Use of Accelerated Solvent Extraction to Improve Laboratory Workflow

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Executive Summary

Accelerated solvent extraction is a sample preparation technique that greatly reduces the amount of time and solvent required to achieve analyte extraction. This technique uses elevated temperature and pressure to accelerate the partitioning of key analytes for a diverse array of sample matrices. Accelerated solvent extraction is used in a broad range of industries and can help the analytical laboratory greatly improve their productivity by reducing the time required to achieve sample extraction.

Keywords

Accelerated solvent extraction, ASE, Soxhlet extraction, liquid-solid extraction, microwave-assisted extraction, sample preparation, analytical laboratory, analytical workflow

Introduction

The modern analytical laboratory is continually striving to develop methods that accomplish the desired results in a more rapid, less expensive, and automated manner to improve productivity. In recent years, substantial improvements such high pump flow rates, smaller column part diameters, and novel detectors have improved analytical techniques tremendously. While these improvements help the laboratory achieve detection limits and resolution at unparalled speeds, they do little to address the cumbersome sample preparation techniques that precede them. Often times, analytical chemists are still seen preparing samples for chromatographic analysis using the same type of Soxhlet apparatus that was used to prepare samples for the first gas chromatograph instruments over 50 years ago. These traditional extraction techniques suffer from several shortcomings and incur high costs for laboratories. They often take several hours per sample, use hundreds of milliliters per sample, and require a great deal of labor and user intervention that lengthens the process of sample preparation.

In addition to the costs associated with sample preparation, studies have also shown that the biggest bottleneck and source of errors in any analytical process occur during sample preparation. Due to substantial amounts of time and solvent required using traditional techniques, it is critical that sample preparation is performed correctly, as any variation in extraction conditions can profoundly affect the percent recoveries of the analytes of interest. In an effort to address cumbersome sample preparation, the technique of accelerated solvent extraction was invented to help bring this vital stage of the workflow up to par with the powerful analytical techniques that exist today.

What Is Accelerated Solvent Extraction?

Accelerated solvent extraction is an automated extraction technique that uses elevated temperature and pressure to achieve extraction from solid and semisolid matrices in very short periods (12-20 minutes per sample). For example, 10 g of sample can be extracted in less than 15 minutes, using less than 15 mL of solvent. There are several physicochemical factors that help accelerated solvent extraction substantially reduce the amount of time and solvent required for extraction and each is described below.

Temperature

Temperature is the most important parameter used in accelerated solvent extraction. As the temperature is increased, the viscosity of the solvent is reduced, thereby increasing its ability to wet the matrix and solubilize the target analytes. This enables the solvent to penetrate the pores of the matrix more easily. It is a well known fact that the use of higher temperatures increases the capacity of solvents to solubilize analytes. For example, the solubility of anthracene increases nearly 13-fold as the temperature increases from 50 to 150 °C. Increasing the temperature also leads to faster diffusion rates. This means that analytes move more quickly from the matrix from which they are extracted to the solvent at higher temperatures. Increased temperature also makes it easier to disrupt solute-matrix interactions (dipole attractions, van der Waals forces, hydrogen bonding, etc.) and remove analytes from the matrix. The net effect is that doing extractions at elevated temperatures means that extractions happen much faster and use less solvent.

Pressure

Temperature alone is not enough to accomplish efficient extractions because many of the organic solvents used in extractions boil at relatively low temperatures. This is one limitation of techniques such as Soxhlet or automated Soxhlet; the highest temperature at which extractions take place is the boiling point of the solvent. If sufficient pressure is exerted on the solvent during the extractions, temperatures above the boiling point can be used. This means that all of the advantages of working at elevated temperature can be realized even with solvents with relatively low boiling points. Operating at elevated pressures also helps the overall extraction process to happen more quickly. Pumping solvent through a packed bed is easier at elevated pressures. Pressurized solvent is forced into the pores of the sample matrix, coming into close contact with analytes in those areas. Hence, the combination of elevated temperature and pressure allows extractions to occur rapidly and completely.

Solvent Composition

For an efficient extraction, the solvent must be able to solubilize the target analytes while leaving the sample matrix intact. The polarity of the extraction solvent should closely match that of the target compounds. The common adage of “like dissolves like” is very applicable in accelerated solvent extraction. Mixing solvents of differing polarities can be used to extract a broad range of compound classes. Generally, if a particular solvent has been shown to work well in a conventional procedure, it will also work well in accelerated solvent extraction.

Solvent choice will also determine the level of coextractables along with the analytes. Generally, the more polar the solvent or solvent mixture, the less selective it will be for extracting analytes of interest. Solvents that exhibit marginal results at ambient conditions may perform adequately under accelerated solvent conditions. Most liquid solvents, including water and buffered aqueous mixtures, can be used in accelerated solvent extraction. Strong acids (HCl, HNO_3, H_2SO_4) are not recommended for use with stainless steel cells because they may damage the cells. However, with the advent of Zirconium based cells, small amounts of these acids can be used. When required, weak acids such as acetic or phosphoric can be used.

Static Extraction Cycles

The use of static extraction cycles was developed to introduce fresh solvent during the extraction process, which helps to maintain favorable extraction equilibrium. This effectively approximates dynamic extraction conditions without the need for troublesome flow restrictors to maintain pressure. Static cycles have proven to be useful for sample types with a very high concentration of analyte, as well as samples with difficult to penetrate matrices. The static time can be adjusted to minimize the total extraction time. For example, three 3-minute static cycles can be used in place of one 10-minute static step. When low temperature extractions are desired (< 75 °C), multiple static cycles should be used to compensate for the smaller amount of solvent introduced during the heat-up step, as the static valve pulses to regulate the pressure.

How Does Accelerated Solvent Extraction Work?

Accelerated solvent extraction was first described in 1995 and 1996 (1–9) and has grown steadily as an extraction technique since that time.

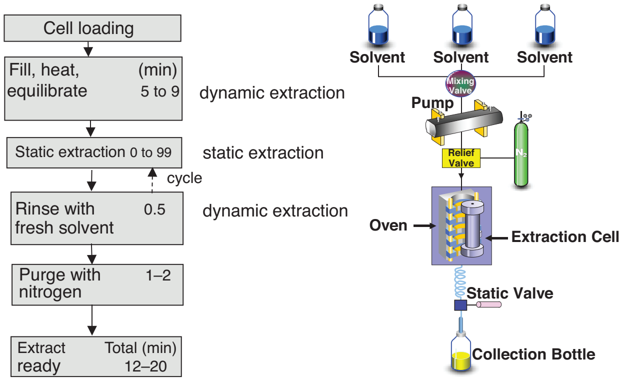

Figure 1. Accelerated solvent extraction process.

Figure 1 shows a schematic of the accelerated solvent extraction process. To perform an extraction, the solid sample is loaded into a sample cell (1 - 100 mL) and the end caps are tightened by hand onto the cells. The filled sample cells are loaded onto a cell tray and collection vessels (bottles or vials) are loaded onto a collection tray. A robotic arm transfers each cell separately into the oven for extraction. The oven is maintained at the selected operating temperature throughout the extractions (room temperature to 200 °C). The cell design and associated fluid apparatus allow operation of the extractions at elevated pressures (1500 psi) to maintain the solvents as liquids at temperatures above their boiling points. The temperature and pressure are controlled independently for each cell regardless of the solvent used, the moisture or mineral content of the sample, or any characteristic of the matrix that might affect the actual extraction temperature. This is an advantage when compared to microwave extraction, in which the actual pressure and temperature of the extraction are influenced strongly by the above-mentioned sample parameters. Once the cell is in placed in the oven, the pump immediately begins to deliver the solvent of choice to the sample cell. Single solvents or premixed solvents can be used from a single collection vessel, or any combination of up to three different solvents can be programmed.

Table 1. Comparison of extraction techniques.

Technique	Sample Size (Grams)	Solvent Used (mL)
Accelerated Solvent Extraction	1-100	5-150
Soxhlet	1-100	300-1000
Microwave	5-10	30-50
FMS PLE	5-100	300-450
Buchi PLE	1-100 (2 systems)	300-750

Once solvent has made its way through the sample cell and reaches the collection vessel, the static valve closes to allow pressurization of the cell. Since the solvent expands as it heats, the pressure in the cell will increase when the static valve closes. When the pressure reaches 200 psi above the set point, the static valve rapidly opens to relieve the pressure and then closes again. The pump also delivers fresh solvent to the cell in an effort to return the pressure to the set point value. This addition of fresh solvent during accelerated solvent extraction is analogous to fresh solvent dripping down from the condenser onto the extraction thimble during Soxhlet extraction. During the first phase of a run, called the heat-up time, the cell contents are heated by the oven to the selected operating temperature. Heat-up times vary between 5 minutes for 100 °C and 9 minutes for 200 °C. After the heat-up time, the extraction enters a static period with a duration selected by the user. Typical static times are 5 minutes, but can vary from 0 to 2000 minutes. After the static time, fresh solvent is pumped through the cell to remove extracted analytes while the sample and solvent are still hot. The user can select the number of times the sample will be in the static mode, and enter this as the number of static cycles.

Following the final solvent rinse, solvent is purged out of the cell (using nitrogen at 150 psi) for a predetermined period of time. The total time for the extraction is usually less than 15 minutes and the amount of solvent used is approximately 1.5 times the volume of the sample cell (for example, about 15 mL for a 10-mL cell). The extracts are delivered to the collection vessels through a filter, and in many cases do not need any additional preparation prior to analysis. Since the extract is diluted by the total volume of extraction solvent plus the rinse solvent, a further concentration step (evaporation, solid-phase concentration step (evaporation, solid-phase extraction, etc.) may be required when performing trace analysis. Upon completion of the purge step, the cell is returned to the tray and the next sample is taken to the oven to begin the extraction process again.

Accelerated solvent extraction current offers both method control (each sample is extracted using the same conditions) and sequence control (each cell can be extracted using different conditions, including different solvents). Accelerated solvent extraction instrumentation also includes many features designed to minimize safety issues with the use of solvents at elevated temperatures and pressures. Among the safety measures in place are flammable vapor sensors, liquid leak detectors, checks for collection vessel overfill conditions, three levels of over pressurization prevention (electronic and mechanical), solvent flow monitoring, and pneumatic source pressure monitoring.

Will Accelerated Solvent Extraction Benefit My Laboratory?

Since its introduction to the market in 1996, accelerated solvent extraction has helped numerous analytical laboratories automate sample preparation and improve overall workflow productivity. This technique is used in numerous industries including environmental, food safety, chemical/petrochem, and pharmaceuticals and has been demonstrated to pair well with gas, liquid, and ion chromatography. Current accelerated solvent extraction instrumentation, the Thermo Scientific™ Dionex™ ASE™ 150 and 300 Accelerated Solvent Extractor systems allow for unattended overnight operation without user intervention. Extraction parameters can be programmed for individual samples or an entire batch of samples that enables the Dionex ASE systems to offer a level of automation and precision that greatly exceeds traditional sample preparation techniques. The Dionex ASE systems are suitable for any analytical laboratory that is looking to improve the efficiency of their extraction process and greatly reduce the amount of solvent, time, and analyst intervention required to obtain extracts with high levels of analytes of interest. Use of the Dionex ASE systems have demonstrated to reduce the error reduction often attributed to sample preparation workflow and has enabled analysts to spend most of their time utilizing the state of the art analytical tools available on the market today.

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- Unattended extraction of up to 24 samples
- Mixing or selection of three different solvents for complex extractions

Figure 2. Accelerated solvent extraction for solid and semisolid samples.

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