

Table 1. Comparison of main approaches for quantification of organic pollutants in soil and sediments by SPME

Approach for controlling matrix effects	Approach for decreasing matrix effects*	Advantages	Disadvantages	Recommendation for on-site application	Analytes [Reference]
Matrix-matched external standard calibration	-	1) Simple	1) Possible only at a high extraction effectiveness 2) Re-calibration is recommended for different soil types	May be used for analytes and fibers providing sufficient extraction effectiveness	petroleum hydrocarbons [48,54,55]; chemical warfare agents [21]; 2-chloroethyl ethyl sulfide [93]
Internal standard calibration	-	1) Efficient matrix effect control 2) High precision and accuracy. No replicates are required 3) Simple operation 4) Efficient control of instrument performance and other errors 5) Single calibration is enough for long time	1) Long equilibration of soil is required after spiking internal standards 2) Concentration of IS should be close to that of analyte 3) Difficult to select IS 4) Expensive isotope-labeled ISs 5) Variable detection limits	1) Simplest and fastest approach 2) Ideal when using isotope dilution	1-methyl-1H-1,2,4-triazole [36]; transformation products of UDMH [57]; phenol [56]; pesticides [39]
Standard addition	-	1) Most efficient matrix effect control	1) Time-consuming: analysis of a single sample requires >4 analyses 2) Range of standard additions must be close to analyte concentration in a sample 3) Long equilibration of soil is required after spiking standards 4) Replicate soil samples must be identical 5) Not suitable for unstable analytes	Feasible when low number of samples are to be analyzed	VOCs [29], synthetic polycyclic musks [44], phenol [53], N-nitrosodimethylamine [57]; brominated flame retardants [94]
Multiple SPME + external standard calibration	-	1) Extraction from a single vial 2) Spiking of samples is not required 3) Simple calibration by injection of solvent-dissolved standards 4) Automation is possible	1) High extraction effectiveness (>5%) is required to achieve sufficient accuracy 2) Time-consuming: analysis of a single sample requires >4 analyses	Possible when extraction effectiveness is >5% and low number of samples are to be analyzed	BTEX [59]; methylisothiocyanate [47]
Matrix-matched external standard calibration	Fiber cooling	1) Higher extraction effectiveness and lower matrix effect 2) High precision and accuracy	1) Extra instrumentation is required 2) Difficult to automate 3) Condensation of water on a fiber and its attachment	May be used with a thermoelectric cooling	BTEX [61]; PAHs [46,62,66,95]; VOCs [66]; organochlorine pesticides [67]
External or internal standard calibration	Preliminary solvent extraction	1) Higher extraction effectiveness and lower matrix effect 2) High precision and accuracy	1) Extra steps of solvent extraction and evaporation 2) Loss of volatile analytes during solvent evaporation	Recommended only for semi-volatile analytes with high affinity to soil and low $K_{fh}$	pesticides [34,68–70,74]; PAHs [72,96–98]; various hydrocarbons [99]
External or internal standard calibration	Derivatization	1) Exhaustive extraction is possible 2) Best choice for unstable analytes	1) Extra step (loading of a reagent onto a coating) 2) Transformation of analytes during transfer from a sample to a fiber surface	Ideal for unstable compounds	Ergosterol [83]; organometallic compounds [79,80]; chemical warfare agents [81]; phenols [82]

Abbreviations: SPME – solid-phase microextraction; IS – internal standard; ES – external standard; SA – standard addition; PAH – polycyclic aromatic hydrocarbons; UDMH – unsymmetrical dimethylhydrazine; \* - conventional methods including sample heating and addition of water may be used for any of the given approach

Table 2. Comparison of approaches, which may be used for on-site quantification of organic pollutants in soil by SPME. *Note:* low (\*), medium (\*\*), high (\*\*\*)

Approach for controlling matrix effects	Approach for decreasing matrix effects*	Range of analytes	Detection limit	Accuracy	Precision	Speed	Simplicity	Ease of automation
Matrix-matched external standard calibration	-	*	**	**	**	**	**	**
Internal standard calibration	-	***	**	**	***	**	***	**
Standard addition	-	***	**	**	*	**	**	**
Multiple SPME + external standard calibration	-	*	**	**	**	*	**	***
Matrix-matched external standard calibration	Fiber cooling	**	***	***	**	**	**	**
External or internal standard calibration	Preliminary solvent extraction	**	**	**	**	*	**	*
External or internal standard calibration	Derivatization	***	***	**	**	*	**	**