

Practice Final Exam Chemistry 312 Spring 2007:**Name(s)**

Answer all the questions in section A, and questions 5 and 6 and up to any three other questions from section B. Pay attention to significant figures (points will be deducted for quoting numerical answers to an inappropriate number of digits). The completed practice exam will be worth 10% of the final exam grade if handed in at the beginning of the final exam.

Section A

1. Your Consulting Laboratory has been approached by the Berkshire Brewing Company to provide analytical support for their entire manufacturing operation (they think it is cost effective to outsource all their analytical work). In the course of conversation with their scientists you realize that the analyses will include the characterization of product odor as well as determination of trace and minor components in a variety of beers. As your lab does not have any modern separation equipment, what would you buy (don't forget to specify the detectors you would need)? (10 points)

You are confident that your lab manager, a UMass Chemistry graduate, can handle the first beer samples, so you take off to Nova Scotia for two weeks. When you come back, you find a list of possible jobs that you need to review. Potential clients have asked about the determination of

- (a) Chlorinated pesticide residues in river water.
- (b) Food dyes in ice cream.
- (c) Fragrance components in Chanel Number 5 (an expensive perfume).
- (d) The aromatic hydrocarbons in gasoline.
- (e) The amino acids in a protein hydrolysate (enzyme catalyzed).
- (f) The inorganic anions in a shower of rain.
- (g) The alcohol content of whisky.
- (h) The lead in seawater.
- (i) The "free" aluminum in lake water (i.e. the aluminum not tightly bound to organic complexing agents or to solid particles).
- (j) The molecular weight distribution of a soluble polymer.

You decide to go with three of these that you could run simultaneously on the three different separation instruments that you have just acquired. Which three analyses might these be? (6 points) What separation technique (6 points) and what detector (6 points) would you use in each case? Give reasons for your choices. (7 points)

2. As the manager of a surface analysis laboratory you have been asked by a chemist working for a steel company to help determine whether she has produced a new type of stainless steel. The hypothesis that you are being asked to test is that the new steel does not rust because it has a strongly adherent surface coating of manganese dioxide. Suggest how this hypothesis might be tested by the use of some surface analytical techniques. (25 points)

3. Describe procedures suitable for the complete dissolution of nine of the following materials for the determination of some trace metal contaminants. (27 points)

(a) paper (b) concrete (c) soil (d) coffee beans (e) bacon	(f) whole blood (g) gold (h) brass (i) table salt (j) antacid tablets
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4. Which of the following statements are true (T) and which are false (F). (1 point each). Pick three statements that you have designated as false and provide explanations as to why these statements are not true. (12 points)

1. It is not possible to establish the accuracy of a new analytical method.
2. Certified reference materials can only be used by government laboratories.
3. The standard additions method of calibration avoids the need for method validation.
4. Method validation involves writing a report for the National Institute of Standards and Technology
5. Matrix effects are always the cause of method inaccuracy.
6. Inappropriate sampling is always the cause of method inaccuracy.
7. There are no standard reference materials for surface analysis methods.
8. Auger electron spectrometry gives no information about the surface chemical environment.
9. The spike recovery method of validation can only be used with liquid samples.
10. Method validation by comparison with the results of another method is only possible for chromatographic methods.
11. X-ray photoelectron spectrometry is also known as electron spectrometry for chemical analysis.
12. Combining a surface analysis technique with ion sputtering provides depth profile information.

Section B. Answer questions 5 and 6 and three others.

5. Answer all of the following parts of the question. (25 points)

(a) What weight of anhydrous calcium carbonate is needed to make 500 mL of a 1000-ppm calcium solution?

(b) A 1000-ppm calcium solution is diluted by taking 5.00 mL and making up to volume in a 100-mL calibrated flask; 10 mL of this solution is then diluted to 250 mL. What is the concentration of Ca in the final solution in ppm?

(c) The UMassChem Corp plans to sell a 10,000 ppm copper solution (for calibration in atomic spectrometry) in 1.00 M nitric acid. What volume of 70% (mass/mass) nitric acid (density 1.42 g/mL) is needed per liter of final solution? What is the concentration of the solution with respect to copper expressed as a mass/volume percentage?

(d) A mixture of acetone and acetic acid contains the same number of moles of each compound. Calculate the mass percentage with respect to each compound.

(e) Ionic strength is defined as $0.5(C_1Z_1^2 + C_2Z_2^2 + \dots + C_nZ_n^2)$ where C_1 to C_n are concentrations in mol L⁻¹ of the various ions in solution, and Z_1 to Z_n are the charges on the corresponding ions. Calculate the ionic strength of a solution that contains 0.50 M magnesium phosphate and 0.50 M ferric acetate.

6. Describe an incident in Neal Stevenson's novel *Zodiac* in which information about chemical composition was needed to "solve a problem" or "take a decision". Name the analyte(s) and the matrix, and suggest how the information might have been obtained, even if this was not the procedure described in the novel. (10 points)

7. Match the following determinations with a spectrophotometric or titrimetric analytical technique that will allow the determination to be performed with the best precision. (4 points each)

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|---|--|
| A | sodium in saliva |
| B | copper in brass |
| C | polynuclear aromatic hydrocarbons separated by gas chromatography |
| D | iron in ferrous ammonium sulfate |
| E | chromium in blood plasma |
| F | arsenic in seaweed |
| 1 | atomic absorption spectrometry with graphite furnace atomization |
| 2 | inductively coupled plasma emission spectrometry |
| 3 | atomic absorption spectrometry with hydride generation and quartz tube atomization |
| 4 | titration with permanganate |
| 5 | infrared absorption spectrometry with a long path-length cell |
| 6 | titration with EDTA |

Each technique may be used only once. Your answer may be in the form A1, B3, C2, etc.

8. Suggest overall analytical procedures for the following analyses. The determination of

- (a) copper, cadmium and lead in pancake mix
- (b) PCBs in the shells of hen's eggs
- (c) iron, nickel and cobalt in chalk
- (d) amino acids in yeast
- (e) iso-octane in gasoline

(25 points)

Pick one of the analyses and explain how you would validate the procedure you have suggested. (5 points)

9. Iron(III) forms a red 1:1 complex with thiocyanate (SCN^-). Thiocyanate itself is colorless. The reaction may be used as the basis of the determination of iron at ppm (parts per million) concentrations, even though the equilibrium constant for the reaction is only 1.00×10^2 . This value is too low for the quantitative determination of iron by titration with thiocyanate, as the product is not 99.9% formed when an equivalent amount of thiocyanate has been added. Explain how the limitation of this low value of the equilibrium constant is overcome in the spectrophotometric procedure. (5 points)

To a 50.00-mL sample of mine waste run-off was added 10 mL of 0.1 M potassium thiocyanate solution and the resulting solution was diluted to 250.0 mL. A single standard was prepared by adding the same amount of thiocyanate solution to 20.00 mL of a solution containing 100.0 mg L^{-1} of iron(III) and, again, the mixture was diluted to 250.0 mL. A blank solution was prepared in the same way with 50.00 mL of water. Absorbances were measured in a 1.00-cm cell in a single-beam spectrophotometer, and the following values were obtained: blank 0.008, standard 0.676, and sample 0.224. Calculate the concentration of iron in the run-off in ppm (15 points) and mol L^{-1} (5 points) What is the molar ratio of thiocyanate to iron in the standard solution? (5 points)

10. In a journal article, the researchers present the results of replicate analyses. The results are quoted as the mean $\pm x$, where x is either the standard deviation or the 95% confidence interval, whichever is the smaller. How many replicate measurements must be made in order that the 95% confidence interval is quoted? (10 points)

m	1	2	3	4	5	6	7	8	9	10
$t(95\%)$	12.71	4.30	3.18	2.78	2.57	2.45	2.36	2.31	2.26	2.23

m is the number of degrees of freedom.

Two analytical methods are to be compared by using each of them to analyze the same samples over a period of several weeks. Each sample is divided into two portions and analyzed by each of the techniques simultaneously. The concentration of the analyte in the samples varies from approximately 1.00 mg kg^{-1} to approximately 100 mg kg^{-1} . The following results are obtained.

sample number	1	2	3	4	5
method 1	1.05	26.4	35.7	89.3	67.9
method 2	1.26	30.5	41.5	99.4	73.8

On the basis of a *paired* t-test, is there a significant difference between the results of the two methods? (10 points). Give reasons for your answer. (5 points). The 95% confidence interval about the mean of a set of data is given by ts/\sqrt{n} , where t is found from tables, s is the standard deviation and n is the number of replicate measurements.

11. Suggest a separation technique and detector that would be suitable for inclusion in an overall method for the determination of the following, and briefly describe an appropriate sample pretreatment procedure.

- (a) nitrate in cranberry juice.
- (b) chlorophyll in oak leaves
- (c) aluminum in lake water.
- (d) iron in iron ore
- (e) lead in neonatal blood (the blood of newly born children).

There is a maximum of 5 points for each part. This maximum will only be awarded if at least 4 *different* techniques are appropriately chosen.

12. For which of the following analyses could atomic spectrometry *not* be used? (10 points). The determination of

- (a) chloride by precipitation of silver chloride with excess silver nitrate.
- (b) vitamin B₁₂ (cyanocobalamin) after HPLC separation
- (c) neon in a mixture of inert gases
- (d) bicarbonate in baking powder
- (e) the solubility of barium sulfate

For those situations for which you think atomic spectrometry cannot be used, explain your answers. (10 points) Draw a schematic diagram of an atomic absorption spectrometer with a graphite furnace atomizer. (5 points).

Possible relevant information.

The formula for the calculation of Student's t is not needed to answer question 10; a *paired* t-test should be used in which the average difference between, or ratio of, the results for the two methods for each sample is examined to see whether it differs significantly from 0, or 1, respectively. Derivatization means the formation of a product from an analyte species, by the addition of a reagent, which can be detected by a particular instrumental technique.

Atomic weights: C 12.011, N 14.00674, H 1.00794, Cl 35.4527, S 32.066, O 15.9994, Ca 40.078,