

Solutions to ASSIGNMENT #1

1. Write a detailed *lab procedure* outlining appropriate masses, volumes and volumetric glassware to prepare a standard solution containing 5.00 ppb P from $\text{KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ as a primary standard. (Note: keep in mind the practical limitations of analytical mass balances (± 0.0001 g) and available volumetric glassware – see Introductory pages of your Lab Manual).

Solution:

This problem involves preparing very dilute solutions with concentrations expressed in terms of the mass of a specific element (P) from appropriate primary standard solids. It is tempting to work this one out by converting the concentration from mass/L of P to mass/L of $\text{KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$. (Note: the mass of the three waters of hydration ($3\text{H}_2\text{O}$) are included in the molar mass). However, if the concentration is in the $\mu\text{g/L}$ range the required mass of $\text{KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ will be impractically small. Remember, a typical mass balance is accurate to ± 0.0001 g (or 0.1 mg), so in order to have three or four significant figures in the resulting standard solution, the mass of primary standard should be > 100 mg. Therefore, the strategy here is to prepare a stock solution of higher concentration than needed and then dilute appropriately to give the desired dilute concentration. There are several ways to approach this; (1) convert mass of element to number of moles and then use the MW of the primary standard to calculate the mass of solid required or (2) use the mass ratio of the primary standard to that of the element to convert mass of element to mass of solid directly. Note, in freshwater 1 ppb = 1 $\mu\text{g/L}$, since density = 1.00 kg/L

Phosphorous:

MW ($\text{KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$) = 190.136 g/mol MW (P) = 30.9738 g/mol

$$5.00 \mu\text{g P/kg} \times \frac{1.00 \text{ kg}}{1 \text{ L}} \times \frac{1 \text{ mol}}{30.9738 \text{ g P}} \times \frac{1 \text{ g}}{1 \times 10^6 \mu\text{g}} = 1.614 \times 10^{-7} \text{ mol P/L}$$

$$= 1.614 \times 10^{-7} \text{ mol/L KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$$

$$1.614 \times 10^{-7} \text{ mol/L KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O} \times \frac{190.136 \text{ g}}{1 \text{ mol}} = 3.069 \times 10^{-5} \text{ g/L KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$$

This would require 0.03069 mg of primary solid to be quantitatively transferred and dissolved in 1.00 L, clearly impractical from a number of perspectives, not the least of which is the high relative error. Therefore, one could dissolve 30.7 mg of $\text{KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ in a 1.00 L volumetric flask, mix thoroughly and pipet 1.00 mL into a second 1.00 L volumetric flask. Or better yet, weigh 306.9 mg into 1.00 L, mix, pipet 10.00 mL into a second 1.00 L flask, mix and pipet 10.00 mL of this sub-stock into a third 1.00 L volumetric flask.

Note: The concentration of a standard solution must be known as precisely as possible and we want to minimize the sources of indeterminate error. In general, it is possible to prepare standard solutions with ~0.1% relative error. The two main contributing factors are; 1) the mass reading from the analytical balance and 2) the volume readings from class A analytical glassware. To minimize the relative error from the mass balance, it is desirable to weigh out a mass > 100 mg. To avoid the propagation of indeterminate error through multiple dilution steps, keep pipet volumes to > 1.00 mL and minimize the number of dilution steps (three or less, if possible).

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2. The phosphorous content of fertilizer is often given as a percentage of phosphorous pentoxide (P_2O_5) even though the phosphorous is present in a number of different chemical forms. A 126 mg sample is digested in nitric acid to convert all of the phosphorous containing species to *ortho*-phosphate, which are precipitated as the quinoline salt of phosphomolybdic acid $(\text{C}_9\text{H}_7\text{N})_2\text{H}_3\text{PMo}_{12}\text{O}_{40}$. The precipitate is then dried and weighed. If the final mass of the precipitate is 346 mg, calculate the weight percent of phosphorous in the fertilizer as P_2O_5 .

Solution:

Working this question back to front and breaking it down into simple steps;

$$\text{mass \% } \text{P}_2\text{O}_5 = (\text{mass } \text{P}_2\text{O}_5 / \text{mass sample}) \times 100\%$$

$$\text{and mass of } \text{P}_2\text{O}_5 = n_{\text{P}_2\text{O}_5} \times \text{MW}(\text{P}_2\text{O}_5)$$

$$\text{MW}(\text{P}) = 30.97$$

$$\text{MW}((\text{C}_9\text{H}_7\text{N})_2\text{H}_3\text{PMo}_{12}\text{O}_{40}) = 2084.0$$

$$\text{MW}(\text{P}_2\text{O}_5) = 141.94$$

$$n_{\text{P}_2\text{O}_5} = n_{\text{ppt}} \times (1 \text{ mol } \text{P}_2\text{O}_5 / 2 \text{ mol ppt})$$

$$n_{\text{ppt}} = 346 \text{ mg} \times (1 \text{ g} / 10^3 \text{ mg}) \times (1 \text{ mol} / 2084.0 \text{ g})$$

$$\text{therefore, } n_{\text{P}_2\text{O}_5} = 8.301 \times 10^{-5} \text{ mol } \text{P}_2\text{O}_5$$

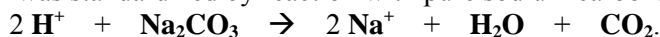
so, mass % P_2O_5 in sample =

$$(8.301 \times 10^{-5} \text{ mol } \text{P}_2\text{O}_5 \times 141.94 \text{ g/mol}) / (126 \text{ mg} \times 1 \text{ g} / 10^3 \text{ mg}) \times 100\% \\ = \mathbf{9.35\% \text{ P}_2\text{O}_5 \text{ (wt/wt)}}$$

Note the N-P-K numbers you may have seen on bags of fertilizer are actually weight percentages of N (as nitrogen), P (as phosphorous pentoxide) and K (as potassium oxide).

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3. A solution of **HCl** was standardized by reaction with pure sodium carbonate.



Due to time limitations, a student was only able to carry out the standardization titration once and has been asked to estimate the uncertainty in the final result by propagating the individual reading errors associated with each measured value. A volume of 7.32 ± 0.04 mL of **HCl** solution was required for complete reaction with 0.0967 ± 0.0002 g of **Na₂CO₃** (FW = 105.989 ± 0.001 g mol⁻¹). Determine the molarity of **HCl** and its absolute uncertainty.

Solution:

$$[\text{HCl}] = \frac{n_{\text{HCl}}}{V_{\text{HCl}}} = \frac{n_{\text{Na}_2\text{CO}_3}}{V_{\text{HCl}}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol Na}_2\text{CO}_3} = \frac{\overset{\text{mass}_{\text{Na}_2\text{CO}_3}}{\text{FW}_{\text{Na}_2\text{CO}_3}}}{V_{\text{HCl}}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol Na}_2\text{CO}_3} = 0.24927837 \pm ? \text{ mol / L}$$

Each measured quantity has an associated experimental reading error which is propagated through the calculation to the final answer according to the rules governed by the type of mathematical operation involved. Recall, we add the absolute errors for addition/subtraction and add the relative errors for multiplication/division. In actual fact, it is the sum of the squares of the absolute errors that are additive for addition/subtraction and the sum of the squares of the relative errors that are additive for multiplication/division (see Table 3.1, textbook for these and other rules for propagating error through calculations).

In absolute terms the errors are reported as,

$$[\text{HCl}] = \frac{0.0967 \pm 0.0004 \text{ g}}{105.989 \pm 0.001 \text{ g / mol}} \times \frac{2 \text{ mol HCl}}{0.00732 \pm 0.00004 \text{ L} \cdot 1 \text{ mol Na}_2\text{CO}_3}$$

Note that there is no error introduced by the mole ratio since it represents an exact number. Converting these absolute errors to relative expressions gives,

$$[\text{HCl}] = \frac{0.0967 \text{ g} (0.21\%)}{105.989 \text{ g / mol} (\pm 0.00094\%)} \times \frac{2 \text{ mol HCl}}{0.00732 \text{ L} (\pm 0.55\%) \cdot 1 \text{ mol Na}_2\text{CO}_3}$$

So adding the squares of the relative errors and taking the square root yields,
Relative error in answer = $[(0.21)^2 + (0.00094)^2 + (0.55)^2]^{1/2} = 0.59\%$

Note, in this case where the relative error of one of the measurements (in this case the titration volume) is significantly larger than the other contributing relative errors, it dominates and is essentially equal to the relative error in the final answer.

Therefore, **[HCl] = 0.24927837 M (±0.59%)**
Since 0.59% of 0.24927837 M = 0.0015 M

We therefore report the final answer in absolute terms as, **[HCl] = 0.249 ± 0.002 M**
(always convert errors back to absolute in final reported values)

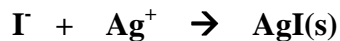
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4. The concentration of a iodide ion in solution can be determined by adding excess AgNO_3 to precipitate all of the iodide as AgI(s) and back-titrating the remaining Ag^+ with KSCN . What is the concentration of iodide (mM), if 50.0 mL of $8.63 \times 10^{-3} \text{ M AgNO}_3$ is added to 100.0 mL sample and 10.20 mL of 0.0325 M KSCN was needed to reach the equivalence point.

Solution:

This is an example of a *back titration*, where the number of moles of I^- present in the original sample = number of moles of Ag^+ reacted = number moles of Ag^+ initially added (from AgNO_3) – number moles Ag^+ remaining (as titrated by KSCN).

The chemistry in this case is:



$$n_{\text{I}^-}(\text{sample}) = n_{\text{Ag}^+}(\text{reacted}) \times 1 \text{ mol I}^- / 1 \text{ mol Ag}^+$$

$$n_{\text{Ag}^+}(\text{reacted}) = n_{\text{Ag}^+}(\text{added}) - n_{\text{Ag}^+}(\text{remaining})$$

$$n_{\text{Ag}^+}(\text{added}) = (50.00 \times 10^{-3} \text{ L})(8.63 \times 10^{-3} \text{ M}) = 4.315 \times 10^{-4} \text{ moles}$$

$$n_{\text{Ag}^+}(\text{remaining}) = (10.20 \times 10^{-3} \text{ L})(0.0325 \text{ M}) = 3.315 \times 10^{-4} \text{ moles}$$

$$\text{Therefore, } n_{\text{I}^-}(\text{sample}) = n_{\text{Ag}^+}(\text{reacted}) = 1.00 \times 10^{-4} \text{ mol}$$

$$\text{So, } [\text{I}^-]_{\text{sample}} = 1.00 \times 10^{-4} \text{ mol} / 0.1000 \text{ L} = 1.00 \times 10^{-3} \text{ mol I}^- / \text{L}$$

$$[\text{I}^-]_{\text{sample}} = \mathbf{1.00 \text{ mM}}$$

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5. Given that a one digit increment of the Hach Digital Titrator™ corresponds to 0.10 mg/L of dissolved oxygen ($\text{O}_2(\text{aq})$), when analyzing a 20.0 mL sample with 0.200 N sodium thiosulfate by the *Winkler method*, calculate the volume of titrant added with each digit increment. Calculate the magnitude and sign of the error (in mg/L of O_2), if one drop of thiosulfate titrant is inadvertently added during the titration. (assume one drop = 30 μL).

Solution:

a) Calculating the volume of each digit increment

Since #equivalents of analytes = #equivalents titrant,

$$N_{\text{O}_2} V_{\text{O}_2} = N_{\text{S}_{2}\text{O}_3} V_{\text{S}_{2}\text{O}_3}$$

And therefore $V_{\text{S}_{2}\text{O}_3}$ is given by,

$$V_{\text{S}_{2}\text{O}_3} = N_{\text{O}_2} V_{\text{O}_2} / N_{\text{S}_{2}\text{O}_3}$$

To solve this we need to convert 0.1 mg/L O_2 into a Normal concentration.

Since the EW of O_2 is 8.0 g/equiv (i.e., $K = 4 \text{ mol e}^-/\text{mol O}_2$ or 4 equiv/mol), we have

$$N_{\text{O}_2} = 0.1 \text{ mg O}_2/\text{L} \times 1 \text{ equiv}/8,000 \text{ mg} = 1.25 \times 10^{-5} \text{ equiv/L}$$

$$\text{So, } V_{\text{S}_{2}\text{O}_3} = (1.25 \times 10^{-5} \text{ equiv/L}) (0.020 \text{ L}) / (0.200 \text{ equiv/L}) = \mathbf{1.25 \times 10^{-6} \text{ L}} \text{ (or } 1.25 \mu\text{L)}$$

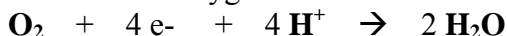
b) Calculating the magnitude and sign of the error of one drop of added titrant

Using equivalents allows us to write;

$$N_{\text{O}_2} = N_{\text{S}_{2}\text{O}_3} V_{\text{S}_{2}\text{O}_3} / V_{\text{O}_2}$$

$$\text{So, } N_{\text{O}_2} = (0.200 \text{ equiv/L}) (30 \times 10^{-6} \text{ L}) / (20.0 \times 10^{-3} \text{ L}) = 3.00 \times 10^{-4} \text{ equiv/L}$$

Converting this concentration to mg/L O_2 requires the mass of one equivalent of O_2 (i.e., the EW). Since one equivalent is the amount that supplies one mole of electrons, we need to know about the change in oxidation state when O_2 reacts. For this, we use the fact that all chemically combined forms of oxygen have a -2 oxidation state. For example,



Therefore, each mole of O_2 reacts with 4 moles of e^- and we have;

$$K = 4 \text{ moles e}^-/\text{mol of O}_2$$

Consequently the EW of $\text{O}_2 = 8.00 \text{ g/equiv}$ and the concentration of O_2 in mg/L is given by;

$$3.00 \times 10^{-4} \text{ equiv/L} \times 8.00 \text{ g/equiv} \times 1000 \text{ mg/g} = 2.4 \text{ mg/L O}_2$$

Since this drop of titrant was added to the sample but not accounted for, the apparent end-point will occur 24 digits (or 2.4 mg/L) short of the true end-point. Thus a drop of titrant inadvertently added will result in a **-2.4 mg/L O_2 determinant error**.

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6. The following data was obtained in a series of volumetric analysis using EDTA. When samples are buffered at pH 10, the EDTA complexes all of the Ca^{2+} and Mg^{2+} ions for *total hardness* analysis. At pH 12, $\text{Mg}(\text{OH})_2$ precipitates and the EDTA will only complex the remaining Ca^{2+} ions thus measuring the *calcium hardness*. Calculate the molar concentration of **Ca** and **Mg** and report the uncertainties in each.

Data Table for the Total and Calcium Hardness of Aqueous Samples

	[EDTA] (M)	V_{EDTA} delivered at pH = 10 (mL)	V_{EDTA} delivered at pH = 12 (mL)
Experimental Mean Value and Error	$(1.024 \pm 0.008) \times 10^{-3}$	23.34 ± 0.22	18.35 ± 0.32
# Replicates in Determining the Mean	3	4	5

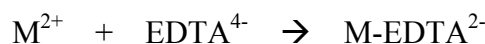
End-points determined using Calmagite indicator.

Sample volumes of 25.00 mL used for each titration.

Absolute errors quoted as experimental standard deviations.

Solution:

The complexation reaction is;



Where M = **Ca** and **Mg** or just **Ca**, depending on the pH

$$[\text{Ca}^{2+} + \text{Mg}^{2+}] = M_{\text{EDTA}} V_{\text{EDTA}}^{\text{pH } 10} / V_{\text{sample}}$$

$$[\text{Ca}^{2+}] = M_{\text{EDTA}} V_{\text{EDTA}}^{\text{pH } 12} / V_{\text{sample}}$$

$$[\text{Mg}^{2+}] = (M_{\text{EDTA}} V_{\text{EDTA}}^{\text{pH } 10} / V_{\text{sample}}) - (M_{\text{EDTA}} V_{\text{EDTA}}^{\text{pH } 12} / V_{\text{sample}})$$

$$[\text{Ca}^{2+} + \text{Mg}^{2+}] = \frac{1.024 \times 10^{-3} (\pm 0.781\%) \times 23.34 \times 10^{-3} (\pm 0.942\%)}{25.00 \times 10^{-3} (\pm 0.12\%)} = 9.56 \times 10^{-4} \text{ M } (\pm 1.23\%)$$

$$= 9.56 (\pm 0.12) \times 10^{-4} \text{ M}$$

$$[\text{Ca}^{2+}] = \frac{1.024 \times 10^{-3} (\pm 0.781\%) \times 18.35 \times 10^{-3} (\pm 1.74\%)}{25.00 \times 10^{-3} (\pm 0.12\%)} = 7.52 \times 10^{-4} \text{ M } (\pm 1.91\%)$$

$$[\text{Ca}^{2+}] = 7.52 (\pm 0.14) \times 10^{-4} \text{ M}$$

Therefore, $[\text{Mg}^{2+}] = (9.56 (\pm 0.12) - 7.52 (\pm 0.14)) \times 10^{-4} \text{ M}$

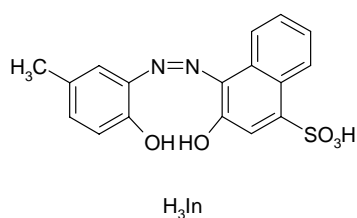
$$[\text{Mg}^{2+}] = 2.04 (\pm 0.18) \times 10^{-4} \text{ M}$$

Note that the relative error for the $[\text{Mg}^{2+}]$ is ~ 9%, whereas that for $[\text{Ca}^{2+}]$ is ~2%. This is because the magnesium conc is determined by difference.

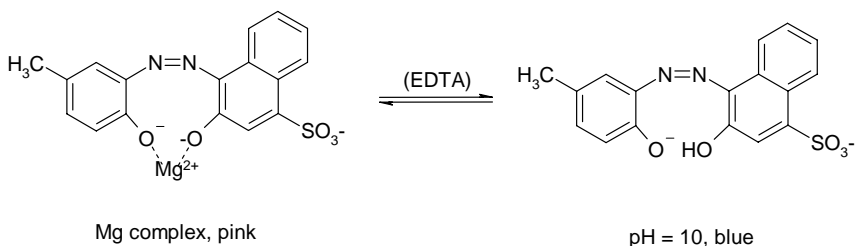
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FYI:

Calmagite is an example of an azo dye (Ar-N=N-Ar), which changes colour depending on the extent of protonation or metal complexation. The structure is shown below in the fully protonated form (H_3In) and the colour of several forms are indicated at various pH (p. 323-324 text). In the EDTA titration of Ca^{2+} and Mg^{2+} , the calmagite complexes with a small portion of free Mg^{2+} to form a pink (wine red) coloured complex. As EDTA is added, it effectively complexes both Ca^{2+} and Mg^{2+} , ($K_f(EDTA-Mg) \sim 10^9$). When all of the available Ca^{2+} and Mg^{2+} is complexed, additional EDTA will remove the Mg^{2+} ion from calmagite, which at pH = 10 (buffered) is in the blue coloured form (HIn^{2-}). For a metal ion indicator to be useful, it must bind less strongly than EDTA.



pH	form	colour
< 2	H_3In	
2 - 8	H_2In^-	pink
8 - 12	HIn^{2-}	blue
> 12	In^{3-}	orange



EDTA (ethylene diamine tetraacetate, $(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2$) is a hexadentate ligand, which forms strong complex ions with divalent metal ions as indicated by the large formation constants (K_f 's) (p. 307-313 text).

CHEM 311

7. The following method is reported in *Standard Methods for the Examination of Water and Wastewater* for the analysis of sodium hypochlorite (**NaOCl**) in bleach.

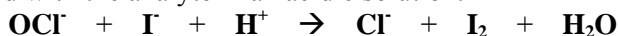
(i) A 20.00 mL sample of bleach is diluted to 100.0 mL.

(ii) A 25.00 mL aliquot of the diluted sample is then transferred into a flask and treated with an excess acidic iodide solution.

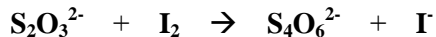
(iii) The iodine thus formed, is titrated with a standard thiosulfate solution.

The chemistry is outlined below (unbalanced equations):

Excess iodide is reacted with the analyte in an acidic solution.



The resulting iodine (I_2) is then titrated with a standardized solution of sodium thiosulfate.



If 25.62 mL of a 0.140 N thiosulfate solution was required to reach the end point, calculate the concentration of **NaOCl** and report as a mass percent **NaOCl**.

Solution:

Conc. **NaOCl** as mass % = mass **NaOCl**/mass sample

Since,

$$N_t \times V_t = N_a \times V_a$$

Where $N_t = 0.140$ eq/L, $V_t = 25.62$ mL and

$V_a =$ volume titrated x dilution factor = 25.00 mL x (20.00 mL/100.00 mL) = 5.00 mL

So

$$N_a = (N_t V_t) / V_a = 0.7174 \text{ eq/L}$$

Another way to think about this is to say that the number of equivalents of titrant ($N_t \times V_t$) = (25/100; i.e., 1/4) the number of equivalents in the original 20.0 mL sample.

Thus,

$$N_a = 4 (N_t \times V_t) / 0.0200 \text{ L} = 0.7147 \text{ eq/L}$$

To convert this to a mass of **NaOCl**, use the EW of **NaOCl**

$$\text{EW} = \text{MW}/K$$

Where $K = 2$ mols e^- /mol **OCl**⁻, since 2 mol of e^- are transferred per mol of **NaOCl** reacted (i.e., as **OCl**⁻ \rightarrow **Cl**⁻ the oxidation state of each **Cl** goes from +1 to -1 and there is one **Cl** undergoing this change in each **OCl**⁻)

So, EW (**NaOCl**) = (74.45 g **NaOCl**/mol) x (1 mol/2 equiv) = 37.453 g **NaOCl**/equiv

Therefore,

Conc. **NaOCl** in g/L = 0.7174 eq/L x 37.453 g **NaOCl**/eq = 26.9 g **NaOCl**/L

Assuming the density of the solution is 1.00 kg/L, this amounts to 26.9 g per 1000 g or **2.69% (by mass)**.

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8. The concentration of dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) in electroplating waste may be determined by titrating with a standardized solution of ferrous ammonium sulphate (FAS).

- a) Calculate the normality of dichromate if a 100.0 mL sample required 14.20 mL of 0.00242 N of FAS to reach the end point (unbalanced reaction given below).
- b) What is the concentration of dichromate - chromium in mg/L?
- c) If the 100.0 mL sample was derived by digesting 565 mg of dried mine tailings, what is the the concentration as ppm of $\text{Cr}_2\text{O}_7^{2-} - \text{Cr}$?



Solution:

a) Since, # equiv of $\text{Cr}_2\text{O}_7^{2-}$ = # equiv of Fe^{2+}

$$N_{\text{Cr}_2\text{O}_7} = N_{\text{Fe}} V_{\text{Fe}} / V_{\text{sample}}$$

and, $V_{\text{sample}} = 100.0 \text{ mL} / 1000 \text{ mL L}^{-1} = 0.1000 \text{ L}$

So # equiv of $\text{Cr}_2\text{O}_7^{2-}$

$$= (0.00242 \text{ equiv/L})(14.20 \text{ mL} \times 1 \text{ L} / 10^3 \text{ mL}) = 3.436 \times 10^{-5} \text{ equiv}$$

Therefore, $N_{\text{Cr}_2\text{O}_7} = 3.436 \times 10^{-5} \text{ equiv} / 0.1000 \text{ L} = \mathbf{3.43_6 \times 10^{-4} \text{ equiv/L}}$

b) Conversion to $M_{\text{Cr}_2\text{O}_7} = N/K$, where $K = 6 \text{ equiv/mol}$ for $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$

So,

$$[\text{Cr}_2\text{O}_7^{2-}] = 5.72_7 \times 10^{-5} \text{ M}$$

and Conc. in mg/L of $\text{Cr}_2\text{O}_7^{2-} - \text{Cr}$

$$= 5.727 \times 10^{-5} \text{ mol Cr}_2\text{O}_7^{2-} / \text{L} \times 2 \text{ mol Cr} / 1 \text{ mol Cr}_2\text{O}_7^{2-} \times 51,996 \text{ mg/mol}$$

$$= \mathbf{5.95_5 \text{ mg Cr}_2\text{O}_7^{2-} - \text{Cr/L}}$$

c) We need to express the conc as a mass ratio:

mass of dichromate – chromium in 100. mL digest per 565 mg of sludge sample.

Thus,

$$\begin{aligned} & (5.955 \times 10^{-3} \text{ g/L Cr}_2\text{O}_7^{2-} - \text{Cr} \times 0.100 \text{ L} \times 10^6 \text{ } \mu\text{g/1 g}) / 0.565 \text{ g} \\ & = 105_4 \text{ } \mu\text{g/g} = \mathbf{1050 \text{ ppm Cr}_2\text{O}_7^{2-} - \text{Cr}} \text{ (i.e., } \sim 0.1 \text{ \% by mass !!!)} \end{aligned}$$