Analytical Arrow-Tip Method – SPME Arrow

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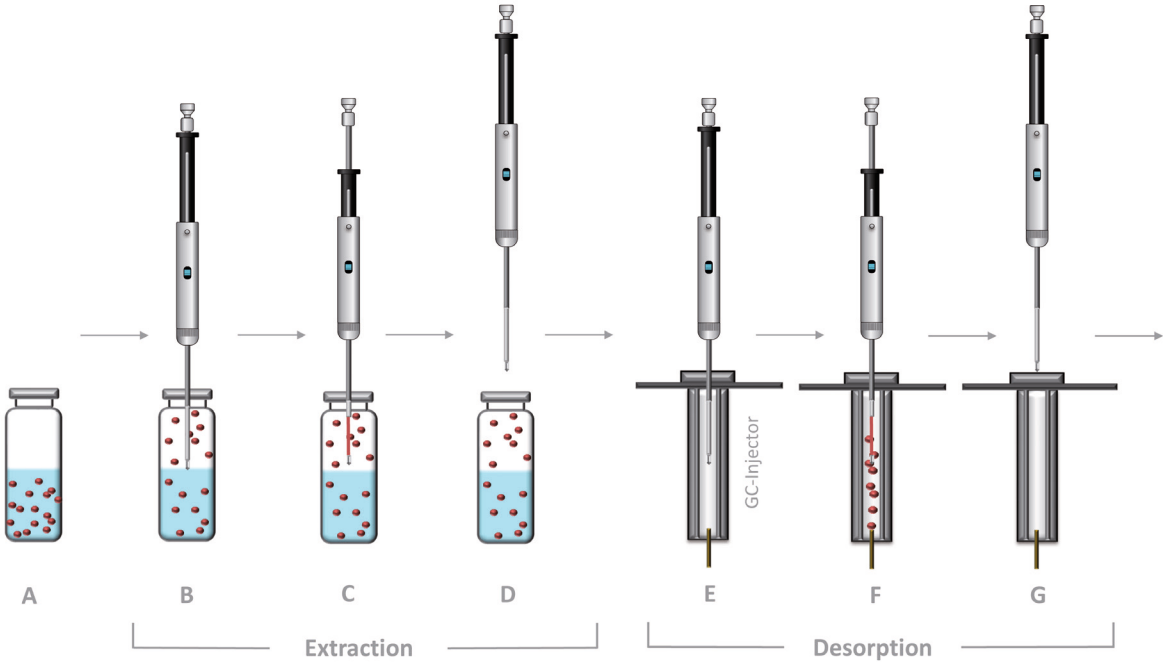

Fig. 1: Diagrammatic illustration of extraction and desorption using *PAL SPME Arrow*

What is SPME?

Given one of the key objectives of analytical sample preparation, which is to extract the analytes from the sample with the highest possible reproducibility rate but with the lowest possible losses and interferences, J. Pawliszyn and his co-workers developed an almost solvent-free, simple and speedy method for doing so in 1989, terming it solid-phase microextraction, SPME.

With regard to sampling, a differentiation is mainly made between two principles. The first involves extracting the volatile analyte from the so-called headspace (HS) above the sample. The second principle applies if the analyte shows semi-polar/polar properties, in which case the fibre can be directly immersed in the sample solution (direct immersion, DI).

How does the classic SPME set up work?

The SPME a syringe-like instrument equipped with a hollow needle. This hollow needle contains an extendable quartz glass fibre, which is coated with a polymer material. The coated fibre is bonded, via a highly heat-resistant epoxy adhesive, to a metal needle, which can be retracted into the said hollow needle to protect the sensitive coating.

What are the pros and cons of using the SPME method?

The key benefits of using the SPME method, in addition to achieving distinctly shorter sample processing times in some cases, are the almost solvent-free operation and the minimisation of matrix interferences, especially when performing headspace-extraction.

Automation of the SPME method is possible using a fibre holder and replaceable fibre inserts, possibly enabling time-savings and a reduction in the level of human sources required. The fibres can be used multiple times (for HS, several hundred times; for DI, several dozen times) but need to be heat-treated or rinsed off between applications.

Given the diverse range of available fibres, a broad applicability to many different compounds on trace level is possible, making the SPME method particularly selective and sensitive. SPME can be used for a wide variety of matrices (solids, liquids, gases).

The sensitivity of the classic SPME application is restricted by a relatively small proportion of fibre material involved, leading partially to a low extraction efficiency.

Furthermore, a certain degree of experience is required for using SPME since e. g. a lack of stability (e. g. creasing) or improper handling (extreme bakeout temperatures) may considerably shorten a fibre's lifetime.

What is the *PAL SPME Arrow*?

The microextraction field is seeing new technological developments. The *PAL (prep and load) SPME Arrow* provides additional benefits in addition to the capabilities of conventional SPME fibres. Its optimised more stable and closed design provides greater protection of the sorption phase, also when making the

transfer. Moreover, the greatly increased sorption phase volume provides for a better extraction yield and an improved sensitivity. *PAL SPME Arrow* is based on a stable stainless steel inner rod which is surrounded by sorption phase. The arrow-like head enables trouble-free penetration of bottle and injector septa. As opposed to the classic SPME fibre, the arrow-like head protects the sorbent and minimises undesirable external interferences and the loss of analytes during the transfer. Combined with the PAL-RTC (robotic tool changer) or RSI (robotic sample injection), the *PAL SPME Arrow* is completely automatic and hence enables high productivity.

How is sampling performed using SPME?

Depending on the properties of the analyte, SPME fibres with a suitable coating material should be selected so that the analyte can selectively adsorb onto the appropriate fibre. The material properties of these fibres vary according to the polarity and pore size of the coating.

To extract the analyte, the appropriate fibre is placed into a closed sample container. The fibre is extended from the hollow needle to enable the analyte to absorb onto the fibre (cf. Figure 1, A-C). Various parameters may impact the speed of this process. Temperature, stirring speed, duration time of the fibre in the sample container, density of the stationary phase, pH value and ionic strength of the sample solution, as well as the headspace size above the sample solution/sample volume should be kept constant to achieve reproducible results. The analytes are extracted and reconcentrated onto the fibre until a partition equilibrium is achieved between sample, headspace, and fibre. Subsequently the fibre is retracted into the protective hollow needle and removed from the sample container (cf. Figure 1, D).

Which desorption possibilities do exist?

SPME applications are possible using gas chromatography (GC), high performance liquid chromatography (HPLC), and capillary electrophoresis (CE). The differences vary according to the desorption process. Volatile compounds can be thermally redesorbed from the fibre in the GC-injector. Subsequently the vaporised and solvent-free sample is transferred to the column via carrier gas. After the fibre has been retracted into the hollow needle and been removed from the injector, the fibre can be used for the next extraction (cf. Figure 1, E-G).

Polar and thermolabile compounds are suited to analysis using HPLC. Desorption occurs either in a stationary mode, in a specially prepared sample chamber with strong eluents and a certain duration time, or dynamically, in a sample loop rinsed by eluents.

Following chromatographic separation and desorption, the compounds can subsequently be analysed using mass spectrometry (MS), tandem mass spectrometry (MS/MS), or other detectors.

Conclusions

The new *PAL SPME Arrow* microextraction technology features an arrow-like design, which enables a higher sensitivity level at trace levels, a greater mechanical stability, and improved protection of the absorbent. Automated sample preparation enables *PAL SPME Arrow* to be used efficiently in many areas. The technology is used for environmental analysis (e. g. determining herbicides in drinking water), for food analysis (e. g. furan and its methyl analogues), for flavouring analysis, as well as in many other fields. SV