Taibah University Faculty of Science Chemistry Department SELECTED TOPICS IN ANALYTICAL CHEMISTRY (CHEM 437) 1 CHEM 437 Instructor: Bader Altayeb E-mail: BTAYEB@taibahu.edu.sa Required textbook: “Sample Preparation Techniques in Analytical Chemistry” 2 Fundamentals of Sample Preparation Schedule of Assessment Tasks for Students During the Semester Assessment task Week Due Proportion of Total Assessment 1 Participation Through the term 5 2 Activity/homework Through the term 5 3 Written Exam (1) To be notified 20 4 Written Exam (2) To be notified 20 5 Oral presentation/or research paper To be notified 10 6 Final Exam (theoretical) To be notified 40 Total 100 3 1. Introduction 4 Content: 1.1.What is meant by sample preparation? 1.2.Purpose Of Sample Preparation 1.3.Overview On Sample Preparation 1.4.Types of Sample 5 Fundamentals of Sample Preparation 1.1.What is meant by sample preparation? v In analytical chemistry, sample preparation refers to the ways in which a sample is treated prior to its analyses. q It is the processes in which a representative piece of material is extracted from a larger amount and readied for analysis. q Sampling and sample preparation have a unique meaning and special importance when applied to the field of analytical chemistry q Most analysis is still done by taking a part (or portion) of the object under study (referred to as the sample) and analyzing it in the laboratory (or at the site). 6 Fundamentals of Sample Preparation ● The purpose of an analytical study is to obtain information about some object or substance. The substance could be a solid, a liquid, a gas, or a biological material. ● The information to be obtained can be varied. It could be the chemical or physical composition, structural or surface properties, or a sequence of proteins in genetic material. ● It is not possible to find every bit of information of even a very small number of samples. For the most part, the state of current instrumentation has not evolved to the point where we can take an instrument to an object and get all the necessary information. 7 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Some common steps involved in the process are shown in Figure 1.1. The first step is sampling, where the sample is obtained from the object to be analyzed. This is collected such that it represents the original object. Sampling is done with variability within the object in mind. For example, while collecting samples for determination of Ca+2 in a lake, it should be kept in mind that its concentrations can vary depending on the location, the depth, and the time of year. The next step is sample preservation. This is an important step, because there is usually a delay between sample collection and analysis. Sample preservation ensures that the sample retains its physical and chemical characteristics so that the analysis truly represents the object under study. 8 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE sample preparation is the next step, Most samples are not ready for direct introduction into instruments. For example, in the analysis of pesticides in fish liver, it is not possible to analyze the liver directly. The pesticides have to be extracted into a solution, which can be analyzed by an instrument. There might be several processes within sample preparation itself. Some steps commonly encountered are shown in Figure 1.2. However, they depend on the sample, the matrix, and the con-centration level at which the analysis needs to be carried out. 9 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Once the sample preparation is complete, the analysis is carried out by an instrument of choice. A variety of instruments are used for different types of analysis, depending on the information to be acquired: For example, chromatography for organic analysis, atomic spectroscopy for metal analysis, capillary electrophoresis for DNA sequencing, and electron microscopy for small structures. 10 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE The sample preparation depends on the analytical techniques to be employed and their capabilities. For instance, only a few microliters can be injected into GC. Sampling, sample preservation, and sample preparation are all aimed at producing those few microliters that represent what is in the fish. It is obvious that an error in the first three steps cannot be rectified by even the most sophisticated analytical instrument. So the importance of the prior steps, in particular the sample 11 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Common analytical instrumentation and the sample preparation associated with them are listed in Table 1.1. 12 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Methods of Quantitation Almost all measurement processes, including sample preparation and analysis, require calibration against chemical standards. The relationship between a detector signal and the amount of analyte is obtained by recording the response from known quantities. Similarly, if an extraction step is involved, it is important to add a known amount of analyte to the matrix and measure its recovery. 13 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Such processes require standards, which may be prepared in the laboratory or obtained from a commercial source. An important consideration in the choice of standards is the matrix. For some analytical instruments, such as x-ray fluorescence, the matrix is very important, but it may not be as critical for others. Sample preparation is usually matrix dependent. It may be easy to extract a polycyclic aromatic hydrocarbon from sand by supercritical extraction but not so from an aged soil with a high organic content 14 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Calibration Curves The most common calibration method is to prepare standards of known concentrations, covering the concentration range expected in the sample. The matrix of the standard should be as close to the samples as possible. For instance, if the sample is to be extracted into a certain organic solvent, the standards should be prepared in the same solvent. The calibration curve is a plot of detector response as a function of concentration. It is used to determine the amount of analyte in the unknown samples. The calibration can be done in two ways, best illustrated by an example. Let us say that the amount of lead in soil is being measured. The analytical method includes sample preparation by acid extraction followed by analysis using atomic absorption (AA). 15 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE 16 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Preservation Of Samples The sample must be representative of the object under investigation. Physical, chemical, and biological processes may be involved in changing the composition of a sample after it is collected. v Physical processes that may degrade a sample are volatilization, diffusion, and adsorption on surfaces. v chemical changes include photochemical reactions, oxidation, and precipitation. v Biological processes include biodegradation and enzymatic reactions. – sample degradation becomes more of an issue at low analyte concentrations and in trace analysis. 17 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE ● The sample collected is exposed to conditions different from the original source. For example, analytes in a groundwater sample that have never been exposed to light can undergo significant photochemical reactions when exposed to sunlight. ● It is not possible to preserve the integrity of any sample indefinitely. Techniques should aim at preserving the sample at least until the analysis is completed. ● A practical approach is to run tests to see how long a sample can be held without degradation and then to complete the analysis within that time. 18 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Ø Common steps in sample preservation are the use of: proper containers, temperature control, addition of preservatives, and the observance of recommended sample holding time. Ø The holding time depends on the analyte of interest and the sample matrix. stable for months, whereas Cr(VI) is stable for only 24 hours. Ø Holding time can be determined experimentally by making up a spiked sample (or storing an actual sample) and analyzing it at fixed intervals to determine when it begins to degrade. 19 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE The changes that take place in a sample are either chemical or biological. ØIn the chemical changes , certain changes occur in the chemical structure of the constituents that are a function of physical conditions. ● Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. 20 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE ● Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. 21 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE 1.4.4. Chemical Changes q A wide range of chemical changes are possible. q For inorganic samples, controlling the pH can be useful in preventing chemical reactions. For example, metal ions may oxidize to form insoluble oxides or hydroxides. q The sample is often acidified with $HNO3$ to a pH below 2, as most nitrates are soluble, and excess nitrate prevents precipitation. q Other ions, such as sulfides and cyanides, are also preserved by pH control. Samples collected for $NH3$ analysis are acidified with sulfuric acid to stabilize the $NH3$ as $NH4SO4$. 22 ● Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. as a general rule, it is best to analyze the samples as soon as possible after collection. ● Samples may also contain microorganisms, which may degrade the sample biologically. Extreme pH (high or low) and low temperature can minimize microbial degradation. Adding biocides such as mercuric chloride or pentachlorophenol can also kill the microbes. 23 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Absorption of Gases from the Atmosphere –Gases from the atmosphere can be absorbed by the sample during handling, for example, when liquids are being poured into containers. Ø–Gases such as $O2$, $CO2$, and volatile organics may dissolve in the samples. v Oxygen may oxidize species, such as sulfite or sulfide to sulfate. v Absorption of $CO2$ may change conductance or pH. This is why pH measurements are always made at the site. v $CO2$ can also bring about precipitation of some metals. v Dissolution of organics may lead to false positives for compounds that were actually absent. – Blanks are used to check for contamination during sampling, transport, and laboratory handling. 24 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE q ORGANIC SPECIES CAN ALSO UNDERGO CHANGES DUE TO CHEMICAL REACTIONS: ● Organics can also react with dissolved gases; for example, organics can react with trace chlorine to form halogenated compounds in treated drinking water samples. In this case, the addition of sodium thiosulfate can remove the chlorine. 25 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Preservation of samples v Preservation methods are limited to pH control, chemical addition, amber or opaque bottles, filtration, refrigeration, and freezing. v To minimize the potential for volatilization or biodegradation between sampling and analysis, keep the sample as cool as possible without freezing. v Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. v Regardless of the nature of the sample, complete stability for every constituent can never be achieved. v At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. 26 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Preservation of samples o Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes, (3) reduce volatility of constituents, (4) reduce absorption effects. 27 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Preservation of samples vSample preservation should be performed immediately upon sample collection vFor composite samples each aliquot should be preserved at the time of collection. vWhen use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4 deg. C until compositing and sample splitting is completed. vChoice of Proper Containers vContainer may :Plastic (P) or Glass (G). vFor metals, polyethylene with a polypropylene cap (no liner) is preferred. 28 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Choice of Proper Containers q The surface of the sample container may interact with the analyte. § The surfaces can provide catalysts (e.g., metals) for reactions or just sites for irreversible adsorption. § For example, metals can adsorb irreversibly on glass surfaces, so plastic containers are chosen for holding water samples to be analyzed for their metal content. These samples are also acidified with $HNO_3$ to help keep the metal ions in solution. ● Organic molecules may also interact with polymeric container materials (plastic container). Plasticizers such as phthalate esters can diffuse from the plastic into the sample, and the plastic can serve as a sorbent (or a membrane) for the organic molecules 29 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE ● Consequently, glass containers are suitable for organic analytes. ● Storing the sample in amber bottles prevents photooxidation of organics (e.g., polynuclear aromatic hydrocarbons). ● Bottle caps should have Teflon liners to preclude contamination from the plastic caps. ● Oily materials may adsorb strongly on plastic surfaces, and such samples are usually collected in glass bottles. ● A sonic probe can be used to emulsify oily samples to form a uniform suspension before removal for analysis. ● Oil that remains on the bottle walls should be removed by rinsing with a solvent and be returned to the sample 30 SAMPLE PREPARATION: AN ANALYTICAL PERSPECTIVE Preservation of samples v Maximum holding time is 24 hours when sulfide is present. v Optionally, all samples may be tested with lead acetate paper before the pH adjustment in order to determine if sulfide is present. vIf sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. vThe sample is filtered and then NaOH is added to pH 12. vSamples should be filtered immediately on-site before adding preservative for dissolved metals. v For samples from non-chlorinated drinking water supplies conc. $H_2SO_4$ should be added to lower sample pH to less than 2. The sample should be analyzed before 14 days. 31 Table 1.3 lists some typical preservation methods. 32