Name: **KEY**

Pledge: I have neither given nor received aid on this test

Chemistry 301 Test #1

Point Total: 100 pts possible

- 8 pts 1. In 2-4 sentences, explain the fundamental basis of quantitative analysis by the following methods. Be complete but succinct.
 - (a) precipitation gravimetry

In precipitation gravimetry, dissolved analyte reacts with excess reagent to form a solid precipitate. The precipitate is filtered, cleaned and dried, and its mass is measured. Since the identify of the analyte's *weighing form* is known, the mass of the analyte in the original solution can be determined, assuming that (i) the precipitate is pure, and (ii) that all of the analyte reacted with the reagent.

(b) titrimetry

In titrimetry, a reagent (the *titrant*) is added to a solution containing the analyte. We measure the quantity (eg, volume) of titrant solution necessary to react with all of the analyte present in the sample solution. From the stoichiometry of reaction between analyte and titrant, the amount of analyte originally present in the dissolved sample can be determined, if the titrant concentration is known.

- 8 pts 2. List the steps that are typically necessary for the analysis of the chemical composition of a material.
 - 1. Decide on the analytical measuring technique (eg, titrimetry, gravimetry, etc)
 - 2. Sample collection and transport (a representative sample should be chosen).
 - 3. Sample treatment (to convert the sample to a form suitable for analysis.)
 - 4. Analysis of the sample using the chosen analytical technique.
 - 5. Calibration or standardization (*if necessary* for quantitation).
 - 6. Data analysis to estimate the analyte concentration in the sample.
- 12 pts 3. The following is a list of solutions that can be used as titrants for various analytical procedures. For each solution, (i) classify the titration by reaction type, and (ii) briefly state (one sentence) how the titrant is standardized.
 - (a) silver nitrate
 - (i) precipitation reaction

(ii) silver nitrate is usually standardized by titrating a known mass of dry, primary standard sodium chloride.

(b) potassium dichromate

(i) redox reaction (it is an oxidant)

(ii) potassium dichromate is a primary standard. Thus, it is dried overnight, weighed, and diluted to a known volume.

(c) sodium hydroxide

(i) acid-base reaction (it is a base)

(ii) sodium hydroxide solution is titrated against a standard potassium hydrogen phthalate (KHP) solution. KHP is a primary standard.

(d) ferrous ammonium sulfate

(i) redox reaction (it is a reductant)

(ii) FAS may be standardized by titrating a standard solution of potassium dichromate, which is available in high enough purity to be considered a primary standard.

- A gravimetric analysis for arsenic in insecticides can be based on precipitation as MgNH₄AsO₄ (220.259 amu). This material tends to precipitate as a colloid. After proper collection, this precipitate can be converted to a superior weighing form, Mg₂As₂O₇ (310.449 amu), by heating to constant mass.
- 8 pts (a) A 1.3567 g insecticide sample yields 127.3 mg of the weighing form. What is the arsenic (74.92159 amu) content of the insecticide?

mol_As := mol_weigh	ing_form·2	g_As := mol_As .74.92159	g_As = 0.0614	originally present in sample
$\operatorname{conc} := \frac{g_\operatorname{As}}{1.3567} \qquad \text{c}$	conc = 4.5289•%	The concentration of As in the insecticide is 4.5289 w/w %		

5 pts (b) If colloid formation cannot be prevented, what might you do to make the precipitate more filterable?

Heating and adding inert electrolyte will cause the colloidal particles to coagulate, making the precipitate more easily filtered.

8 pts (c) Contamination by coprecipitation is always a concern in gravimetric analysis. What types of contamination would you be worried about in this case? What might you do to minimize or eliminate these types of contamination?

With a colloidal precipitate, the most likely source of contamination would be due to surface adsorption, due to the high relative surface area of the precipitate. This form of coprecipitation may be minimized by digestion of the precipitate and by thorough cleaning with dilute, inert electrolyte.

Lattice ion substitution is another possible form of coprecipitation that might affect colloids. Redissolution and reprecipitation is often the only method to reduce this problem, when it occurs (it is less likely than surface adsorption).

12 pts 5. In the most common version of the Mohr method of argentometric titration, potassium chromate is used as a chemical indicator. The endpoint is marked by the appearance of a red precipitate, silver chromate. Explain in some detail, using chemical equations when appropriate, why the change in color gives a good approximation to the equivalence point of an argentometric titration.

A chemical indicator causes the solution to change color at some point during the titration - the point at which the change occurs is taken to be the endpoint of the titration, when all of the analyte has reacted with the titrant. Let's first consider the case of the argentometric titration of cyanide using the Mohr method.

The titration reaction for the Mohr method is

$$Ag^+(aq) + X^-(aq) \Rightarrow AgX(s)$$
 K_T

where X^- is the analyte. The reaction between indicator and titrant produces a red precipitate, whose appearance signifies the endpoint:

$$2Ag^{+}(aq) + CrO_{4}^{2-}(aq) \Rightarrow Ag_{2}CrO_{4}(s) \qquad \qquad K_{IN}$$

For this titration to be successful, it is desirable that the silver precipitates the analyte more readily than the indicator: in other words, that $K_T >> K_{IN}$.

The red chromate precipitate will appear once the concentration of titrant (Ag^+) has risen to a certain level. The concentration of Ag^+ will increase dramatically near the equivalence point, since the analyte will be almost gone:

[insert sketch of titration curve here]

Once the concentration of Ag^+ has risen to the point where the solubility product of Ag_2CrO_4 has been exceeded, then the red precipitate will form, signifying the endpoint. This color change will happen near the equivalence point, since it is at this point in the titration when the Ag^+ concentration rises so abruptly.

10 pts 6. A sample of phosphate (94.97136 amu) detergent weighing 0.6637 g was dissolved in water and titrated with 0.1216 M HCl. The endpoint was observed after addition of 28.33 mL of HCl titrant. What is the concentration of phosphorus (30.97376 amu) in the sample in (a) w/w %? (b) ppm?

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mol_titrant := 0.028330.1216mol_titrant = 3.444910^{-3}mol_analyte := mol_titranta 1:1 reactiong_analyte := mol_analyte \cdot 30.97376g_analyte = 0.1067conc := \frac{g_analyte}{0.6637}conc = 16.0769\%The concentration of phosphate in the<br/>detergent is 16.08 w/w %, or 160,770 ppm.
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¹² pts 7. In a little detail, outline a procedure for the analysis of iron in a water-soluble powder by titration with cerric sulfate. You don't have to be specific (ie, don't give concentrations and volumes) but you should be as complete as possible – in other words, be sure to include all of the necessary steps and describe how they would be executed. You should also include a balanced chemical equation for the titration reaction.

1. Dry the powder overnight, let it cool and weigh out several portions before dissolving in water. Each portion is to be titrated.

2. As with any redox titration, potentiometric endpoint detection is possible with a Pt electrode. Thus, during the titration, the potential of a Pt electrode will be monitored as the titrant is added. In other words, this is to be a potentiometric titration. Since the titrant is an oxidant, the potential, E_h , will become progressively more oxidizing (ie, positive) as the titration progresses.

3. Prepare the titrant solution and standardize it by titrating against a known mass of sodium oxalate, Na₂C₂O₄, which is a primary standard. The standardization titration is $2Ce^{4+} + C_2O_4^{2-} \rightleftharpoons 2Ce^{3+} + 2CO_2$

4. Since cerric sulfate is an oxidant, it is necessary to convert the iron in the solution to its reduced ferrous form. This is done by passing the solution through a reduction column (eg, containing zinc amalgam – a Jones Reductor).

5. Titration proceeds by adding the cerric titrant solution to the dissolved samples. The titration reaction is

$$Ce^{4+} + Fe^{2+} \Rightarrow Ce^{3+} + Fe^{3+}$$

6. Data analysis follows. The endpoint can be identified from the first or second derivatives of the plot of $E_{\rm H}$ against titrant volume (assuming a volumetric titration). The titration has a 1:1 stoichiometry, so the number of moles of cerric cations needed to reach the endpoint will equal the number of moles of iron present in the original solution. This number is converted to a mass and divided by the mass of the dry sample originally dissolved to obtain the iron concentration.

- 8. A 1.00 mL aliquot of fish oil was analyzed for organic nitrogen using the Kjeldahl method. After digestion, the distilled ammonia was collected in a solution of boric acid that contained a small amount of methyl red indicator. This solution then required 62.6 mL of 0.125 M HCl to reach the endpoint.
- 9 pts (a) Briefly describe the chemistry of this determination. Specifically, what happens during
 (i) digestion, (ii) distillation, and (iii) titration? Supplement your explanations with balanced chemical equations.

The sample is digested in concentrated sulfuric acid, which converts the organic nitrogen into inorganic ammonium, NH_4^+ . This solution is basified by adding sodium hydroxide, which converts the ammonium into ammonia:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O.$$

The liberated ammonia is distilled into the flask containing excess boric acid, with which it reacts:

 $NH_3 + H_3BO_3 \rightarrow NH_4^+ + H_2BO_3^-$

After distillation, the solution consists of a mixture of unreacted boric acid, H_3BO_3 , and dihydrogen borate, $H_2BO_3^-$. This mixture is titrated with HCI; the titration reaction is $H_3O^+ + H_2BO_3^- \rightarrow H_2O + H_3BO_3$

where the hydronium ion, H_3O^+ , is from the dissociation of HCl. Thus, for every mole of ammonia originally formed, one mole of HCl must be added to reach the titration endpoint, which is indicated by the change in color of the methyl red indicator.

8 pts (b) Calculate the nitrogen (14.00674 amu) content of the original sample in mg/mL.

conc := $\frac{g_analyte \cdot 1000}{mL_sample}$	conc = 109.6027	The concentra fish oil sample	tion of nitrogen in the e is 109.6 mg/mL.
mol_analyte := mol_titrar	t g_analyte := mol_an	alyte · 14.00674	g_analyte = 0.1096
mL_sample := 1.00	mol_titrant := 0.06260.125	mol_titra	$tant = 7.8250 \cdot 10^{-3}$