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Introductory Chapter: Evolution of Sample Preparation

Massoud Kaykhaii

1. Importance of sample preparation in chemical analysis

The start of chemistry as a science can be dated back to the time that the textbook “*Traité élémentaire de chimie*” was written by French chemist Antoine-Laurent Lavoisier in 1789. This book can be regarded as the beginning of entry on measurement in chemistry. Lavoisier wrote: “When 16 ounces of alcohol are burnt in an apparatus properly adapted for collecting all the water disengaged during the combustion, we obtain from 17 to 18 ounces of water” [1], which clearly shows that a “gravimetric analysis” was performed during his experiments. In today’s modern chemical analysis, still balances are the basis of all measurements. An analytical method is carried out to help us gather “analytical data” to solve problems. From a general point of view, these data can be either qualitative or quantitative. Qualitative analysis tries to find an answer to the question yes/no to the presence of a particular analyte in a sample, while quantitative analysis provides an answer to the basic question of “how much” of an analyte of interest presents in a sample. There is another term, semiquantitative analysis, which concerns whether the analyte is below or above a certain concentration. Each chemical analysis needs to be performed in several consecutive steps; sampling, sample preparation (including dilution, filtration, deproteinization, derivatization, centrifugation, purification, isolation and separation, extraction and preconcentration), quantitative analysis (i.e., introducing (the extract of) sample into an analytical instrument), statistical evaluation of the obtained data (i.e., instrument’s output), and making decision. Extraction is the major part of sample preparation and separation and can be considered as the partition of a solute between two immiscible solvents. One solvent contains samples with analytes and the second one is the extraction phase. It should be noted that before completion of each step, the next step cannot be started. Moreover, the raise of any error in each step means that the chemical analysis process needs to be repeated from the same step. It is well known that what causes most errors in chemical analysis is the sample preparation step (**Figure 1**) [2]. This step is also the most time-consuming and also is highly laborious [3]. Even having the highest expertise and best laboratory chemical, devices, and glassware, total systematic and random errors for sampling and sample preparation can occur from a few percentages to several orders of magnitude. As a result, any progress, improvement, or optimization in this “bottle neck” step of a chemical analysis process greatly boosts performance of the overall analysis, including precision, accuracy, and rapidity of the method. On the other hand, while analytical instrumentation in the recent years has continued to benefit from improvements such as tiny size, fastness, high resolution, low cost of capital investment, maintenance, and operation, still their limit of detection is not enough to be able to directly analyze a sample with ultra-trace amounts of a particular analyte. Besides, interferences from the matrix of the sample and its incompatibility (due to the dirtiness of real samples) with an

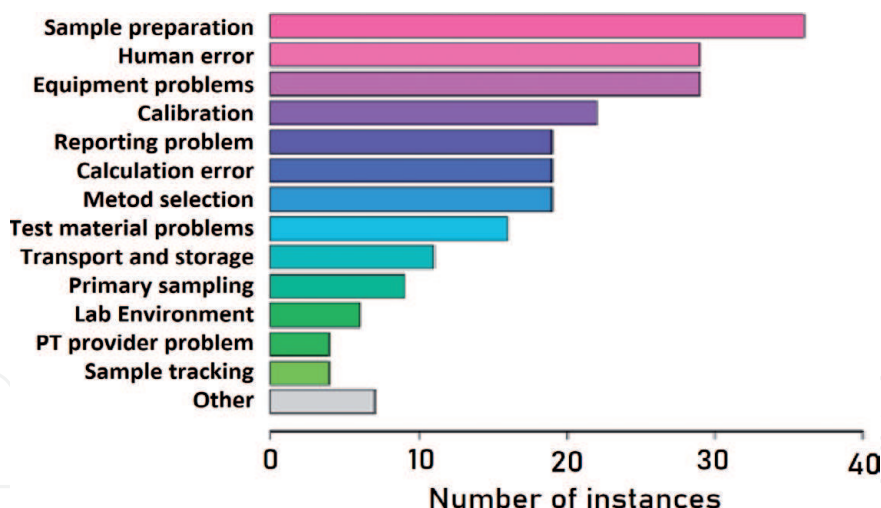


Figure 1.
Causes of error in chemical analysis (copyright 2013, Royal Society of Chemistry. Reprinted from Ref. [2] with permission).

analytical instrument make a cleanup and sample preparation step indispensable. Even with higher concentration of the analyte, this step is necessary for protecting instruments, for example, to increase the life of chromatographic columns.

2. Exhaustive and nonexhaustive extraction

Traditionally, sample preparation consisted of sample dissolution, purification, and extraction that were carried out with liquid-liquid extraction (LLE). For many

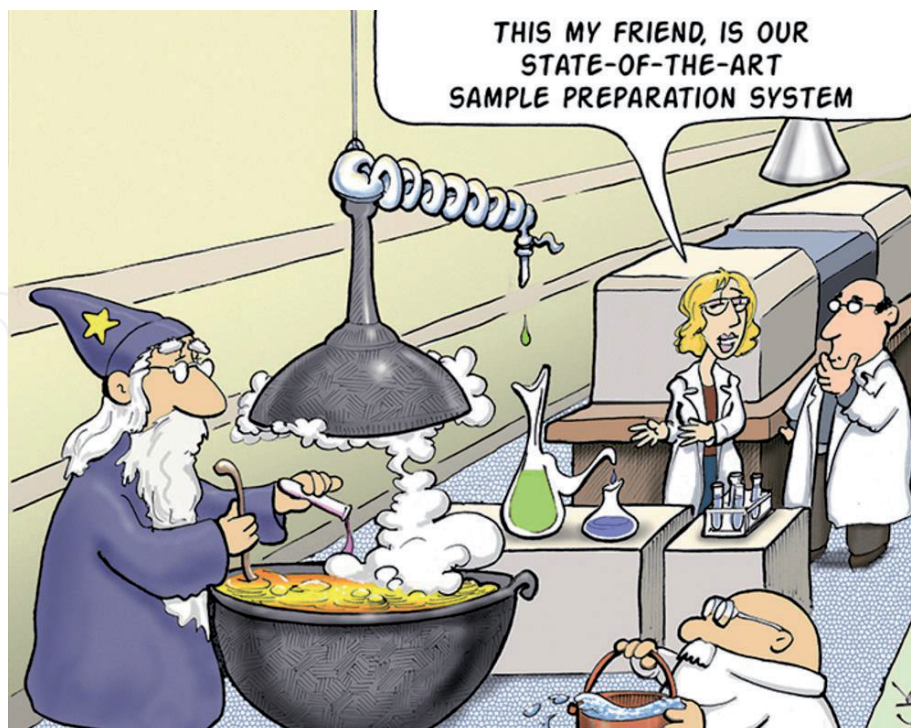


Figure 2.
“They have the very best instrumentation, for example to determine the composition of drinking water at the sub-parts per trillion level with triple quadrupole mass specs and gas chromatography. But do you know what their sample preparation is? They take one liter of water, add 100 ml of dichloromethane, shake it for half an hour. Then they put the dichloromethane in a vial, evaporate it down to 0.5 ml—don’t worry, it’s just going into the air—and then they inject. We need to do something about that...” Courtesy of Analytical Scientist, 27/7/2014.

years, classical extraction methods as sample preparation tools were in use. For example, Soxhlet extractor invented in 1879 by Franz von Soxhlet still is widely in use.

Depending on the receiving phase in contact with the sample solvent, extraction can be either sorbent-based (in case of solid extracting phase) or solvent-based (in case of liquid extracting phase). Through the years, both methods are applied in many formats and versions and are simple and effective. They are classified as exhaustive extraction techniques, which mean a significant amount of the target analyte is extracted to the receiving phase during extraction. The disadvantages with liquid-liquid extraction include the use of large volumes of organic solvent (**Figure 2**), cumbersome glassware, and high cost. Furthermore, LLE often creates emulsions with aqueous samples that are difficult to extract, and it is not easily automated. These limitations were overcome with solid-phase extraction (SPE) invention in the mid-1970s. Besides reduction of volume of organic solvents, SPE showed advantages such as miniaturization of the device, multiclass compound extraction and automation, and/or high-throughput determination [4]. Solvents in the order of 100 ml, which are needed in LLE, are reduced to a few milliliters in SPE. Moreover, normal phase, reversed phase, ion exchange, mixed mode, and selective sorbents (such as molecularly imprinted polymers) are now available commercially to cover any type of analytical extraction.

3. Miniaturized extraction

Solid-phase microextraction (SPME) is a simple and efficient, solventless sample preparation method, invented by J. Pawliszyn in 1989 as an attractive choice primarily applied for volatile organic compounds extraction applications [5]. This method opened a new door to the sample preparation technique, known as microextraction methods nowadays. Microextraction methods are based on equilibrium between sample solution (or its headspace) and extraction phase, which has much smaller volume than the sample itself. While there were major drawbacks such as fragility of the SPME fibers, its majority of applications was limited to gas chromatography; after commercialization, it became the most popular microextraction. In 1999, J. Namiesnik proposed the term green analytical chemistry (GAC) [6], and then 12 principles of GAC were proposed by A. Gałuszka et al. as: 1. direct analytical techniques, 2. minimize sample size and number of samples, 3. in situ measurements, 4. integration of analytical processes and operations to reduce energy and reagents usage, 5. automation and miniaturization of methods, 6. avoid derivatization, 7. avoid waste generation and provide appropriate waste management, 8. multi-analyte or multi-parameter methods, 9. minimize the use of energy, 10. preferable use of reagents obtained from renewable sources, 11. elimination of toxic reagents, 12. increase of the safety of the operator [7]. All these rules are compliant in microextraction methods, which resulted in these newly introduced techniques becoming at the center of attention of analytical chemistry researchers (**Figure 3**) [8]. These techniques were also greener sample preparation methods in terms of waste generation and energy consumption. From the point of view of the above 12 principles, methods of in-field analysis can be considered as the foremost green techniques, which were in use before microextraction. These techniques became even more efficient and greener by the introduction of smart phones into analytical chemistry as the detection and data analysis/transmission devices [9]. Specialized sample preparations, such as self-assembly of analytes on nanoparticles for surface enhancement, have also evolved in parallel. Another aspect that makes microextraction methods more in demand is because modern analytical chemistry tends to prepare methods that are more around interdisciplinary research areas in biotechnology, environmental science, and materials science, etc.

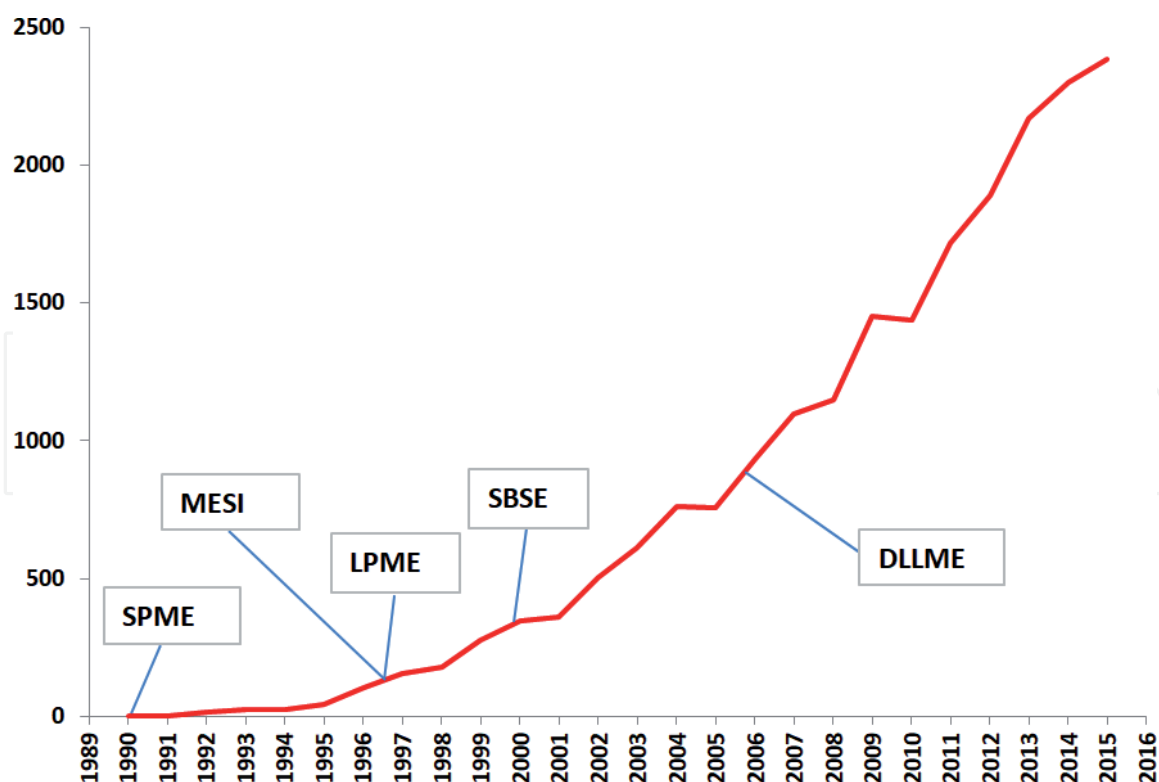


Figure 3.

Number of papers published since the introduction of SPME on applications of microextraction to chemical analysis. SPME, solid-phase microextraction; MESI, membrane extraction with a sorbent interface; LPME, liquid-phase microextraction; SBSE, stir bar sorptive extraction; DLLME, dispersive liquid-liquid microextraction (copyright 2017 Taylor & Francis Group, LLC. Reprinted from Ref. [8] with permission).

Analytical microextraction can be defined as a sample preparation step using volumes in the microliter or nanoliter range of extracting phase (solid, semisolid polymeric, or liquid material) [4]. They include 12 principles of GAC for sample treatment, especially in terms of miniaturization, in-field analysis, automation, and rapidity. These techniques are equilibrium-based extraction methods, which mean that the analyst may not know when equilibrium is reached, and the equilibrium distribution may necessitate multiple extractions [10]; this is the main drawback of these techniques. Besides SPME, analytical chemists invented a wide range of other microextraction techniques, including: single-drop microextraction, microextraction in packed syringe, membrane extraction with a sorbent interface, liquid-phase microextraction, dispersive liquid-liquid microextraction, accelerated solvent extraction, vortex-assisted microextraction, dispersive solid-phase extraction, pressurized liquid extraction, fabric phase sorptive extraction, micro solid-phase extraction, microwave-assisted solvent extraction, stir bar sorptive extraction, quick, easy, cheap, effective, rugged, and safe extraction (QuEChERS), magnetic solid-phase extraction, salt saturated single-drop microextraction, micro-cloud point extraction, matrix solid-phase dispersion, pipette tip micro solid-phase extraction, and many more.

Unluckily, in many universities and analytical chemistry textbooks, importance and steps of sampling and sample preparation are not mentioning during analytical courses. It is always to be remembered that because of the importance of these steps in the generation of precise and accurate qualitative, semiquantitative, and quantitative analytical data, such skills are subject of great importance to be taught to the students. In terms of routine application of miniaturized microextraction methods in standard operating procedures, microextraction requires more time, but once the procedure is optimized, these methods are more convenient, greener, and more economical in comparison to traditional exhaustive extraction methods.

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