Perspectives and challenges of on-site quantification of organic pollutants in soils using solid-phase microextraction

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Abstract

This review explores the current state-of-the-art and progress towards on-site quantification of organic pollutants in soils with solid-phase microextraction (SPME). In spite of many available methods, only few publications report on-site analyses of soil samples by SPME. To date, the only application of SPME for the on-site quantification of organic pollutants in soil was devoted to trichloroethylene. Problem of matrix effects limiting quantification by external standard calibration is discussed. Efficiencies of available approaches for decreasing and controlling matrix effects are evaluated and compared. SPME from a soil sample headspace with internal standard calibration was identified as one of the promising approaches to achieve fast, simple, precise and accurate on-site quantification of a wide range of organic pollutants in soil. Cold-fiber SPME has a greatest development potential because it is capable of providing lowest detection limits along with a minimum matrix effect. Perspectives for future development of the field are outlined.

Keywords: solid-phase microextraction; organic pollutants; on-site soil analysis; matrix effect control; exhaustive extraction; internal standard.

Abbreviations: BTEX, benzene, toluene, ethylbenzene and xylenes; GC, gas chromatography; IR, infrared; IS, internal standard. MW, microwave-assisted; MS, mass spectrometry; PAH, polycyclic

aromatic hydrocarbons; SPME, solid-phase microextraction; UA, ultrasonic-assisted; VA, vacuum-assisted; UV, ultraviolet; VOC, volatile organic compounds.

Contents

1. Introduction

Monitoring of toxic organic chemicals in soil is a very important element of environmental and food safety systems all around the world [1,2]. Concentrations of pesticides and herbicides, petroleum hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, munitions and rocket fuel residuals, chemical warfare agents, and pharmaceuticals are of a highest concern. Quantification of pollutants in soil is required to: a) verify if a soil quality conforms to safety standards; b) estimate temporal and spatial trends in pollutants' concentrations; c) develop efficient soil remediation technologies; and d) find the source or epicenter of pollution and map polluted areas. Soil is often either the sink or source of pollutants exchanged with water, air and biosphere.

Compared to air and water, pollution of soil is very non-homogeneous and often local due to a slower diffusion of chemicals [3,4]. Therefore, monitoring of soil always requires taking and analyzing greater number of samples. Often many samples must be taken, transported to the lab and analyzed before a decision can be made on further sampling. For example, at least two days are required to determine concentrations of rocket fuel residuals in soil at a site of burned-out rocket stage landing in Central Kazakhstan because analytical laboratory is located 1200 km from landing sites [4]. In the case of accidental rocket crash, when hundreds of tons of rocket fuel are spilled, quick decision making may be crucial. In addition, during transportation of samples, analytes may be decomposed [4], thus leading to non-accurate results and to higher uncertainties in risk assessment. Besides the distance or lack of resources, the lack of readily available methods for on-site analyses is a challenge.

Therefore, on-site analysis of soil samples has advantages because transportation of samples to an analytical laboratory is not required [5]. These could be summarized as follows:

- higher accuracy and reliability of measurements;
- faster data collection and decision making; and
- ability to analyze more samples at a lower cost.

Spectroscopic methods (UV, IR and Raman) are often used for on-site measurements [6]. Instrumentation for these methods is quite simple and reliable. However, to achieve sufficient selectivity, sensitivity and accuracy, they often require time- and labor-consuming derivatization. In most cases, every analyte requires a specific derivatization reagent to offset matrix effects.

Recent developments in portable chromatographic and mass spectrometric instrumentation made on-site analysis possible [7,8]. Portable gas chromatography (GC) and gas chromatography – mass spectrometry (GC-MS) instruments became very efficient, sensitive and affordable, thus making it possible to move quantification of many volatile and semi-volatile organic contaminants to the field without a significant loss of methods' performance. GC-MS is an ideal method for on-site measurements because of a reliable operation and ability to simultaneously identify and quantify a large number of analytes. Recent advances in a fast gas chromatography made on-site analysis faster, less expensive and more efficient [9,10].

To make an on-site analysis of soils possible, efficient sample preparation methods are required. On-site methods must be simple, fast, inexpensive, and capable of automation. The use of conventional solvent extraction methods [11,12] complicates the process, especially when

concentration and cleanup stages are necessary [13]. Therefore, in most cases they are not suitable for on-site application to soil analyses.

Headspace (HS) sampling represents a simpler alternative for on-site sample preparation [11]. It was successfully applied in combination with portable GC for rapid on-site quantification of benzene, toluene, ethylbenzene and xylenes (BTEX) in soils of a former chemical plant located in northeast China [14]. Broader adoption and application of HS sampling is limited by its poor detection limits for semivolatile analytes and the problem of a matrix effect.

Solid-phase microextraction (SPME) is one of most popular sampling and sample preparation techniques [15] developed by Janusz Pawliszyn and co-workers from the University of Waterloo, Canada [16]. It is based on extraction of analytes from a sample to a polymer coating (Fig. 1) followed by a thermal desorption in the inlet of a gas chromatograph. SPME combines extraction, pre-concentration and cleanup into a single stage. SPME is a very simple technology, especially when extracting from headspace above a sample [17]. Most methods based on SPME fulfill the requirements of a green analytical chemistry [18]. In the best case, they require weighing of a soil sample in a vial, extraction of analytes by exposing the fiber into a headspace above a sample and complete desorption into GC that, at the same time, cleans the fiber and makes it reusable and ready for analysis of the next sample. Such approach is often used for screening purposes [4,19–22] when the main goal is to identify compounds of greatest concern present in analyzed sample.

No other known sample preparation methods may provide similar simplicity that is also combined with high sensitivity. Therefore, SPME has an enormous potential for on-site measurements in environmental analysis [13,23–26]. In spite of this fact, application of SPME for quantification of organic pollutants in soils is often limited by poor accuracy of measurements [27–31] mainly caused by a matrix effect. The same problem exists also for other solid samples [32]. Several approaches are used to decrease and control matrix effect, however most of them make an on-site analysis complex and inexpedient. The aim of this review is to evaluate available approaches for quantification of organics in soil by SPME and perspectives of their application for on-site measurements. It does not focus at specific applications of SPME for soil analysis because they may be found in other available review papers. In this review, only methods based on a conventional SPME by a fiber are considered because this approach does not require additional instrumentation, and, therefore, more suitable for on-site analysis.

Figure 1.

2. Problem of a matrix effect

SPME is an equilibrium method [33] (Fig. 1). Even at constant extraction conditions, a mass of an analyte extracted by a SPME fiber depends on its affinity to a sample, thus causing a matrix effect [29,30,34]. In the case of headspace SPME, the affinity of analyte to a sample is represented by an analyte distribution constant (coefficient) between a headspace and a sample (K_{hs}) that is equal to a ratio of equilibrium concentrations of an analyte in headspace ([C_h]) and a sample ([C_s]) [33]. All soil samples have different physical chemical properties and affinity to analytes [35] (Fig. 2). SPME effectiveness (1) is primarily affected by the following soil characteristics:

- concentration of organic carbon (humus and fragments of plants);
- mechanical composition:
    - particle size distribution;
    - porosity;
- water content;
- pH;
- concentration of water-soluble salts;
- active functional groups at a surface of soil particles.

Figure 2.

$$R = m_f / m_0 = (K_{fh} \cdot K_{hs} \cdot V_f \cdot 100\%) / (K_{fh} \cdot K_{hs} \cdot V_f + K_{hs} \cdot V_h + m_s) \qquad \textbf{(1)}$$

where:

R – extraction effectiveness, %

m_f - analyte mass in a fiber coating after extraction, ng

m_0 - analyte mass in a soil sample before extraction, ng

V_f – volume of a fiber coating, mL

m_s – mass of soil sample, g

V_h – volume of a headspace above sample, mL

K_{fh} – analyte distribution constant between fiber and headspace, dimensionless

K_{hs} - analyte distribution constant between headspace and sample, g/mL.

Because of so many affecting factors, extraction effectiveness of analytes from different soils may easily vary by an order of magnitude [36]. This makes quantification of organic compounds using a simple external standard approach inaccurate. If an analyte extraction effectiveness from an analyzed sample is higher than that from external standard calibration samples, the apparent measured concentration will be higher, too.

The magnitude of a matrix effect depends on analyte properties, the most important of which are: a) hydrophobicity, b) volatility, c) acidity/basicity. For example, an increase of a water content in soil increases the SPME effectiveness for hydrophobic compounds while polar compounds become stronger retained by wet soil [20,36].

According to Eq. (1), analytes with a stronger affinity to a SPME polymer coating are less prone to be matrix-affected (Fig. 3). These compounds may be completely extracted from a sample to a fiber coating. Due to a hydrophobic nature of most fiber coatings, these compounds also have hydrophobic nature. For compounds with log K_{fh} = 6, decrease of log K_{hs} from 0 to -3 results in a drop of an extraction effectiveness by a factor of 2.2. For polar compounds having lower affinity to a fiber, a variability of an extraction effectiveness may theoretically reach two orders of a magnitude.

Figure 3.

An extraction effectiveness may be increased by an optimization of SPME parameters (Fig. 4). For soil samples, this may be achieved by increasing an extraction temperature and time, fiber coating volume, addition of water, other solvents or salt, and cooling a fiber [37]. A matrix effect may be decreased by an addition of excess water to a soil sample prior to an extraction [20,38]. However, it may result in a loss of an extraction effectiveness of polar analytes because of their stronger affinity to water than to soil [20,36]. Addition of water is not recommended when extraction temperature needs to be >100 °C due to the risk of vial explosion after the evaporation of water. When conducting SPME above soil-water mixtures, agitation [39], ultrasonic [40,41] or microwave [42–44] radiations may be used to enhance the transfer of analytes from a sample to a fiber; these methods are called ultrasound-assisted (UA) and microwave-assisted (MA) SPME, respectively.

Figure 4.

Method detection limits are also affected by soil properties [36]. If the extraction effectiveness is 100%, for a mass of soil sample 1 g and typical GC-MS sensitivity 1 pg, detection limits may reach 1 pg/g. For most analytes, detection limits of 1-10 ng/g may be achieved after optimization.

Other sample preparation methods including headspace sampling and solvent extraction have the problem of a matrix effect.

3. Methods for quantification of organic pollutants in soil samples using SPME

As was shown in the previous section, quantification of organic pollutants in soil using SPME is complicated by a matrix effect caused by different extraction effectiveness of analytes from samples. In the case of exhaustive (R>90%) extraction, calibration plot "S = f (m_a)" may be obtained by introducing different masses of analytes (m_a) to the GC column and measuring peak areas (S) [45]. An analyte peak area on a chromatogram of an analyzed sample is used to find the mass of analyte in a fiber coating (m_a) that is equal to a mass of analyte in a sample. This is possible only for most hydrophobic compounds with high K_{fh} values, e.g., organochlorine pesticides and polycyclic aromatic hydrocarbons (PAHs) [45,46].

When exhaustive extraction is not practically possible, sufficient quantification accuracy may be achieved using approaches based on (1) controlling matrix effects; and (2) decreasing matrix effects. Matrix effects may be controlled by matrix matched external standard calibration, internal standard calibration, standard addition and multiple SPME. For a substantial decrease of matrix effects, fiber cooling, preliminary solvent extraction or derivatization may be applied. For achieving even greater accuracy, approaches for both decreasing and controlling matrix effects can be involved in a single analytical method.

3.1 Methods based on controlling matrix effects

3.1.1 Matrix-matched external standard calibration

Quantification of soil organic pollutants by SPME is a complex analytical task due to the matrix effect. Simple 'detector response vs. analyte concentration in a sample' (external standard) calibration may be used only if an extraction effectiveness is reasonably high [45]. A calibration plot is obtained by analyzing soil samples having different analyte concentrations typically prepared using a 'clean'

soil with physical chemical properties similar to those of typically analyzed soils, so called matrix-matched calibration [47–51]. Every soil sample is characterized by its own K_{hs} and, therefore, own slope factor of a calibration plot (Fig. 5). A separate calibration plot has to be obtained for every soil type to avoid under- or overestimation of measured concentrations. In addition, determination of a soil type and its properties is not trivial [52]. This necessitates a thorough knowledge of soil and testing of soil itself in addition to an expertise in chemical analyses.

Figure 5.

Precision and accuracy of an external standard calibration is also affected by a competition between analytes and matrix components [31]. Optimization of extraction parameters for achieving a higher extraction effectiveness may result in increased responses of matrix components and even higher competition.

Another important issue for consideration when analyzing trace concentrations of volatile organic compounds (VOCs) in soil by headspace SPME is caused by a possible presence of analytes in a gas above samples due to ambient air contamination [53]. For example, 19 mL of air (above 1 g of a soil sample in a 20-mL vial) with benzene concentration 50 μg/m^3 contains 950 pg of analyte that corresponds to a benzene concentration in soil of 950 pg/g (or 0.95 μg/kg). Without consideration of this issue, end-users may obtain overestimated concentrations or false positives, e.g., by detecting analytes in a non-contaminated soil. Effect of this factor is difficult to control because VOCs concentrations in air, especially indoor or lab air are not stable. To overcome this issue, sample-to-headspace volumes ratio may be increased.

External standard calibration is often used for determination of total petroleum hydrocarbons representing a large class of compounds with a wide range of volatility and polarity [48,54,55]. Such tasks are especially complex because of different matrix effects to all analytes. For example, heavy oil fractions will be more affected by the concentration of organic carbon in soil while light hydrocarbons will be more affected by porosity of soil particles. In most cases, calibration is performed using matrix-matched soil samples and petroleum taken from the analyzed site. Addition of excess water minimizes a matrix effect, however a polar organic solvent must be added to avoid formation of an oil film on a water surface [48].

3.1.2 Internal standard calibration

Addition of an internal standard to the analyzed soil sample prior to analysis makes it possible to control a matrix effect using a response to the added compound [33,45,56]. When a soil sample has higher than usual affinity to the analyte, its affinity to the internal standard will be higher than usual, too. If physical chemical properties of internal standard and analyte are similar, dependence of analyte to internal standard responses ratio versus their concentration ratio will be the same for all soil samples (Fig. 5). Selection of a suitable internal standard may be quite complex because of many soil properties affecting its retention. Isotopically labeled internal standards provide highest accuracies because they have analyte-like properties and differ only slightly by a molecular weight [30,53]. However, they are quite expensive and require mass spectrometric detection.

In addition to a matrix effect, internal standard method allows decreasing other errors of analysis including loss of SPME fiber coating effectiveness and instrument performance (leaks, detector sensitivity, etc.). Accuracy of an internal standard method is much higher than that of classic external standard calibration. Using internal standard calibration, methods for quantification of phenols [56], VOCs [30] and transformation products of unsymmetrical dimethylhydrazine [36,57] (rocket fuel) based on SPME have been developed.

To achieve high accuracy of the method, internal standard must be distributed in the sample and retained in the same way as an analyte [27,28,36]. Uniform distribution of internal standard over a whole sample and its penetration to all pores may require a long time; most researchers used >24 h equilibration times. Pore sizes can vary with the types and condition of the soil, therefore, they also affect the rate of analyte diffusion. If an analyte has very high affinity to certain soil particles, internal standard molecules will not be able to substitute analyte molecules there [36]. Increase of a temperature, water addition, and stirring may be required to achieve proper equilibration and accuracy [36]. At higher temperatures, a complete soil equilibration may be observed immediately after spiking an internal standard.

3.1.3 Standard addition calibration

Standard addition approach is similar to an external standard calibration, but calibration samples are prepared using an analyzed soil sample and different concentrations of added analyte [44,53,58]. Typically, 4-5 vials (e.g., 20-mL) with replicate soil samples (e.g., 1.00 g) are prepared and spiked by equal volumes (e.g., 10 μL) of analyte solutions in water or another solvent having different

concentrations (e.g., 0, 1, 3, 5 and 10 mg/L corresponding to a concentration of standard addition 0, 10, 30, 50 and 100 μg/kg).

A calibration plot is then obtained for every analyzed sample. The equilibration of a soil after spiking standard additions is required because injected analyte must be distributed in the same way as analyte molecules already present in the analyzed sample [53]. Compared to the internal standard method, analysis of a single sample by a standard addition requires at least four analyses to obtain an accurate linear 'peak area vs. concentration of a standard addition' plot. Different style of injection may result in a slight difference in a mechanical composition of replicate and calibration samples leading to a low precision [53]. In this case, to achieve a sufficient accuracy, a higher number of calibration standards must be analyzed. A standard addition approach was used for quantification of VOCs [29], synthetic polycyclic musks [44], phenol [53] and N-nitrosodimethylamine [57] in soil samples by SPME.

3.1.4 Multiple SPME

As was shown above, non-exhaustive extraction leads to a variability in extraction effectiveness and variability in matrix effects. However, the total amount of analyte in a sample vial may be determined by making several (3-5) consecutive extractions and analyses [59,60]. A total mass of analyte in an analyzed sample (m_{total}) decreases after each consecutive extraction by the value directly proportional to a relative extraction effectiveness and may be determined using the formula: $m_{total} = m_1 / (1 - \beta)$, where m_1 – mass in the fiber after 1st extraction, and β – coefficient determined using the linear calibration plot '$\log m_i = (1\text{-}i) \log \beta + \log m_1$', where i – number of extraction step, m_i – mass extracted at this step. Log β is equal to a slope factor of the obtained linear plot. Mass of the analyte in the fiber may be determined using a calibration plot obtained by analyzing its liquid standards.

Number of required steps is directly proportional to β. At $\beta > 0.95$ (corresponds to an extraction effectiveness of 5%), the use of the multiple SPME approach is not recommended because many extraction steps are required to achieve reasonable accuracy. Therefore, application of the method for polar analytes is practically impossible. The method was successfully applied for determination BTEX [59] and pesticides [47]. Multiple SPME may have problems with accuracy caused by losses of analytes via septum hole and leaks after its first puncture.

3.2 Quantification approaches based on decreasing matrix effects

3.2.1 Fiber cooling

Increase of a temperature results in an increase of K_{hs}, however it results in a decrease of K_{fh}. To overcome this issue, SPME fiber may be cooled during an extraction process. It substantially increases extraction effectiveness and decreases a matrix effect. By cooling a fiber, exhaustive extraction becomes possible for broader ranges of analytes and matrices [46,61–63]. Fiber cooling can be accomplished by liquid CO_2, thermoelectric effect or circulating cooled fluids. Many different fiber cooling devices have been developed [63]. They provide different temperature gradients between sample and fiber. Compared to CO_2 cooling, thermoelectric cooling can provide a smaller temperature gradient (<70 °C). However, thermoelectric cooling system (Fig. 6) [64] is simpler in use, has lower cost, smaller size, lower weight and provides more accurate temperature control. As such, it could be considered for field use.

Figure 6.

Fiber cooling may be automated after slight modification of widely spread commercial autosamplers CTC Combi-PAL [46,65] and Gerstel MPS [66]. The use of a modified septumless head of GC injector minimizes septa coring allowing 200 automated injections without maintenance [66]. SPME with cooled fiber was successfully applied for determination of VOCs [61], PAHs [62,63,66], pesticides [67], dioxins and furans [22] in soil samples. The main problem of this approach is a complex and often large instrumentation, poor reliability and precision [63]. Temperature gradients inside a sample vial may cause condensation of water capable of absorbing polar compounds.

3.2.2 Preliminary solvent extraction

Different extraction effectiveness of analytes from soil is the main reason for a matrix effect. To avoid this, analytes may be preliminary extracted from soil to a suitable solvent [9,38,50,68–71]. Most organic solvent extracts are not compatible with SPME fibers which may be damaged by swelling. In this case, solvent substitution to water is required. SPME effectiveness for analyses of water-based samples is less affected by their composition. Therefore, matrix effect is significantly decreased, and proper accuracy is achieved using a simple external standard calibration. In addition, a recovery of analytes from water may be increased by addition of a strong electrolyte. Compared to

a headspace mode, direct immersion SPME provides a quicker extraction of analytes having poor volatility, e.g., pesticides and herbicides [34,68–70].

Ultrasonic-assisted (UA) [72,73] and microwave-assisted (MA) [70,74,75] extractions allow faster and greater recoveries of analytes from soil samples with lower volumes of organic solvents. Extraction effectiveness of PAHs from soil to water was successfully increased by addition of ionic liquids [76] or micellar solutions [77].

Methods based on preliminary solvent extraction are still characterized by a matrix effects, which may be minimized by standard addition, internal standard calibration and multiple SPME. For quantification of tributyltin in sediments, Yang et al. [75] combined a standard addition approach with an internal standard calibration. Replicate samples were spiked with standards containing different concentrations of analyte and the same concentration of an internal standard. Calibration plot represented a dependence of a responses ratio of an analyte and internal standard versus a concentration of the added analyte. Compared to the ordinary standard addition approach, this method provides higher accuracy because effects of all key external factors are controlled.

3.2.3 Derivatization

When determining organic pollutants in soil by a headspace SPME, derivatization may be used to convert analytes to a more volatile, stable and less polar compounds, improve selectivity, extraction effectiveness and decrease a matrix effect [78]. There are two main options for derivatization when analyzing soil by SPME: in-matrix [79–82] and on-fiber [83,84]. Most methods involving derivatization are similar to classic sample preparation approaches and, before SPME, they require extraction to an organic solvent [83], an aqueous solution of acid [79,81] or a sub-critical water [80] containing derivatizing agent. This is followed by a cleanup and evaporative concentration. In-matrix derivatization is a better choice when analyzing compounds having low stability, low volatility and high polarity. This approach significantly broadens the range of soil pollutants that may be determined by SPME. Derivatization-based methods are available for organometallic compounds [79,80], chemical warfare agents [81], phenols [82] and ergosterol [83].

On-fiber derivatization may be done using two different options – by saturating a fiber with reagent before or after analyte extraction. Theoretically, on-fiber derivatization may be used for a quick exhaustive extraction of volatile analytes. It requires a reagent with low volatility and high affinity to the fiber coating. In this case, volatile analytes reach the fiber, react with a reagent and

remain in a coating in derivatized forms. Currently, exhaustive SPME methods involving on-fiber derivatization are not available for soil samples.

4. Applicability of different SPME-based approaches for on-site soil analysis

As was shown in sections 2 and 3, matrix effects make quantification of organic pollutants in soil using SPME very complicated. Each of the developed approaches has its own advantages and problems (Table 1). A preferred method for field application, must be simple, fast, inexpensive and require a minimum amount of additional materials and equipment. Automation may be important when many samples need to be analyzed. To quickly obtain the highest possible amount of information on-site, a method should allow simultaneous quantification and qualification of multiple analytes. Final selection of the method should be done based on the following requirements: the range of analytes and their concentrations, detection limits, speed of analysis, number of analyzed samples, and acceptable accuracy.

Table 1.

In spite of many available methods, only few publications report on-site analyses of soil samples by SPME [9,85,86]. They range from 1997 to 2008. Such low number of real applications may be caused by a poor suitability of most available methods for an on-site quantification, mainly due to their insufficient accuracy, reliability, and simplicity. Another reason is a limited availability of field instrumentation in analytical laboratories of SPME method developers. This review should help method developers in making their methods more suitable for an on-site application.

The only application of SPME for the on-site quantification of organic pollutants in soil was devoted to trichloroethylene [9]. Using fast GC in combination with photoionization detector (PID), > 500 soil samples were analyzed during 10 days for study of migration of the pollutant. SPME was conducted after preliminary analyte extraction by methanol followed by spiking extract aliquot to water.

The main drawback of methods based on a preliminary solvent extraction is the additional extraction step typically requiring toxic organic solvents. However, this approach is most popular among method developers due to its greater reliability and simple transfer from conventional to SPME-based methods. Currently, this approach is recommended for on-site quantification of analytes

having high affinity to soil, poor volatility and/or low stability when application of simpler approaches does not provide desired accuracy. To decrease extraction time and labor expenses, ultrasonic-, microwave-assisted or accelerated solvent extraction [68,70] should be involved. In addition, selection of a method based on a preliminary solvent extraction must be justified for on-site measurements because direct injection of extracts to the instrument may often represent a simpler and more accurate alternative. The main advantage of SPME over direct injection is a better selectivity leading to a lower mass of matrix ingredients injecting to an instrument, a higher signal-to-noise ratio for analytes and less frequent instrument maintenance. However, SPME represent an additional sample preparation stage, and its application may result in a decreased precision and accuracy of the method.

Considering the pros and cons discussed above, SPME from soil sample headspace with internal standard calibration seems to have the best potential for an on-site application because it provides the best combination of speed, automation, detection limits and accuracy, especially when using isotopically labeled standards (Table 2). For faster equilibration, higher temperature and addition of water may be used. When analyzing many on-site samples, equilibration step does not significantly affect overall time of analysis. All method procedures (spiking standards, soil equilibration and extraction) may be completely automated using commercial autosamplers. The ‘ideal’ internal standard-based method is represented in Figure 7. When excess water is added, UA-SPME is recommended for enhancing extraction process. Microwave-assisted (MA)-SPME is less suitable for on-site analyses because it requires quite large extraction system equipped with condenser. Compared to a standard addition, analysis of only one replicate sample is possible. Calibration may be done in the lab before departure to the field, its repetition is not required because the method controls not only a matrix effect, but all other variables affecting an analytical signal. This represents a major time saving and it increases instrument throughput. This is very important because it takes time to create a sufficient vacuum in a MS detector in the field, the level of which affects sensitivity of GC-MS instrument. Few internal standards may be used to simultaneously quantify multiple analytes. Therefore, all standards of analytes do not need to be brought to the field.

Table 2.

Figure 7.

When exhaustive extraction of analytes is possible, external standard calibration may be a better choice [45]. However, this approach may be used only for a limited number of very hydrophobic

analytes. In addition, exhaustive extraction often requires long extraction times resulting in a drop of analysis speed. To accelerate an extraction process and decrease equilibration time, vacuum-assisted (VA) SPME may be used [87,88]. VA SPME was successfully downsized [89] and may be used for on-site analyses, however, with a limited level of automation. Fiber cooling increases an extraction effectiveness and method accuracy, but the method requires additional instrumentation, which is not commercially available yet. Thermoelectric fiber cooling is more suitable for an on-site application compared to other cooling methods because of a simpler and more reliable operation, smaller dimensions and easier automation [66].

Instead of an exhaustive extraction, multiple SPME may be used for analytes of wider polarity and volatility ranges. Compared to a standard addition method, it does not require soil equilibration after spiking standards. However, the use of this method is associated with a longer analysis time because analysis of one sample requires at least four consecutive extractions to obtain a proper linearity and accuracy of 'm = f (i)' plot. It may be used in the field when high speed of analysis is not required.

SPME from soil sample headspace in combination with a standard addition approach is very close to a multiple SPME based on its specifications. However, before extraction, soil samples need to be homogenized and equilibrated after spiking standards leading to a longer analysis time. At the same time, standard addition provides higher accuracy because calibration plot is obtained for every sample. Compared to multiple SPME, it may be used for analytes having low extraction effectiveness. In contrast with non-labeled internal standards, physicochemical properties of a spiked analyte are the same as properties of the analyte already present in soil. Therefore, the matrix effect control using standard addition is more efficient. Application of the method combining internal standard and standard addition may be more suitable for on-site analyses of very important samples due to a higher accuracy.

5. Further development of the field

Methods that may be used for an on-site quantification of soil organic pollutants by SPME have many problems including insufficient accuracy, speed of analysis and simplicity. However, the field is relatively new; it is multidisciplinary, it has many knowledge gaps and a significant potential for the development.

SPME from a soil sample headspace with internal standard calibration is the simplest and fastest approach for on-site quantification of organic pollutants of soil. However, it may be further improved by increasing soil equilibration rate after soil spiking with internal standards. A universal multi-analyte method may be developed using a set of internal standards and a proper mathematical model allowing prediction of an analyte retention by soil. During a method development and optimization, it is important to use an accuracy as a dependent variable instead of a typically used response because, in most cases, accuracy is a main limiting factor of a method quality. To quickly estimate an accuracy, sample may be spiked with an internal standard before starting an experiment, and an analyte to internal standard responses ratio may be determined and related to the theoretical value.

Standard addition method may be improved by increasing its precision. At a sufficient precision, the number of analyzed replicate samples required for achieving proper accuracy may be decreased to the theoretical minimum - two (without and with standard addition). Therefore, it is important to discover and eliminate reasons of insufficient precision when analyzing replicate soil samples spiked with standards of analytes.

Cold fiber approach has a significant potential for a development because theoretically it may provide lowest detection limits and highest accuracies for most volatile and semivolatile analytes. Further development of the method instrumentation is crucial for making it more portable and increasing sample-fiber temperature gradients.

Development of new efficient and selective fiber coatings may provide an increase in K_{fh} and a decrease of a matrix effect [90,91]. High selectivity is important for higher method accuracy because it minimizes a competition between analytes and matrix components. In this respect, molecularly imprinted polymers have a great potential [92]. Fibers may be saturated with derivatizing agents having their high affinity for achieving exhaustive extraction of chemically active analytes. On-fiber derivatization has a significant potential because of a wide variety of commercially available derivatization reagents. Universal derivatization reagents may be used to determine a wide range of non-volatile compounds.

6. Conclusion

Thus, solid-phase microextraction has a significant (yet not realized) potential in application for an on-site quantification of organic pollutants in soil. To achieve a sufficient accuracy, a matrix effect must be minimized or controlled using a set of available methods. Methods for on-site analysis should

be simple, robust, fast and inexpensive. SPME was applied on-site only for quantification of trichloroethylene after organic solvent extraction and dilution by water. Most available methods for quantification of organic pollutants in soil using SPME are based on a preliminary solvent extraction for transferring analytes from soil to less matrix-affected water. However, these methods are more complex and time-consuming compared to many conventional methods based on direct injection of extracts to the instrument.

Methods based on SPME over soil or soil-water slurry are simpler, faster and have greater potential for an on-site application. Matrix-matched external standard calibration may be used when extraction effectiveness is high enough. Exhaustive extraction may be achieved for hydrophobic compounds with a low volatility or by a cold fiber SPME. Multiple SPME may be used to predict the total amount of analyte present in a sample. Standard addition and internal standard allow efficient matrix effect control, but samples must be properly equilibrated after spiking with standards prior to analysis. Among these methods, internal standard method has an advantageous combination of speed, simplicity, cost of analysis and accuracy when using isotopically labeled standards. Multiple SPME and standard addition may be used on-site when a high speed of analysis is not required.

Among all available methods, cold fiber SPME has a highest potential because it is capable of providing lowest detection limits along with minimal matrix effect. Its instrumentation requires improvement to achieve highest sample-fiber coating temperature gradients, proper reliability and level of integration to portable instruments. Internal and external standard methods could be improved by developing efficient equilibration techniques of spiked soil samples, discovering and eliminating other sources of uncertainty.

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Figure captions:

Figure 1. Solid-phase microextraction of organic pollutants from soil. Reprinted with permission from Elsevier [36].

Figure 2. Main soil characteristics affecting SPME effectiveness of organic pollutants from soil and causing a matrix effect

Figure 3. Calculated effect of log K_{fh} on a decline of an extraction effectiveness at different changes of log K_{fs}. *Note:* 100 μm PDMS fiber, soil mass 1 g, vial volume 20 mL.

Figure 4. Calculated effect of log K_{fh} on the extraction effectiveness at different log K_{hs}. *Note:* 100 μm PDMS fiber, soil mass 1 g, vial volume 20 mL.

Figure 5. Illustration of a matrix effect on external and internal standard calibration plots

Figure 6. (A) Schematics and (B) picture of the prototype of cold fiber SPME device based on a thermoelectric cooling. Reprinted with permission from Elsevier [64].

Figure 7. Visual representation of the proposed simple, fast and accurate internal standard based SPME method most suitable for on-site quantification of organic pollutants in soil

Table captions:

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

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