Analytical Cumulative Exam - September 11, 2004
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This exam deals with analytical problem solving. Six situations are given below for which you are to formulate a solution strategy. Your strategies will be evaluated based on the following criteria:

a. If not already stated in the problem, what chemical parameters must be measured and how do they relate to solving the problem?

b. What analytical method(s) will be used to measure these chemical parameters and why are these method(s) best suited for this application? (Note: It may be that several methods are equally suitable. If that is the case, simply choose one for the remaining questions below.)

c. How will samples be acquired? Are there any special procedures that must be followed or special problems that must be overcome?

d. How will samples be prepared for analysis? Again, are there any special procedures that must be followed or special problems that must be overcome?

e. Is quantitative analysis needed? If so, what will you use as standards? If standards are not likely to be commercially available, how will you make them? What approach will you use for quantitative analysis (calibration curve, standard addition) and why is it the best approach for this application?

Analytical Problems (Question 1 is worth 10 points; Questions 2-7 are worth 15 points each)

1. This problem concerns an analytical measurement strategy for the compound benzo(a)pyrene whose structure is given below. This compound is both a carcinogen and a mutagen.

![Structure of benzo(a)pyrene](image)

Aldrich Chemical sells reagent grade benzo(a)pyrene that is listed as 98% pure. The 2% impurity is due to other C_{20}H_{12} isomers. Suggest a fast, simple, relatively inexpensive method that Aldrich could use as a quality control check to make sure that the material they sell is at least 98% pure.

2. Nitrate and sulfate are two major inorganic constituents of atmospheric aerosols. The concentrations of these ions in airborne particles have important environmental ramifications. Therefore, there is a need to develop analytical methods which can accurately determine small amounts (nanograms to micrograms) of these ions in particulate samples collected from the atmosphere. In a typical set-up, air is drawn through a Teflon coated quartz filter by a small pump for a specified period of time. The filter is removed and rinsed with water. The concentrations of nitrate and sulfate in the rinse-water are then determined. How would you quantitate trace levels of nitrate and sulfate in these solutions? (Note that there are many different water-soluble organic and inorganic species in aerosol particles. Other major
inorganic components include sodium, ammonium, magnesium, calcium, chloride and carbonate ions.)

3. Omeprazole (Prilosec®) is a drug used to treat acid reflux (Gastroesophageal Reflux Disease). Omeprazole is a white crystalline powder which decomposes at about 155 °C. It is a weak base solubile in methanol and isopropanol, and slightly soluble in water. Typically, omeprazole is administered to a patient in delayed-release capsules containing 10-50 mg. The capsules degrade slowly in the digestive tract and release the drug over a 3 hour period. Once in blood plasma, omeprazole metabolizes rather quickly, with a half-life of less than 1 hour. Omeprazole has a molecular formula of C₁₇H₁₉N₃O₃S and the structure shown below. Devise a method to quantitate the amount of omeprazole in a patient’s blood stream as a function of time after the capsule is ingested.

4. Mercury is a significant contaminant in the ocean. It has a tendency to bioaccumulate in aquatic organisms – shark and swordfish are particularly susceptible to bioaccumulation, but white tuna is also of great concern because so much of it is consumed by the general population. Devise a method that the food and drug administration could use to quickly screen many cans of tuna for the amount of mercury. Concentration levels are typically on the order of 200 ng mercury per gram of tuna; concentrations over about 1 µg/g would be of great concern.

5. The structure of a styrene-butadiene copolymer is shown below. The average molecular weight is typically between 20,000 and 100,000 g/mol. Your company would like to analyze a sample of a competitor's product (the sole of an athletic shoe) containing this copolymer to determine exactly what material they are using. Two pieces of information are required: 1) the molecular weight distribution – both the average molecular weight and the width of the distribution (commonly referred to as the polydispersity) and 2) the relative amounts of styrene and butadiene that were used to make the copolymer (i.e. the relative values of n and m below). Explain how you would obtain this information. Note that styrene-butadiene copolymers are nonvolatile (they decompose upon heating) but they are slightly soluble in toluene.

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\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \\
\text{O} & \quad \text{CH}_2 \\
\text{S} & \quad \text{CH}_2 \\
\text{N} & \quad \text{CH}_3 \\
\text{H}_3\text{CO} & \quad \text{OCH}_3
\end{align*}
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6. In a recent A-page article in the August 1, 2004 issue of *Analytical Chemistry*, the possibility of using breath tests for diagnosing diseases is briefly discussed. The basic idea is that the distribution of volatile inorganic (O₂, CO₂, CO, NO) and/or organic (major products of metabolism such as ethane, acetone, methanol plus hundreds if not thousands of other species) compounds in breath may be altered in a characteristic way when a person is in a specific disease state. Devise a strategy to quantify the amounts of these species in exhaled air. Preferably, the method(s) used will be suitable for use in a clinical setting.

7. Arsenic is a continuing problem in drinking water. If arsenic is present in the bedrock underlying a groundwater source, it can be released into the water. Ingestion of high levels of arsenic over several years can cause cancer as well as neurological and cardiovascular problems. When inorganic arsenic is ingested [As(OH)₃ and AsO(OH)₃, As(III) and As (V) respectively] it is metabolized by biomethylation to species such as As(CH₃)ₓ(OH)ᵧ and AsO(CH₃)ₓ(OH)ᵧ where x+y=3. Because the methylated species are thought to be less toxic than the respective inorganic forms, biomethylation is thought to be an important detoxification mechanism for human exposure to arsenic. Devise a method that can be used to determine the amounts of these species in urine and/or blood samples of people exposed to arsenic in drinking water.