of Ca^{2+} expressed in: a) molarity; b) meq Ca^{2+} / L serum; c) ppm of Ca^{2+} by weight?

a) $$\frac{102.5\;\mu g\;Ca^{2+}}{mL\;serum}\,\frac{1g\;Ca^{2+}}{10^6\mu g\;Ca^{2+}}\,\frac{1\;mol\;\;Ca^{2+}}{40.08\;\;g\;Ca^{2+}}\,\frac{10^3mL\;serum}{1L\;serum} = 2.56\cdot10^{-3}M$$

b) $$\frac{2.56\cdot10^{-3}mol\;Ca^{2+}}{L\;serum}\,\frac{2\;eq\;Ca^{2+}}{1\;mol\;Ca^{2+}}\,\frac{10^3meq\;Ca^{2+}}{1\;eq\;Ca^{2+}} = \frac{5.12\;meq\;Ca^{2+}}{1\;L\;serum}$$

c) $$\frac{102.5\;\mu g\;Ca^{2+}}{mL\;serum}\,\frac{mL\;\;serum}{1.053\;g\;serum} = 97.3\;p.p.m.$$

9. How many grams of $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$ (molecular weight: 392.14 g/mol) should be dissolved and diluted to 250 mL to prepare an aqueous solution of 1.0 g/mL density and 1 ppm (by weight) of Fe^{2+}? DATA: Fe: 55.85 g/mol.

$$250\ \text{mL soln.}\frac{1\ \text{g soln.}}{1\text{mL soln.}}\frac{1\mu\text{g }\ \text{Fe}^{2+}}{1\text{g soln.}}\frac{1\ \text{mg}}{10^3\mu\text{g}}\frac{392.14\ \ \text{mg FeSO}_4(\text{NH}_4)_2\text{SO}_4\cdot 6\text{H}_2\text{O}}{55.85\ \ \text{mg Fe}^{2+}}=1.75\ \text{mg}$$

10. How many mL of 37wt% HCl and density 1.18 g/mL are required to prepare 100 mL of 6M HCl?

$$100\ \text{mL}\frac{6\ \text{mol HCl}}{10^3\text{mL}}\frac{36.45\ \text{g HCl}}{\text{mol HCl}}\frac{100\ \text{g soln}}{37\ \text{g HCl}}\frac{1\,\text{mL soln}}{1.18\ \text{g soln}}=50.09\ \text{mL}$$

11. What volume of concentrated 36wt% hydrochloric acid and density 1.1791 g/mL would be necessary to prepare 50 mL of 12wt% HCl and density 1.0526 g/mL?

$$50\,\text{mL}\frac{1.0526\,\text{g}}{1\,\text{mL}}\frac{12\,\text{g HCl}}{100\,\text{g}}\frac{100\,\text{g soln}}{36\,\text{g HCl}}\frac{1\,\text{mL soln}}{1.1791\,\text{g soln}}=14.88\,\text{mL}$$

12. What volume of a stock NaOH solution should be taken to prepare 1 L of a 1N NaOH solution if it has been found that 20.0 mL of stock NaOH neutralize exactly 40.0 mL of 0.95 N HCl?

40.0 mL · 0.95 meq HCl/mL = 20.0 mL · x N $\text{NaOH}_{\text{stock}}$ ⇒ $\text{NaOH}_{\text{stock}}$ is 1.9 N

1 L · 1 eq NaOH/L = y L · 1.9 eq $\text{NaOH}_{\text{stock}}$/L ⇒ y = 0.526 L $\text{NaOH}_{\text{stock}}$ = 526 mL $\text{NaOH}_{\text{stock}}$

13. 7 g of NaCl are dissolved in 43 g of H_2O. Calculate the weight percentage of the solution.

$$\frac{7\text{g NaCl}}{43\ \text{g soln.}}\frac{100}{100}=\frac{16.28\,\text{g NaCl}}{100\,\text{g soln.}}=16.28\,\text{wt.\% NaCl}$$

14. A concentrated nitric acid, with a density of 1.405 g/mL, contains 68.1% by weight of HNO_3. Calculate the molarity and normality of this acid.

$$\frac{1.405\ \text{g soln.}}{1\ \text{mL soln.}}\frac{68.1\text{g HNO}_3}{100\ \text{g soln.}}\frac{\text{mol HNO}_3}{63\,\text{g HNO}_3}\frac{10^3\text{mL soln.}}{1\text{L soln.}}=15.19\ \text{M HNO}_3=15.19\ \text{N HNO}_3$$

15. Calculate the molarity of a solution containing 9.0 g of $H_2C_2O_4$ in a volume of 500.0 mL.

$$\frac{9\,\text{g H}_2\text{C}_2\text{O}_4}{500\,\text{mL soln}}\frac{\text{mol H}_2\text{C}_2\text{O}_4}{90\,\text{g H}_2\text{C}_2\text{O}_4}\frac{10^3\ \text{mL soln}}{\text{L soln}}=0.2\,\text{M H}_2\text{C}_2\text{O}_4$$

16. An exactly weighed 180 g of NaOH are dissolved in 400 g of water. The density of the resulting solution is 1.340 g/mL. Calculate the concentration of this solution in a) weight percent; b) grams per liter; c) molarity and d) molality.

a) $\frac{180\,\text{g NaOH}}{580\,\text{g soln}}\frac{100}{100}\cong\frac{31\,\text{g NaOH}}{100\,\text{g soln}}=31\text{wt\% NaOH}$

b) $\frac{180\,\text{g NaOH}}{580\,\text{g soln}}\frac{1.340\,\text{g NaOH}}{\text{mL soln}}\frac{10^3\,\text{mL soln}}{\text{L soln}}\cong 416\,\text{g NaOH/L soln}$

c) $\frac{180\,\text{g NaOH}}{580\,\text{g soln}}\frac{1.340\,\text{g NaOH}}{\text{mL soln}}\frac{\text{mol NaOH}}{40\,\text{g NaOH}}\frac{10^3\,\text{mL soln}}{\text{L soln}}=10.4\,\text{M NaOH}$

d) $\frac{180\,\text{g NaOH}}{400\,\text{g solvent}}\frac{1000\,\text{g solvent}}{\text{Kg solvent}}\frac{\text{mol NaOH}}{40\,\text{g NaOH}}\cong 113\,\text{m}$

17. 6 g of KCl are added to 80 g of a 12% KCl solution. Calculate the weight percent KCl of the resulting solution.

$80\,\text{g soln}\frac{12\,\text{g KCl}}{100\,\text{g soln}}=9.6\,\text{g KCl};$ $\frac{(9.6+6)\,\text{g KCl}}{(80+6)\,\text{g soln}}\frac{100}{100}=18.14\,\text{wt\%}\quad\text{KCl}$

18. A solution with a volume of 100 mL contains 0.2083 g of barium chloride. a) How many moles of barium chloride, barium ion and chloride ion are present in this solution? b) What is the molarity of the solution? c) What weight of barium and chloride is present in the solution? d) Find the weight of silver nitrate required to precipitate the chloride from the solution and the weight of silver chloride obtained; e) What volume of 0.100 M silver nitrate solution is needed to precipitate all the chloride? f) How many milliliters of silver nitrate solution containing 10.0 g of the salt per liter are needed to precipitate the chloride? g) With what weight of aluminum sulfate will the solution react and how much barium sulfate will be obtained?

a) $0.2083\,\text{g BaCl}_2\frac{\text{mol BaCl}_2}{208.24\,\text{g BaCl}_2}=1.00\cdot10^{-3}\,\text{mol BaCl}_2$

$0.2083\,\text{g BaCl}_2\frac{\text{mol BaCl}_2}{208.24\,\text{g BaCl}_2}\frac{\text{mol Ba}}{\text{mol BaCl}_2}=1.00\cdot10^{-3}\,\text{mol Ba}$

$0.2083\,\text{g BaCl}_2\frac{\text{mol BaCl}_2}{208.24\,\text{g BaCl}_2}\frac{2\,\text{mol Cl}}{\text{mol BaCl}_2}=2.00\cdot10^{-3}\,\text{mol Cl}$

b) $\frac{0.2083\,\text{g BaCl}_2}{100\,\text{mL soln}}\frac{\text{mol BaCl}_2}{208.24\,\text{g BaCl}_2}\frac{10^3\,\text{mL soln}}{\text{L soln}}=0.01\,\text{M BaCl}_2$

c) $1.00\cdot10^{-3}\,\text{mol Ba}\frac{137.34\,\text{g Ba}}{\text{mol Ba}}=1.37\cdot10^{-1}\,\text{g Ba}$

$2.00\cdot10^{-3}\,\text{mol Cl}\frac{35.45\,\text{g Cl}}{\text{mol Cl}}=7.09\cdot10^{-2}\,\text{g Cl}$

d) $Cl^- + Ag^+ \leftrightarrows AgCl$

$$2.00\cdot10^{-3}\ \text{mol Cl}\,\frac{\text{mol Ag}}{\text{mol Cl}}\,\frac{\text{mol AgNO}_3}{\text{mol Ag}}\,\frac{169.87\,\text{g AgNO}_3}{\text{mol AgNO}_3}=3.40\cdot10^{-1}\ \text{g AgNO}_3$$

$$2.00\cdot10^{-3}\ \text{mol Cl}\,\frac{\text{mol Ag}}{\text{mol Cl}}\,\frac{\text{mol AgCl}}{\text{mol Ag}}\,\frac{143.32\,\text{g AgCl}}{\text{mol AgCl}}=2.87\cdot10^{-1}\ \text{g AgCl}$$

e) $$100\,\text{mL soln}\,\frac{1.00\cdot10^{-3}\ \text{mol BaCl}_2}{1000\,\text{mL soln}}\,\frac{2\,\text{mol Cl}}{\text{mol BaCl}_2}\,\frac{\text{mol AgNO}_3}{\text{mol Cl}}\,\frac{1000\,\text{mL AgNO}_3}{0.1\,\text{mol AgNO}_3}=2.00\,\text{mL AgNO}_3$$

f) $$\frac{10\,\text{g AgNO}_3}{\text{L}}\,\frac{\text{mol AgNO}_3}{169.87\,\text{g AgNO}_3}=5.89\cdot10^{-2}\ \text{M}$$

$$100\,\text{mL}\,\frac{1.00\cdot10^{-3}\text{mol BaCl}_2}{10^3\ \text{mL}}\,\frac{2\,\text{mol Cl}}{\text{mol BaCl}_2}\,\frac{\text{mol AgNO}_3}{\text{mol Cl}}\,\frac{10^3\ \text{mL}}{5.89\cdot10^{-2}\ \text{mol AgNO}_3}\cong3.40\,\text{mL}$$

g) $3\ BaCl_2 + Al_2(SO_4)_3 \leftrightarrows 3\ BaSO_4 + 2\ AlCl_3$

$$1.00\cdot10^{-3}\ \text{mol BaCl}_2\,\frac{1\,\text{mol Al}_2(\text{SO}_4)_3}{3\,\text{mol BaCl}_2}\,\frac{342.14\,\text{g Al}_2(\text{SO}_4)_3}{\text{mol Al}_2(\text{SO}_4)_3}=0.11\,\text{g Al}_2(\text{SO}_4)_3$$

$$1.00\cdot10^{-3}\ \text{mol BaCl}_2\,\frac{3\,\text{mol BaSO}_4}{3\,\text{mol BaCl}_2}\,\frac{233.40\,\text{g BaSO}_4}{\text{mol BaSO}_4}=0.23\,\text{g BaSO}_4$$

19. How many moles are in: a) 6.75 g of aluminum oxide; b) 0.232 g of sodium sulfate; c) 250.0 mL of a 0.264 M solution of sodium borate (tetraborate, $Na_2B_4O_7$); d) 2.50 litres of a solution containing 8.264 g of potassium dichromate; e) 100.0 mL of a solution containing 3.72 mgL^{-1} hydrochloric acid.

a) $$6.75\,\text{g Al}_2\text{O}_3\,\frac{\text{mol Al}_2\text{O}_3}{101.96\,\text{g Al}_2\text{O}_3}=6.62\cdot10^{-2}\ \text{mol Al}_2\text{O}_3$$

b) $$0.232\,\text{g Na}_2\text{SO}_4\,\frac{\text{mol Na}_2\text{SO}_4}{142.06\,\text{g Na}_2\text{SO}_4}=1.63\cdot10^{-2}\ \text{mol Na}_2\text{SO}_4$$

c) $$250.00\,\text{mL Na}_2\text{B}_4\text{O}_7\,\frac{0.264\,\text{mol Na}_2\text{B}_4\text{O}_7}{10^3\ \text{mL}}=6.60\cdot10^{-2}\ \text{mol Na}_2\text{B}_4\text{O}_7$$

d) $$\frac{8.264\,\text{g K}_2\text{Cr}_2\text{O}_7}{2.5\,\text{L soln}}\,\frac{\text{mol K}_2\text{Cr}_2\text{O}_7}{294.20\,\text{g K}_2\text{Cr}_2\text{O}_7}=1.12\cdot10^{-2}\ \text{mol K}_2\text{Cr}_2\text{O}_7$$

e) $$100\,\text{mL}\,\frac{3.72\,\text{mg HCl}}{10^3\ \text{mL}}\,\frac{\text{mol HCl}}{36.45\cdot10^3\,\text{mg HCl}}=1.02\cdot10^{-5}\ \text{mol HCl}$$

20. How many grams are in: a) 0.160 moles of chloroform; b) $0.120\cdot10^{-3}$ moles of acetic acid; c) 16.0 moles of sodium nitrite; d) 20.7 mL of a 3.0 M phosphoric acid solution; e) 5.5 mL of a 0.50 M solution of potassium ferrocyanide (potassium hexacyanoferrate (II)).

a) $0.160\,\text{mol}\,HCCl_3\,\frac{119.35\,\text{g}\,HCCl_3}{\text{mol}\,HCCl_3}=19.09\,\text{g}\,HCCl_3$

b) $0.120\cdot10^{-3}\,\text{mol}\,CH_3COOH\frac{60\,\text{g}\,CH_3COOH}{\text{mol}\,CH_3COOH}=7.2\cdot10^{-3}\,\text{g}\,CH_3COOH$

c) $16.0\,\text{mol}\,NaNO_2\,\frac{69\,\text{g}\,NaNO_2}{\text{mol}\,NaNO_2}=1104\,\text{g}\,NaNO_2$

d) $20.7\,\text{mL}\,H_3PO_4\,\frac{3.0\,\text{mol}\,H_3PO_4}{1000\,\text{mL}}\frac{97.97\,\text{g}\,H_3PO_4}{\text{mol}\,H_3PO_4}=6.1\,\text{g}\,H_3PO_4$

e) $5.5\,\text{mL}\frac{0.50\,\text{mol}\,K_4Fe(CN)_6}{1000\,\text{mL}}\frac{368.25\,\text{g}\,K_4Fe(CN)_6}{\text{mol}\,K_4Fe(CN)_6}=1.0\,\text{g}\,K_4Fe(CN)_6$

21. In neutral medium, silver ions react with the carbonate ion to form a precipitate of silver carbonate. Calculate: a) how many grams of sodium carbonate are needed to react completely with 1.75 g of silver nitrate; b) how many grams of silver nitrate are necessary to react with 200.0 mL of a 0.150 M sodium carbonate solution; c) how many grams of silver carbonate are formed when 5.00 g of sodium carbonate are mixed with 2.45 g of silver nitrate; d) how many grams of silver carbonate are formed when 5.00 g of sodium carbonate are mixed with 30.0 g of silver nitrate; e) how many grams of silver carbonate are formed when 200.0 mL of 0.200M sodium carbonate are mixed with 300.0 mL of 0.300 M silver nitrate. $2\,Ag^+ + CO_3^{2-} \leftrightarrows Ag_2CO_3$.

a)

$$1.75\,\text{g}\,AgNO_3\,\frac{\text{mol}\,AgNO_3}{169.87\,\text{g}\,AgNO_3}\frac{\text{mol}\,Ag^+}{\text{mol}\,AgNO_3}\frac{\text{mol}\,CO_3^{2-}}{2\,\text{mol}\,Ag^+}\frac{\text{mol}\,Na_2CO_3}{\text{mol}\,CO_3^{2-}}\frac{105.98\,\text{g}\,Na_2CO_3}{\text{mol}\,Na_2CO_3}=0.55\,\text{g}\,Na_2CO_3$$

b) $200.0\,\text{mL}\frac{0.150\,\text{mol}\,Na_2CO_3}{10^3\,\text{mL}}\frac{2\,\text{mol}\,AgNO_3}{\text{mol}\,Na_2CO_3}\frac{169.87\,\text{g}\,AgNO_3}{\text{mol}\,AgNO_3}=10.2\,\text{g}\,AgNO_3$

c) $5.00\,\text{g}\,Na_2CO_3\,\frac{10^3\,\text{mmol}\,Na_2CO_3}{105.98\,\text{g}\,Na_2CO_3}=47.17\,\text{mmol}\,Na_2CO_3$

$2.45\,\text{g}\,AgNO_3\,\frac{10^3\,\text{mmol}\,AgNO_3}{169.87\,\text{g}\,AgNO_3}=14.42\,\text{mmol}\,AgNO_3$

Ag is the limiting reagent; it will consume 7.21 mmol sodium carbonate to generate 7.21 mmol of silver carbonate:

$$7.21\,\text{mmol}\,Ag_2CO_3\,\frac{275.74\cdot10^{-3}\ \text{g}\,Ag_2CO_3}{\text{mmol}\,Ag_2CO_3}=1.99\,\text{g}\,Ag_2CO_3$$

d) $$5.00\,\text{g}\,Na_2CO_3\,\frac{10^3\ \text{mmol}\,Na_2CO_3}{105.98\,\text{g}\,Na_2CO_3}=47.17\,\text{mmol}\,Na_2CO_3$$

$$30.0\,\text{g}\,AgNO_3\,\frac{10^3\ \text{mmol}\,AgNO_3}{169.87\,\text{g}\,AgNO_3}=176.6\,\text{mmol}\,AgNO_3$$

In this occasion it is the carbonate which is the limiting reagent; it will be able to react with 94.34 mmol $AgNO_3$ to generate 47.17 mmol of Ag_2CO_3.

$$47.17\,\text{mmol}\,Ag_2CO_3\,\frac{275.74\cdot10^{-3}\ \text{g}\,Ag_2CO_3}{\text{mmol}\,Ag_2CO_3}=13.00\,\text{g}\,Ag_2CO_3$$

e) $$200\,\text{mL}\,Na_2CO_3\,\frac{0.200\cdot10^{-3}\ \text{mmol}\,Na_2CO_3}{1000\,\text{mL}}=40\,\text{mmol}\,Na_2CO_3$$

$$300\,\text{mL}\,AgNO_3\,\frac{0.300\cdot10^{-3}\ \text{mmol}\,AgNO_3}{1000\,\text{mL}}=90\,\text{mmol}\,AgNO_3$$

Na_2CO_3 is the limiting reagent; as many millimoles of silver carbonate will be formed.

$$40\,\text{mmol}\,Ag_2CO_3\,\frac{275.74\cdot10^{-3}\ \text{g}\,Ag_2CO_3}{\text{mmol}\,Ag_2CO_3}=11.03\,\text{g}\,Ag_2CO_3$$

22. Just 2 drops of nitric acid of 1.4 g/mL density and 70wt/wt% are added onto 5 mL of 1.12wt/vol% of Fe^{2+} solution. Calculate if they will be enough to oxidize all Fe^{2+} to Fe^{3+}. DATA: 1 drop = 0.05 mL. The unbalanced reaction that takes place is $Fe^{2+} + HNO_3 \leftrightarrows Fe^{3+} + NO$.

The half-reactions involved are:

$NO_3^- + 4\,H^+ + 3\,e^- \leftrightarrows NO + 2\,H_2O$ $\quad$ $Fe^{3+} + 1\,e^- \leftrightarrows Fe^{2+}$

Net balanced reaction: $3\,Fe^{2+} + NO_3^- + 4\,H^+ \leftrightarrows 3\,Fe^{2+} + NO + 2\,H_2O$

$$5\,\text{mL}\,\frac{1.12\,\text{g}\,Fe^{2+}}{100\,\text{mL}}\,\frac{10^3\ \text{mmol}\,Fe^{2+}}{55.85\,\text{g}\,Fe^{2+}}=1.00\,\text{mmol}\,Fe^{2+}$$

$$2\,\text{drops}\,\frac{0.05\,\text{mL}}{1\,\text{drop}}\,\frac{14\,\text{g}\,\text{soln}}{\text{mL}}\,\frac{70\,\text{g}\,HNO_3}{100\,\text{g}\,\text{soln}}\,\frac{10^3\ \text{mmol}\,HNO_3}{63\,\text{g}\,HNO_3}=1.5\,\text{mmol}\,HNO_3$$

According to the stoichiometry of the balanced reaction, the oxidation of 1 mmol Fe^{2+} requires one third mmol HNO_3; since we have 1.5 mmol HNO_3, they are more than enough (we would only need 0.33 mmol HNO_3).

23. Classify the following systems by their increasing donor strength of hydrogen ion: acetic acid (pK = 4.8); hydrocyanic acid (pK = 9.2); hydrofluoric acid (pK = 4.2) and hypochlorous acid (pK = 7.5).

HF > H_3C-COOH > HClO > HCN

24. For each of the following equilibria, identify the acids and bases (Bronsted-Lowry or Lewis), in the forward and reverse reactions.

a) $HClO_2 + H_2O \leftrightarrows ClO_2^- + H_3O^+$
b) $OCl^- + H_2O \leftrightarrows HOCl + OH^-$
c) $NH_3 + H_2PO_4^- \leftrightarrows NH_4^+ + HPO_4^{2-}$

a) $HClO_2$ **(a1)** + H_2O **(b2)** $\leftrightarrows$ ClO_2^- **(b1)** + H_3O^+ **(a2)**
b) OCl^- **(b1)** + H_2O **(a2)** $\leftrightarrows$ HOCl **(a1)** + OH^- **(b2)**
c) NH_3 **(b1)** + $H_2PO_4^-$**(a2)** $\leftrightarrows$ NH_4^+ **(a1)** + HPO_4^{2-} **(b2)**

25. Calculate the pH, pOH and $[OH^-]$ in the solutions that have the following hydrogen ion concentration: a) $3 \cdot 10^{-12}$ M; b) $9 \cdot 10^{-4}$ M; c) $6 \cdot 10^{-7}$ M; d) 1.0 M.

a) pH = 11.52; pOH = 2.48; $[OH^-] = 3.31 \cdot 10^{-3}$ M

b) pH = 3.04; pOH = 10.96; $[OH^-] = 1.10 \cdot 10^{-11}$ M

c) pH = 6.22; pOH = 7.78; $[OH^-] = 1.66 \cdot 10^{-8}$ M

d) pH = 0; pOH = 14; $[OH^-] = 1 \cdot 10^{-14}$ M

26. Calculate pOH, $[OH^-]$ and $[H^+]$ in the solutions that have the following pH: a) 0.0; b) 7.52; c) 3.3; d) 10.90; e) 14.00.

a) pOH = 14; $[OH^-] = 1.00 \cdot 10^{-14}$ M; $[H^+] = 1$ M

b) pOH = 6.48; $[OH^-] = 3.31 \cdot 10^{-7}$ M; $[H^+] = 3.02 \cdot 10^{-8}$ M

c) pOH = 10.7; $[OH^-] = 2.00 \cdot 10^{-11}$ M; $[H^+] = 5.01 \cdot 10^{-4}$ M

d) pOH = 3.1; $[OH^-] = 7.94 \cdot 10^{-4}$ M; $[H^+] = 1.26 \cdot 10^{-11}$ M

e) pOH = 0; $[OH^-] = 1$ M; $[H^+] = 1.00 \cdot 10^{-14}$ M

1.2 Data Handling

Degrees of Freedom	Confidence interval				
	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.60
5	1.48	2.02	2.57	4.03	6.86
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.40
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
11	1.36	1.80	2.20	3.11	4.44
12	1.36	1.78	2.18	3.06	4.32
13	1.35	1.77	2.16	3.01	4.22
14	1.34	1.76	2.14	2.98	4.14
∞	1.29	1.64	1.96	2.58	3.29

Critical values for rejection quotient **Q**			
Number of observations	90% confidence	96% confidence	99% confidence
3	0.94	0.98	0.99
4	0.76	0.85	0.93
5	0.64	0.73	0.82
6	0.56	0.64	0.74
7	0.51	0.59	0.68
8	0.47	0.54	0.63
9	0.44	0.51	0.60
10	0.41	0.48	0.57

Helpful readings on this topic may be found at:

http://hdl.handle.net/10171/27818

http://hdl.handle.net/10171/27822

27. A student performs a quadruplicate analysis of a sample of Cu, obtaining the following results: 52.68; 53.17; 52.73 and 52.67. Applying the different known criteria, can the disperse data be rejected? Use the 95% confidence level.

a) Criterion Q:

$$Q_{\exp} = \frac{|x_q - x_n|}{w} = \frac{|53.17 - 52.73|}{53.17 - 52.67} = 0.88$$

$$Q_{crit(n=4;96\%)} = 0.85$$

Since Q_{exp}>Q_{crit}, that result must be discarded.

Note that this Q_{crit} corresponds to 96% confidence level and therefore for a value of 95% mentioned in the exercise, that value would be even lower.

b) Criterion s:

$$\bar{x} = 52.69; \quad s = 0.032; \quad t_{(n=3;95\%)} = 4.30$$

$$\mu = 52.69 \pm 0.032 \cdot 4.30 = 52.69 \pm 0.14$$

The upper margin of the interval would be: 52.69 + 0.14 = 52.83, then the doubtful value has to be rejected.

c) Criterion **d:**

52.68	-0.01
53.17	
52.73	+0.04
52.67	-0.02
$\bar{x} = 52.69$	$\bar{d} = 0.003$

52.69 ± 4·(0.03) =52.69 ± 0.01.

We see that the doubtful result, also by this method, must be rejected.

28. A group of measurements results in an average value of 15.74, with the data presenting a standard deviation of 0.38. What is the confidence interval for a 99% probability?

If we consider that 10 measurements have been made (the statement does not set the number):

$$\mu = \bar{x} \pm \frac{s \cdot t}{\sqrt{n}} = \bar{x} \pm s_m \cdot t = 15.74 \pm \frac{0.38 \cdot 3.25}{\sqrt{10}} = 15.74 \pm 0.39$$

29. Seven analyses of the phosphorus content in a fertilizer result in 16.2; 17.5; 15.4; 15.9; 16.8, 16.3 and 17.1%. Find the standard deviation and the confidence interval for a 95% probability.

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} = 0.72 \qquad \mu = \bar{x} \pm \frac{s \cdot t}{\sqrt{n}} = \bar{x} \pm s_m \cdot t = 16.5 \pm \frac{0.72 \cdot 2.45}{\sqrt{7}} = 16.5 \pm 0.7$$

30. A series of determinations of the Zn content of a vitamin preparation were carried out with the following results: 14,1; 15.2; 14.8; 15.5; 15.3; 14.6 and 14.9 mg of Zn per capsule. Find: a) the average value of the sample; b) the standard deviation of the results and c) the estimated value of the true mean with a 95% probability.

a) $\bar{x} = \frac{\sum_n x_n}{n} = 14.9$

b) $s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} = 0.474$

c) $\mu = \bar{x} \pm \frac{s \cdot t}{\sqrt{n}} = \bar{x} \pm s_m \cdot t = 14.9 \pm \frac{0.474 \cdot 3.71}{\sqrt{7}} = 14.9 \pm 0.66$

Consequently: $\mu = 14.9 \pm 0.7$

Reminder: the number of degrees of freedom, ν, is equal to the number of observations minus 1, ν = n-1.

31. The weight percentage of an organic compound in a given sample yielded the following values: 30.3; 31.1; 32.6; 36.7 and 28.9. Decide whether the value 36.7 can be discarded with a confidence level of 90% according to the Q test.

$$Q_{exp} = \frac{|x_q - x_n|}{w} = \frac{|36.7 - 32.6|}{36.7 - 28.9} = 0.53$$

$$Q_{crit(n=5;90\%)} = 0.64$$

$Q_{exp} < Q_{crit} \Rightarrow$ the result should be included.

32. Express correctly the result of: 0.64 (± 0.01) + 3.21 (±0.03) - 2.86 (±0.02) = ?

$$s_y = \sqrt{(s_a)^2 + (s_b)^2 + (s_c)^2} = \sqrt{(0.01)^2 + (0.03)^2 + (0.02)^2} = 0.04$$

0.64 (± 0.01) + 3.21 (±0.03) - 2.86 (±0.02) = 0.99 ± 0.04

33. Express correctly the result of: 1.278 (± 0.001) + 0.045 (± 0.002) – 14.6 (± 0.1) =?

1.278 (± 0.001) + 0.045 (± 0.002) – 14.6 (± 0.1) = -13.277 (±?)

$$s_y = \sqrt{(s_a)^2 + (s_b)^2 + (s_c)^2} = \sqrt{(0.001)^2 + (0.002)^2 + (0.1)^2} = 0.1_{000}$$

The result cannot be expressed with more than 1 decimal place, so rounding the correct result is: -13.3 ± 0.1

34. Express correctly the result of: 3.40 (± 0.01) + 0.065 (± 0.003) – 4.3 (± 0.1) = ?

3.40 (± 0.01) + 0.065 (± 0.003) – 4.3 (± 0.1) = -0.8 ± ?

$$s_y = \sqrt{(s_a)^2 + (s_b)^2 + (s_c)^2} = \sqrt{(0.01)^2 + (0.003)^2 + (0.1)^2} = 0.1$$

Result: -0.8 ± 0.1

35. Calculate: $\frac{10.03(\pm 0.01) \cdot 3.61(\pm 0.03)}{4.97(\pm 0.04)} = ?$

$$(s_y)_r = \frac{s_y}{y} = \sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_c}{c}\right)^2} = \sqrt{\left(\frac{0.01}{10.03}\right)^2 + \left(\frac{0.03}{3.61}\right)^2 + \left(\frac{0.04}{4.97}\right)^2} = 0.012$$

$$s_y = 0.012 \cdot 7.29 = 0.09$$

$$\frac{10.03(\pm 0.01) \cdot 3.61(\pm 0.03)}{4.97(\pm 0.04)} = 7.29 \pm 0.09$$

36. Calculate $\frac{24.08(\pm 0.02) \cdot 4.871(\pm 0.01)}{2.63(\pm 0.03)}$ =?

$$\frac{24.08(\pm 0.02) \cdot 4.871(\pm 0.01)}{2.63(\pm 0.03)} = 44.5_{89} \pm ?$$

$$(s_y)_r = \frac{s_y}{y} = \sqrt{\left(\frac{0.02}{24.08}\right)^2 + \left(\frac{0.01}{4.871}\right)^2 + \left(\frac{0.03}{2.63}\right)^2} = 0.0116_{19}$$

s_y = 44.5 · 0.0116 = 0.5_{162}

Result can be reported as: 44.5 ± 0.5

37. Calculate $\frac{41.04(\pm 0.01) \cdot 2.13(\pm 0.02)}{8.15(\pm 0.03)}$ = ?

$$\frac{41.04(\pm 0.01) \cdot 2.13(\pm 0.02)}{8.15(\pm 0.03)} = 10.7 \pm ?$$

$$(s_y)_r = \frac{s_y}{y} = \sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_c}{c}\right)^2} = \sqrt{\left(\frac{0.01}{41.04}\right)^2 + \left(\frac{0.02}{2.13}\right)^2 + \left(\frac{0.03}{8.15}\right)^2} = 0.01$$

$S_y = 10.72 \cdot 0.01 = 0.10$

Then, the proper result is: $\dfrac{41.04(\pm 0.01)\cdot 2.13(\pm 0.02)}{8.15(\pm 0.03)} = 10.7 \pm 0.1$

38. A laboratory technician measures every hour the conductivity of distilled water obtaining the following measurements throughout his workday: 2.014, 2.027, 2.012, 2.041, 2.006, 2.038, 2.019 and 2.025 μΩ /cm; a) Calculate the S/N ratio for that set of values; b) How many more measurements would be needed to obtain a S/N = 1000? c) If the S/N ratio obtained for 20 replicates was 125, how many measurements would be needed to ensure a S/N of 600?

$$\frac{S}{N} = \sqrt{n}\,\frac{S_x}{\sqrt{\sum_{i=1}^{n}(S_x - S_i)^2}} = \frac{\bar{x}}{\sigma_{n\text{-}1}}$$

Since the universe of data available is less than 20, it is statistically more correct to recourse to σ_{n-1} (s_{n-1}).

a) $\dfrac{S_8}{N_8} = \dfrac{\bar{x}}{\sigma_{n-1}} = \dfrac{2.023}{0.012} \cong 169$

b) We may calculate in the first place the S_1/N_1 value, and then try to obtain the value of n to ensure that ratio to reach 1000:

$$\frac{S}{N} = 169 = \sqrt{8}\,\frac{S_1}{N_1};\quad \frac{S_1}{N_1} \cong 60;\quad 1000 = \sqrt{n}\,60;\quad n \cong 278$$

In short, to get a S/N of 1000 would require 270 additional measures.

c) $\dfrac{S_{20}}{N_{20}} = 125 = \sqrt{20}\,\dfrac{S_1}{N_1};\quad \dfrac{S_1}{N_1} = \dfrac{125}{\sqrt{20}} = 28;\quad 600 = \sqrt{n}\,28;\quad n \cong 460$

39. The S/N ratio obtained after four replicates of an analysis was 225. How many measurements are needed to ensure the S/N to become 500?

$$\frac{S}{N} = \sqrt{n}\,\frac{S_x}{N_x};\quad \frac{S_4}{N_4} = \sqrt{4}\,\frac{S_1}{N_1} \Rightarrow \frac{S_1}{N_1} = 112.5;\quad 500 = \sqrt{n}\cdot 112.5;\quad n = 19.75 \cong 20$$

40. Calculate the Fellgett advantage in the signal-to-noise ratio when averaging: a) 558 spectra b) 1200 spectra c) 3750 spectra.

$$\frac{S}{N}=\frac{n}{\sqrt{n}}\cdot\frac{S_x}{N_x}=\sqrt{n}\cdot\frac{S_x}{N_x}$$

a) n = 558 → Fellgett advantage: $\sqrt{558}=23.62$

b) n = 1200 → Fellgett advantage: $\sqrt{1200}=34.64$

c) n = 3750 → Fellgett advantage: $\sqrt{3750}=61.24$

41. Two series of experiments were done in order to study the sensitivity of a method to determine quinine in tonic water. In the first one, 11 repetitive measurements were made for the blank (tonic water without any quinine as supplied by the manufacturer) and the following fluorescence intensity data were obtained: 0.70, 0.74, 0.72, 0.71, 0.73, 0.71, 0.73, 0.74, 0.70, 0.69 and 0.75. In another series of experiments, increasing amounts of quinine were added to prepare 7 artificial samples with the results shown below in the table; a) Estimate the limit of detection (LOD) and the limit of quantification (LOQ) of the method; b) Establish the calibration curve.

Quinine (μg mL^{-1})	1.0	2.0	3.0	4.0	6.0	8.0	10.0
Fluorescence Intensity (a.u.)	25.1	46.0	65.2	86.0	127.1	166.8	208.1

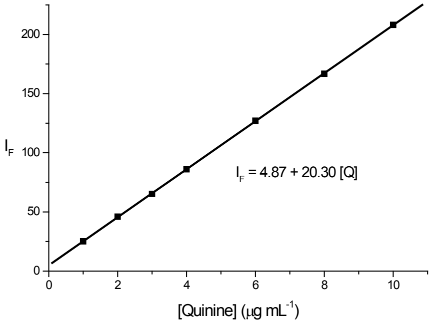
a) $\bar{x}_{blank}=0.72$; $\sigma_{n\text{-}1blank}=0.019$

LOD: $S=\bar{x}+3\sigma_{n-1blank}=0.72+3(0.019)=0.777$

That concentration of analyte giving this signal is the detection limit expressed in units of concentration.

LOQ: $S=\bar{x}_{blank}+10\sigma_{n-1\ blank}=0.72+10(0.019)=0.91$

b) From pairs of data provided, we can construct the calibration curve.



42. We need to know the accuracy of a new and fast immunological method (Method A) for the determination of phenol in water with respect to a classical and slower chromatographic method (Method B). To this end, a double series of experiments were carried out with both methods applied to the same sample aliquots. The results expressed in μg L^{-1} are as follows:

    Method A: 1.7, 1.8, 2.1, 2.2, 1.7, 1.9, 1.5, 1.3, 1.9, 1.7, 1.8, 1.4

    Method B: 1.60, 1.82, 1.73, 1.81, 1.70, 1.73

    Justify what method you would choose for the determination of phenol.

We can calculate the standard deviation of the two sets of measures as well as the respective S/N ratios.

A) $\sigma_{n-1} = 0.265$; $\bar{x} = 1.75$; S/N = 6.60

B) $\sigma_{n-1} = 0.080$; $\bar{x} = 1.73$; S/N = 21.62

Although in the method A ratio S/N is sufficient, the dispersion of data is remarkable with respect to case B. From the standpoint of reproducibility of results is more prudent to continue using the method B. Now if the accuracy of the results is not very relevant (e.g. if you just want to know the presence or absence of the compound) and what is crucial is the speed of analysis, one could resort to the method A.

43. In order to study the sensitivity of a voltammetric method intended for the determination of Zn in drinking water, two series of experiments have been done. In the first, 15 repetitive measurements of the blank (deionized water containing no Zn) were carried out to obtain the following intensity values: 5.25, 5.72, 5.04, 5.43, 5.14, 5.98, 5.61, 6.02, 5.33, 5.47, 5.36, 5.68, 5.39, 5.26 and 5.30 μA. In another series of experiments increasing amounts of Zn were added to prepare 9 samples with the results depicted in the table below. a) Estimate the limit of detection and limit of quantification of the method; b) Establish the calibration curve; c) Estimate the linearity limit of the calibration.

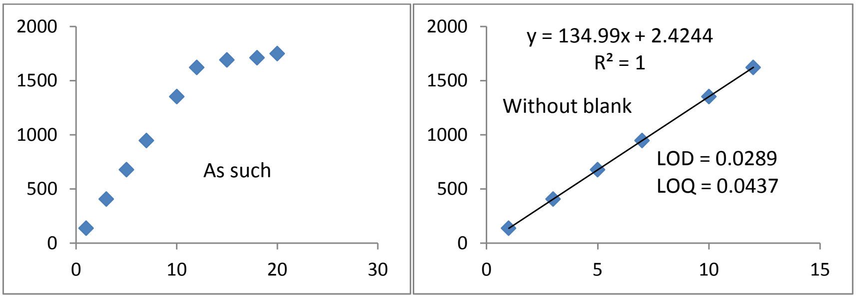
Zn (μg mL^{-1})	1.0	3.0	5.0	7.0	10.0	12.0	15.0	18.0	20.0
Intensity (μA)	137.0	407.6	677.5	947.9	1352.1	1622.2	1690	1710.5	1750.0

a) $\bar{x}_{blank} = 5.47$; $\sigma_{n-1blank} = 0.286$;

LOD: $S = \bar{x}_{blank} + 3\sigma_{n-1blank} = 5.47 + 3(0.286) = 6.328$

LOQ: $S = \bar{x}_{blank} + 10\sigma_{n-1\,blank} = 5.47 + 10(0.286) = 8.33$

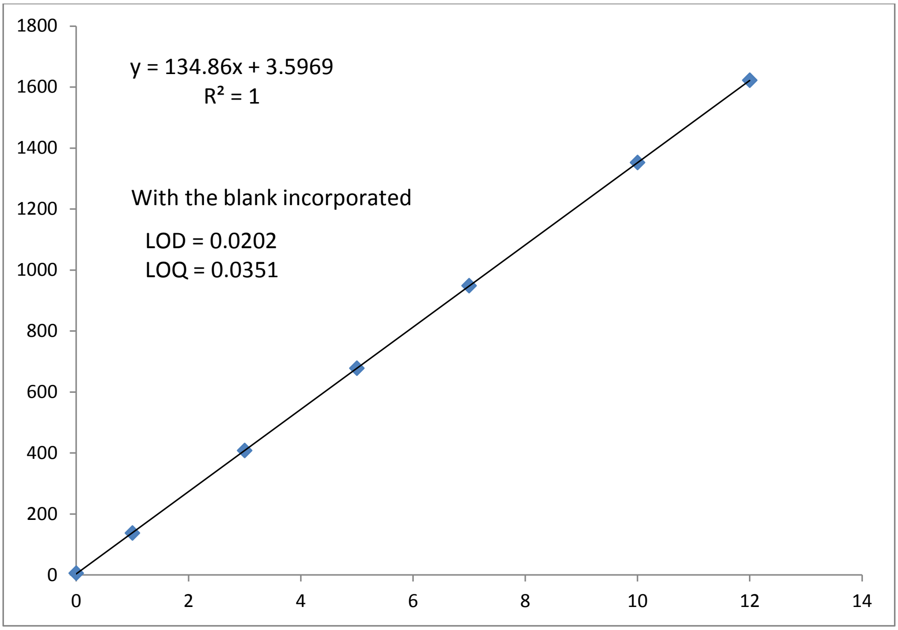
b) From the plotting of pairs of data, it is evident that linearity ceases to exist beyond 12 ppm of Zn. Accordingly, only the first 6 pairs of data are used to estimate the calibration line:



We can calculate both LOD & LOQ according to the equation for this line:

<u>LOD:</u> for I = 6.328 μA ⇒ [Zn] = 0.029 ppm (μg/mL)

<u>LOQ:</u> for I = 8.33 μA ⇒ [Zn] = 0.044 ppm (μg/mL)

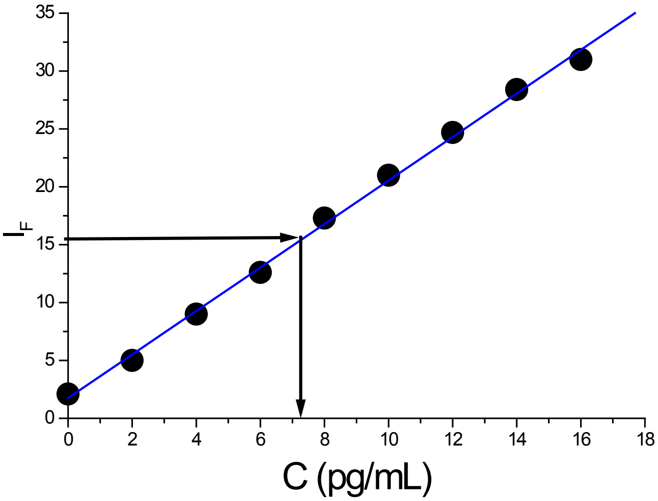


c) The linearity for the calibration will be: 0.044 ppm ≤ [Zn] ≤ 12 ppm

44. Anthracene can be quantified in very low concentrations thanks to its fluorescent emission. Using the data in the Table: a) Build the calibration line for the anthracene; b) Calculate the slope and the ordinate at the origin; c) Calculate the standard deviations of the ordinate, slope and regression; d) Calculate the concentration of an unknown sample that provides a signal of 15.6; e) Calculate the relative standard deviation of the sample concentration; f) Calculate the relative standard deviation of the sample concentration if the value of the fluorescent intensity is the average of 5 measurements.

Concentration (pg/mL)	I_F
0	2.1
2	5.0
4	9.0
6	12.6
8	17.3
10	21.0
12	24.7
14	28.4
16	31.0

For help, you may wish to have a look at the notes in: http://hdl.handle.net/10171/27822



I_F = 1.74889 (± 0.33285) + 1.88 (± 0.03496) · C(pg/mL)

r = 0.99879 ± 0.54154

For the signal 15.6 we interpolate a C = 7.4 pg/mL, which can also be reached in the plot..

$$S_{xx} = \sum x_i^2 - \frac{(\sum x_i)^2}{n} = 816 - \frac{5184}{9} = 240$$

$$S_C = \frac{S_r}{b}\sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(\overline{y_C} - \overline{y})^2}{b^2 S_{XX}}} = \frac{0.54154}{1.88}\sqrt{\frac{1}{1} + \frac{1}{9} + \frac{(15.6 - 16.79)^2}{(1.88)^2 \cdot (240)}} = 0.30$$

$$S_C = \frac{S_r}{b}\sqrt{\frac{1}{m}+\frac{1}{n}+\frac{(\overline{y_C}-\overline{y})^2}{b^2 S_{XX}}} = \frac{0.54154}{1.88}\sqrt{\frac{1}{5}+\frac{1}{9}+\frac{(15.6-16.79)^2}{(1.88)^2\cdot(240)}} = 0.16$$

45. Lithium can be used as a good internal standard in the determination of Na by the atomic emission technique. From the data provided in the table, calculate the content of Na present in the unknown sample. Compare the accuracy of the result obtained with that which would be obtained with the normal calibration using only the standard Na solutions.

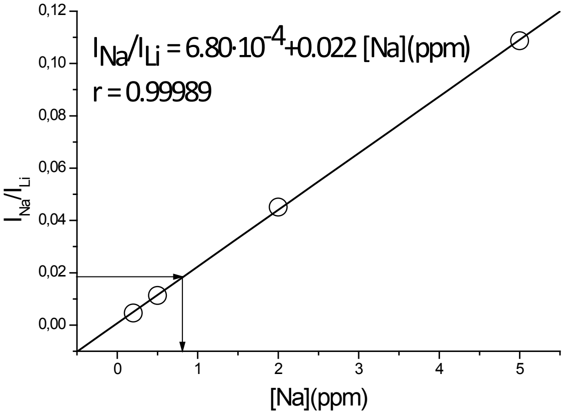
Solution	I (u.a.) Na	I (u.a.) Li
0.2 ppm Na + 500 ppm Li	0.22	48
0.5 ppm Na + 500 ppm Li	0.53	47
2.0 ppm Na + 500 ppm Li	2.30	51
5.0 ppm Na + 500 ppm Li	5.00	46
Sample + 500 ppm Li	0.88	48

We calculate the ratios of intensities for the Na signal with respect to the internal standard of Li:

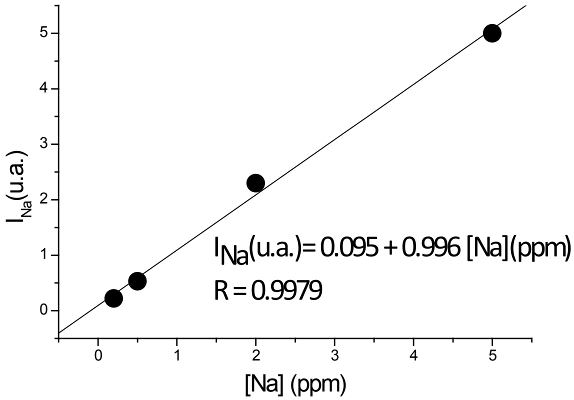
Solution	I (u.a.) Na	I (u.a.) Li	I_{Na}/I_{Li}
0.2 ppm Na + 500 ppm Li	0.22	48	$4.58\cdot10^{-3}$
0.5 ppm Na + 500 ppm Li	0.53	47	$11.28\cdot10^{-3}$
2.0 ppm Na + 500 ppm Li	2.30	51	$45.10\cdot10^{-3}$
5.0 ppm Na + 500 ppm Li	5.00	46	$108.70\cdot10^{-3}$
Sample + 500 ppm Li	0.88	48	$18.3\cdot10^{-3}$

From the interpolation in the graph we obtain an approximate value of 0.8 ppm of Na.

We can also calculate it from the calibration line, solving the equation of the straight line for the the concentration for an intensity ratio of $18.3\cdot10^{-3}$, obtaining 0.80 ppm.



If we carry out the calibration exercise just with the Na standards:



We check that there is a worse linearity (smaller R). In addition, we will calculate the standard deviations of the ordinate, the slope and the regression that will allow us to calculate the relative standard deviation of the sample concentration.

In the first case the calibration can be written as:

$I_{Na}/I_{Li} = 6.80321 \cdot 10^{-4} (\pm 6.19331 \cdot 10^{-4}) + 0.02168 (\pm 2.28872 \cdot 10^{-4})$ [Na] (ppm)

r = 0.99989. $s_r = 8.70543 \cdot 10^{-4}$

In the second case, the line with the corresponding deviations is:

$I_{Na} = 0.09478 (\pm 0.1237) + 0.99622 (\pm 0.04571)$ [Na] (ppm)

r = 0.9979. $s_r = 0.17388$

If we now apply the formulas to calculat S_C:

$$S_{xx} = \sum x_i^2 - \frac{(\sum x_i)^2}{n} = 29.29 - \frac{59.29}{4} = 14.47$$

$$S_C = \frac{S_r}{b}\sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(\overline{y_C} - \overline{y})^2}{b^2 S_{XX}}} = \frac{8.70543 \cdot 10^{-4}}{0.02168}\sqrt{\frac{1}{1} + \frac{1}{4} + \frac{(18.3 \cdot 10^{-3} - 42.415 \cdot 10^{-3})^2}{(0.02168)^2 \cdot (14.47)}} = 0.04$$

In the second case (calibration without internal standard):

$$S_C = \frac{S_r}{b}\sqrt{\frac{1}{m}+\frac{1}{n}+\frac{(\overline{y_C}-\bar{y})^2}{b^2\,S_{xx}}} = \frac{0.17388}{0.99622}\sqrt{\frac{1}{1}+\frac{1}{4}+\frac{(0.88-2.0125)^2}{(0.99622)^2\cdot(14.47)}} = 0.20$$

That is to say that the result would be expressed as:

0.80 ± 0.04 ppm Na,in the case of using internal standard, whereas:

0.80 ± 0.20 ppm Na, would be reported in the case of using the classical external standard calibration, which we can see makes a lot of a difference.