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INCREASING THE VISIBILITY AND KNOWLEDGE BASE ON AIR QUALITY WITH BIG DATA AND ITS IMPACT ON THE POPULATION HEALTH

Erasmus+ KA220 Cooperation Partnerships

EVALUATION OF AIR SAMPLES

A Comprehensive Guide for Analytical Chemistry with Emphasis on SPME–GC/MS

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1. Introduction

Air quality assessment is a key discipline within analytical chemistry, with significant implications for public health, environmental protection, and industrial safety. This document describes a standardized method for sampling and analysis of air using sampling bags and SPME coupled with GC-MS. The method is suitable for both indoor and outdoor air analysis, with a focus on volatile organic compounds (VOCs). The combination of headspace solid-phase microextraction (HS-SPME) and GC-MS enables sensitive, solvent-free detection and identification of airborne compounds.

Air quality affects the daily lives of millions of people and is regulated by strict legislation at both national and international levels. Therefore, proper sampling, analysis, and data interpretation are essential for:

- Monitoring emissions from industrial sources
- Assessing air quality in residential areas
- Controlling workplace environments
- Research on atmospheric processes
- Forensic analysis of contamination

2. BASIC PRINCIPLES OF AIR SAMPLING

Air sampling is a complex process that requires careful planning and execution in order to obtain representative and reliable results. The quality of the analysis is directly dependent on the quality of the collected sample.

2.1 Types of Sampling

2.1.1 Active Sampling

Active sampling involves the use of a pump to actively draw air through a sorbent material or filter. This approach allows for:

- Control of the sampling flow rate
- Accurate determination of the sampled air volume
- Pre-concentration of analytes on a smaller amount of sorbent
- Shorter sampling duration

2.1.2 Passive Sampling

Passive sampling is based on the principle of molecular diffusion of analytes toward a sorbent material. The advantages of passive sampling include:

- Simplicity of use
- Independence from electrical power supply
- Low operational costs
- Suitability for long-term monitoring

Factors Affecting Air Sampling

Factor	**Effect on Sampling**
Temperature	Affects diffusion rate, sorption efficiency, and analyte stability
Humidity	May cause condensation and influence sorption of polar compounds
Airflow velocity	Influences mixing of air masses and passive sampling rate
Atmospheric pressure	Requires correction of sampled volume to standard conditions

Compounds Suitable for SPME–GC Analysis

The success of SPME–GC analysis is strongly dependent on the physicochemical properties of the analytes. The method is most suitable for volatile to semi-volatile organic compounds that exhibit sufficient affinity for the stationary phases of SPME fibers. The key factors include volatility, polarity, and thermal stability of the analytes.

For successful SPME analysis, analytes must meet several fundamental criteria. Volatility is the primary factor, with an optimal boiling point range between 50 and 300 °C**,** while compounds with boiling points in the range of 80–250 °C are considered ideal. Highly volatile compounds (below 50 °C) are difficult to retain on the fiber and may be lost during handling. In contrast, high-boiling compounds (above 300 °C) require very high desorption temperatures and are often incompletely released from the fiber.

The molecular weight of analytes should typically be below 300 Da**,** ensuring sufficient volatility under GC conditions. The polarity of the analyte must be compatible with the stationary phase of the SPME fiber. Non-polar compounds are best extracted using non-polar fibers such as PDMS, whereas polar analytes require polar or bipolar coatings.

Thermal stability is another critical parameter, as analytes must withstand desorption temperatures (typically 200–320 °C**)** without degradation. Reactive compounds may interact with the fiber coating or decompose at elevated temperatures, leading to inaccurate results.

Additionally, sufficient partitioning between the air matrix and the fiber coating is essential, as it governs the efficiency of analyte extraction onto the fiber.

Representation of the SPME–GC Analytical Procedure



Fiber extraction

Selection of an appropriate SPME fiber is crucial for achieving optimal sensitivity and selectivity. Each fiber type exhibits specific properties suited for different classes of analytes.

Table I: Overview of commonly used SPME fibers, including their polarity, temperature range, and typical applications.

FIBER TYPE	THICKNESS (MM)	POLARITY	TEMPERATURE RANGE	SUITABLE ANALYTES
PDMS	100, 30, 7	Non-polar	200–280 °C	Hydrocarbons, esters
PDMS/DVB	65	Moderately polar	200–270 °C	VOCs, alcohols, ketones
CAR/PDMS	75	Bipolar	200–320 °C	C_2–C_{12} hydrocarbons, aldehydes
DVB/CAR/PDMS	50/30	Multimodal	200–270 °C	C_3–C_{20} VOCs, amines
PA	85	Polar	200–320 °C	Polar VOCs, phenols
PEG	60	Polar	200–250 °C	Alcohols, acids
CWR/DVB	70	Polar	200–265 °C	Polar VOCs, alcohols

The selection of an appropriate SPME fiber is a critical step in method development, as it directly influences extraction efficiency, sensitivity, and selectivity. The choice depends primarily on the physicochemical properties of the target analytes, particularly their polarity, volatility, and molecular size. Non-polar fibers such as PDMS are suitable for hydrocarbons and other non-polar compounds, whereas polar coatings (e.g., PA, PEG) are more effective for polar analytes. Multimodal fibers, such as DVB/CAR/PDMS, provide broader applicability and are often used for complex mixtures of volatile organic compounds.

SPME Procedure – Step by Step

1. Conditioning of the SPME fiber in the GC injector (according to the manufacturer's recommendations)
2. Verification of fiber cleanliness (blank analysis)
3. Attachment of the SPME holder to the sampling bag via a septum
4. Insertion of the fiber into the air sample inside the bag
5. Sorption at a constant temperature for a defined period (15–30 min)
6. Retraction of the fiber back into the needle
7. Transfer of the fiber to the GC injector
8. Thermal desorption at an optimized temperature (250 °C, 2 min)
9. Immediate post-desorption conditioning for subsequent analysis



Figure 1: Sorption of analytes onto the SPME fiber and subsequent injection into the GC/MS system

GC/MS Conditions for SPME

SPME requires specific GC/MS parameter settings to ensure optimal desorption and efficient separation of analytes.

- **Injector:** Split/splitless injector equipped with an SPME liner, temperature set to **250 °C**
- **Desorption: 2 minutes in splitless mode**, followed by split mode (**split ratio 1:20**)
- **Column: DB-624** (30 m × 0.25 mm × 1.4 µm) or alternatively **DB-WAX**
- **Oven temperature program: 40 °C (5 min), ramp 5 °C/min to 220 °C (10 min hold)**
- **MS ionization:** Electron ionization (**EI, 70 eV**), scan range **m/z 35–350**
- **Transfer line temperature: 280 °C**
- **Solvent delay: 3 minutes**

Evaluation of Results

In this study, the analysis is primarily focused on the **qualitative identification of volatile organic compounds (VOCs)** present in air samples rather than their exact quantification. The GC–MS system enables the separation of individual compounds and their subsequent identification based on characteristic mass spectra and retention times.

Identification of analytes is performed by comparing the obtained mass spectra with reference spectra from spectral libraries (e.g., NIST), supported by retention behavior and, where applicable, literature data. The results provide information about the **presence or absence of specific compounds**, as well as the overall chemical profile of the sampled air.

Due to the nature of SPME as an equilibrium-based extraction technique, the response of individual compounds is influenced by multiple factors, including fiber affinity, extraction conditions, and matrix effects. Therefore, peak areas obtained from chromatograms are considered **semi-quantitative at best** and are primarily used for relative comparison between samples rather than absolute concentration determination.

This approach is particularly suitable for screening purposes, such as identifying potential sources of contamination, detecting off-odors, or comparing different environments. For accurate quantification, additional calibration procedures and the use of internal standards would be required.

Main Categories of Analyzable Compounds

Aromatic Hydrocarbons (BTEX)

Benzene, toluene, ethylbenzene, and xylenes (BTEX) represent ideal analytes for SPME due to their optimal volatility and strong affinity for non-polar fibers. Benzene, with a boiling point of 80.1 °C and a molecular weight of 78.11 g/mol, is best extracted on a 100 µm PDMS fiber at room temperature. Typical ambient concentrations range from 1 to 100 µg/m³.

Toluene (b.p. 110.6 °C) shows higher affinity for PDMS fiber than benzene and occurs at higher ambient concentrations (5–500 µg/m³). For ethylbenzene and xylenes, with boiling points around 135–145 °C, the 65 µm PDMS/DVB fiber is often preferable, providing better selectivity and higher sorption capacity for these semi-volatile aromatic hydrocarbons.

BTEX — Structural Formulas

Benzene: C_6H_6

Toluene: $C_6H_5–CH_3$ (methylbenzene)

Ethylbenzene: $C_6H_5–CH_2CH_3$

o-Xylene: $C_6H_4(CH_3)_2$ (1,2-dimethylbenzene)

m-Xylene: $C_6H_4(CH_3)_2$ (1,3-dimethylbenzene)

p-Xylene: $C_6H_4(CH_3)_2$ (1,4-dimethylbenzene)

Analyte	MW (g/mol)	B.P. (°C)	Recommended Fiber	Typical Conc.

Benzene	78.11	80.1	PDMS 100 µm	1–100 µg/m³
Toluene	92.14	110.6	PDMS 100 µm	5–500 µg/m³
Ethylbenzene	106.17	136.2	PDMS/DVB 65 µm	1–200 µg/m³
o-Xylene	106.17	144.4	PDMS/DVB 65 µm	1–300 µg/m³
m,p-Xylene	106.17	138–139	PDMS/DVB 65 µm	2–400 µg/m³

Aliphatic Hydrocarbons

Saturated aliphatic hydrocarbons in the C_5–C_{15} range are well suited for SPME analysis due to their chemical stability and predictable interaction with non-polar fibers. Normal alkanes from n-pentane to n-decane are best analyzed with 100 µm PDMS fiber, which provides high capacity for non-polar molecules. Shorter chains (C_5–C_7) require lower sorption temperatures to minimize losses, while longer alkanes (C_{10}–C_{15}) need higher desorption temperatures for complete release.

Cycloalkanes exhibit somewhat different behavior compared to their linear analogs and are often better analyzed with 65 µm PDMS/DVB fiber, which offers improved selectivity due to π-electron interactions with divinylbenzene. Branched isoalkanes generally have lower boiling points than corresponding normal alkanes, which may require use of 75 µm CAR/PDMS fiber for better sorption of more volatile isomers.

Unsaturated hydrocarbons, including alkenes and alkynes, are excellently analyzed using DVB/CAR/PDMS fiber owing to π–π interactions between the unsaturated bonds of the analyte and aromatic structures in the fiber. These compounds, however, are more prone to oxidation, requiring prompt analysis and protection from light.

Aliphatic Hydrocarbons — Examples

n-Pentane: $CH_3(CH_2)_3CH_3$ (C_5H_{12})

n-Decane: $CH_3(CH_2)_8CH_3$ $(C_{10}H_{22})$

Cyclohexane: C_6H_{12} (cyclic)

1-Hexene: $CH_2{=}CH{-}(CH_2)_3{-}CH_3$ (C_6H_{12})

Isooctane: $(CH_3)_3CCH_2CH(CH_3)_2$ (2,2,4-trimethylpentane)

Halogenated Hydrocarbons

Halogenated organic compounds represent one of the most important groups of environmental contaminants suitable for SPME-GC analysis. Their high chemical stability,

favorable distribution coefficients, and often high toxicity make their monitoring a priority task.

Chlorinated alkanes such as chloroform, carbon tetrachloride, and 1,1,1-trichloroethane are excellently analyzed using 65 µm PDMS/DVB fiber. These substances have moderate volatility and exhibit good affinity for the polar groups of divinylbenzene. Their use as industrial solvents and their persistence in the environment require sensitive analytical methods with detection limits in the ng/m³ range.

Chlorinated alkenes, particularly trichloroethylene (TCE) and perchloroethylene (PCE), are common contaminants in groundwater and soil air. For their analysis, 75 µm CAR/PDMS fiber is optimal, utilizing both π–π interactions with unsaturated bonds and dispersion forces with chlorine substituents. Vinyl chloride requires special attention due to its high volatility and carcinogenic effects.

Freons and other fluorinated compounds are primarily analyzed with 100 µm PDMS fiber, although their analysis may be more challenging due to the lower polarizability of fluorine. Brominated substances, including trihalomethanes formed during water disinfection and polybrominated diphenyl ethers (PBDEs) used as flame retardants, often require DVB/CAR/PDMS fiber for optimal sorption.

Halogenated Compounds — Key Structures

Chloroform: $CHCl_3$

Carbon tetrachloride: CCl_4

Trichloroethylene (TCE): $ClCH{=}CCl_2$

Perchloroethylene (PCE): $Cl_2C{=}CCl_2$

Vinyl chloride: $CH_2{=}CHCl$

CFC-12 (Freon-12): CCl_2F_2

Compound Class	Examples	Recommended Fiber	Application
Chloroalkanes	$CHCl_3$, CCl_4, 1,1,1-TCA	PDMS/DVB 65 µm	Solvents, contamination
Chloroalkenes	TCE, PCE, vinyl chloride	CAR/PDMS 75 µm	Remediation, OHS
Freons	CFC-11, CFC-12, HCFC-22	PDMS 100 µm	Refrigerants, ozone
Brominated	Bromoform, PBDEs	DVB/CAR/PDMS	Disinfection, flame ret.

Oxygenated Organic Compounds

Oxygenated organic compounds constitute a diverse group of analytes with varying SPME extraction requirements depending on their polarity and hydrogen-bonding capability. Their analysis often demands polar or bipolar fibers.

Lower alcohols (C_1–C_8) are best analyzed using 65 µm PDMS/DVB or 85 µm PA fibers. Methanol and ethanol require special attention due to their high polarity and strong hydrogen bonding. PA fiber with its polyacrylate stationary phase is most suitable for these polar alcohols, owing to the presence of carboxyl groups capable of interacting with the hydroxyl group of the alcohol. Higher alcohols (C_3–C_8) can also be analyzed with PDMS/DVB fiber, which provides a compromise between polar and non-polar interactions.

Aldehydes present a particular challenge for SPME analysis due to their reactivity and tendency toward oxidation. Formaldehyde often requires derivatization before analysis, while higher aldehydes (C_2–C_{10}) are successfully analyzed with 75 µm CAR/PDMS or 65 µm PDMS/DVB fibers. Acetaldehyde requires short sorption times due to fast kinetics and potential loss during prolonged exposure. Benzaldehyde and other aromatic aldehydes are excellently analyzed using DVB/CAR/PDMS fiber thanks to a combination of π–π interactions and polar forces.

Ketones generally exhibit better stability than aldehydes and are more suitable for standard SPME protocols. Acetone is analyzed with 65 µm PDMS/DVB fiber, though attention must be paid to possible interference with n-propanol. MEK (2-butanone) and higher ketones yield good sensitivity with PDMS/DVB or DVB/CAR/PDMS fibers. Cyclic ketones such as cyclohexanone often require longer sorption times due to steric hindrance.

Oxygenated Compounds — Formulas

Methanol: CH_3OH

Ethanol: C_2H_5OH

Formaldehyde: $HCHO$ (methanal)

Acetaldehyde: CH_3CHO (ethanal)

Benzaldehyde: C_6H_5CHO

Acetone: CH_3COCH_3 (propan-2-one)

MEK: $CH_3COC_2H_5$ (butan-2-one)

Cyclohexanone: $C_6H_{10}O$

Terpenes and Biogenic VOCs

Terpenes emitted by plants represent an important group of biogenic volatile organic compounds (BVOCs) with a significant impact on air quality both indoors and outdoors.

Their analysis by SPME-GC is highly efficient due to optimal volatility and good compatibility with available fibers.

α-Pinene, the most common terpene emitted by coniferous trees, is excellently analyzed using 100 µm PDMS fiber at room temperature. Its high concentration near wood-based materials and its use as a biomarker of indoor air quality make its determination a routine part of interior monitoring. The stability of α-pinene under SPME conditions allows long-term sample storage without significant degradation.

Limonene, the characteristic terpene of citrus fruits, requires special attention due to its susceptibility to oxidation by atmospheric oxygen, forming various oxidation products. For its analysis, 65 µm PDMS/DVB fiber is suitable, providing better selectivity than purely non-polar PDMS. Samples containing limonene should be analyzed as soon as possible after collection, ideally within 6 hours.

Camphene and 3-carene, terpenes emitted by various species of pine and other conifers, are analyzed with 100 µm PDMS fiber. Their lower volatility compared to α-pinene requires longer sorption times (typically 30–45 minutes) to achieve optimal sensitivity. Isoprene, emitted by deciduous trees, requires 75 µm CAR/PDMS fiber due to its high volatility and unsaturated structure.

Terpenes — Molecular Formulas

α-Pinene: $C_{10}H_{16}$ (bicyclic monoterpene)

Limonene: $C_{10}H_{16}$ (monocyclic monoterpene, 4-isopropenyl-1-methylcyclohexene)

Camphene: $C_{10}H_{16}$ (bicyclic monoterpene)

3-Carene: $C_{10}H_{16}$ (bicyclic monoterpene)

Isoprene: $CH_2{=}C(CH_3){-}CH{=}CH_2$ (C_5H_8, 2-methyl-1,3-butadiene)

Terpene	Source	Fiber	Note
α-Pinene	Conifers	PDMS 100 µm	Stable, good sorption
Limonene	Citrus	PDMS/DVB 65 µm	Oxidation-prone
Camphene	Pine	PDMS 100 µm	Low volatility
3-Carene	Various woods	PDMS 100 µm	Biomarker
Isoprene	Deciduous trees	CAR/PDMS 75 µm	Highly volatile

Substituted Aromatic Compounds

Aromatic compounds bearing various functional groups require careful SPME fiber selection according to the nature of the substituents and their interactions with the stationary phase. The combination of π–π interactions of the aromatic ring with specific interactions of functional groups allows achieving high selectivity and sensitivity.

Phenols and their derivatives represent one of the most challenging groups for SPME analysis due to the strong hydrogen bonds of the hydroxyl group. The 85 μm PA fiber with polyacrylate stationary phase is the most suitable choice owing to the presence of carboxyl groups capable of accepting a hydrogen bond from the phenolic OH group. The 70 μm CW/DVB fiber (Carbowax/DVB) provides an alternative option for phenols through the combination of polar polyethylene glycol and aromatic divinylbenzene.

Anilines and their derivatives exhibit basic properties due to the lone electron pair on nitrogen. The 65 μm PDMS/DVB fiber is often optimal because divinylbenzene can interact with the aromatic system of aniline, while PDMS provides a non-polar environment for alkylanilines. The 85 μm PA fiber may be more suitable for substituted anilines with additional polar groups.

Nitrobenzenes are characterized by strong electron-accepting properties of the nitro group, which affect the electron density of the aromatic ring. DVB/CAR/PDMS fiber is the ideal choice due to the combination of π–π interactions with both aromatic components of the fiber and dipolar interactions with the polar nitro group. Chlorobenzenes behave similarly to unsubstituted benzene and are best analyzed with 100 μm PDMS or 65 μm PDMS/DVB fiber.

Substituted Aromatics — Formulas

Phenol: C_6H_5OH

Aniline: $C_6H_5NH_2$

Nitrobenzene: $C_6H_5NO_2$

Chlorobenzene: C_6H_5Cl

2,4-Dichlorophenol: $C_6H_3Cl_2OH$

Compounds Unsuitable for SPME-GC Analysis

Although SPME is a versatile technique for the analysis of a wide range of organic compounds, certain categories of substances are unsuitable for this method or require a specialized approach.

Very volatile substances with boiling points below 50 °C present significant problems due to losses during sample handling. These compounds are difficult to retain on the fiber at room temperature and are rapidly released during transfer to the GC injector. Examples include permanent gases, lower alkanes (methane, ethane), and highly volatile halogens.

At the opposite end of the spectrum, non-volatile substances with boiling points above 300 °C require extremely high desorption temperatures exceeding the thermal limits of available fibers. These compounds are often incompletely desorbed or decompose at the required temperatures. High-molecular-weight paraffins, wax esters, and polymers fall into this category.

Strongly polar substances, especially lower carboxylic acids, amines, and low-molecular-weight alcohols, exhibit low affinity for available SPME fibers and often prefer the aqueous phase over the organic stationary phase of the fiber. These compounds may require derivatization or special polar fibers that are not commercially available.

Reactive substances pose a particular challenge because they can react with the fiber material or decompose at high desorption temperatures. Higher aldehydes may polymerize, unsaturated compounds may oxidize, and some organometallic compounds decompose even at moderate temperatures.

Optimization Strategies for Different Analyte Classes

Low-Molecular-Weight VOCs (C_2–C_5)

Low-molecular-weight volatile organic compounds require a specialized approach to SPME analysis due to their high volatility and low affinity for most available fibers. The 75 µm CAR/PDMS fiber is the optimal choice owing to the high sorption capacity of activated carbon (Carboxen) for small molecules.

Sorption temperature plays a critical role — lowering it to 5–15 °C significantly improves retention of volatile analytes on the fiber. This cooling can be achieved using a thermostat or ice bath, with care to prevent condensation of atmospheric moisture on the fiber. Sorption time should be relatively short (5–10 minutes) due to the fast kinetics of small molecules and the risk of reaching equilibrium followed by analyte loss.

Desorption requires a higher temperature (280 °C) for complete release of analytes from Carboxen pores, but the thermal limits of the fiber must be respected. Cryofocusing in the GC injector can significantly improve peak shape and analytical sensitivity by trapping analytes at low temperature and their subsequent rapid release.

Polar Organic Compounds

Polar organic compounds require a fundamentally different approach to SPME optimization compared to non-polar analytes. Fiber selection is critical — the 85 µm PA fiber with polyacrylate stationary phase is often optimal due to the presence of polar carboxyl groups. The 70 µm CW/DVB fiber provides an alternative through the combination of polar polyethylene glycol and aromatic divinylbenzene.

Sorption temperature may be increased to 40–60 °C to improve sorption kinetics for polar compounds, which often exhibit slower diffusion to the fiber compared to non-polar analytes. Higher temperature also reduces sample viscosity and improves mass transport. However, analyte stability at elevated temperature must be monitored.

Sample humidity represents a significant interfering factor, as water competes with polar analytes for sorption sites on the fiber. Controlling relative humidity below 50% is often necessary for reproducible results. The salt-out effect, achieved by adding sodium chloride or other salts, can increase the activity of polar analytes and improve their extraction onto the fiber.

Derivatization represents an alternative approach for very polar substances. In-situ derivatization directly on the fiber or off-line derivatization before SPME can convert polar analytes into less polar derivatives more suitable for standard SPME analysis.

Derivatization Reactions — Examples

DNPH derivatization of formaldehyde:

$$HCHO + (NO_2)_2C_6H_3NHNH_2 \rightarrow (NO_2)_2C_6H_3NHN{=}CH_2 + H_2O$$

Silylation of phenol with BSTFA:

$$C_6H_5OH + (CH_3)_3SiNHSi(CH_3)_3 \rightarrow C_6H_5OSi(CH_3)_3 + \ldots$$

Acetylation of amine:

$$R{-}NH_2 + CH_3COCl \rightarrow R{-}NHCOCH_3 + HCl$$

Matrix Effects in Air Samples

In complex air samples, various matrix effects may occur that affect the efficiency of SPME extraction and the reproducibility of results. Understanding these phenomena is essential for developing robust analytical methods.

Competitive sorption arises when high concentrations of interfering substances compete with target analytes for sorption sites on the fiber. This effect is particularly pronounced during analysis of industrial emissions containing solvent or hydrocarbon mixtures across a wide concentration range. Solutions may include sample dilution, use of a more selective fiber, or changes to sorption conditions.

Air humidity represents one of the most common interfering factors. Water condensation on the fiber can block sorption sites and alter analyte distribution coefficients. Hydrophobic fibers such as PDMS are less sensitive to humidity than polar fibers. Sample drying using desiccants or permeation membranes may be necessary when analyzing samples with high relative humidity.

Particles and aerosols can contaminate the fiber and cause memory effects or alter sorption properties. Air filtration before SPME or the use of protective fiber covers can minimize these problems. Reactive substances in the sample can chemically react with the fiber material or with analytes, producing artifacts or loss of sensitivity.

Matrix Effect	Cause	Solution
Competitive sorption	High conc. of interferents	Sample dilution, selective fiber
Humidity	Water condensation on fiber	Drying, hydrophobic fiber
Particles	Fiber contamination by dust	Filtration, protective covers
Reactive species	Chemical reaction on fiber	Inert fiber, lower temperatures
Memory effect	Incomplete desorption	Longer/higher desorption, cleaning

Application Areas of SPME-GC by Analyte

Indoor Air Quality Monitoring

Indoor air quality monitoring represents one of the most important applications of SPME-GC analysis, given that people spend most of their time in enclosed spaces.

Formaldehyde emitted from composite materials, particleboard, and adhesives requires a specialized approach due to its high polarity and reactivity. Derivatization with 2,4-dinitrophenylhydrazine or special fibers capable of its direct sorption is often employed.

BTEX compounds originating from paints, varnishes, adhesives, and cleaning products are excellently analyzed by standard SPME protocols. Their concentrations indoors often exceed outdoor levels several-fold, enabling the use of short sorption times and achievement of good detection limits.

Terpenes emitted from wood-based materials, particularly α-pinene and limonene, serve as indicators of natural material use and their emission potential. 2-Ethyl-1-hexanol released from PVC flooring and plastic materials represents a significant marker of plastic materials in interiors. Total volatile organic compounds (TVOC) provide an integral parameter for evaluating overall indoor air quality.

Industrial Emissions and Fugitive Leaks

Industrial applications of SPME-GC analysis cover a broad spectrum of sectors and emission types. In the petrochemical industry, C_5–C_{10} hydrocarbons, BTEX compounds, and their derivatives are primarily analyzed. Fugitive emissions from valves, flanges, and pumps often contain complex hydrocarbon mixtures requiring separation on polar columns and identification by mass spectrometry.

The plastics industry produces characteristic monomer and additive emissions. Styrene from polystyrene production, acrylonitrile from ABS plastics, and vinyl chloride from PVC are priority analytes with strictly regulated limits. Their analysis requires specific fibers and optimized GC temperature programs.

Paint shops and coating facilities emit solvent mixtures including toluene, xylenes, butyl acetate, and other esters and ketones. High concentrations of these substances can cause SPME fiber saturation, necessitating sample dilution or shorter sorption times. The chemical industry often requires specialized approaches depending on the type of production, and identification of unknown substances using spectral libraries and retention indices may be necessary.

Industrial Monomers — Formulas

Styrene: $C_6H_5CH{=}CH_2$ (vinylbenzene, C_8H_8)

Acrylonitrile: $CH_2{=}CHCN$ (C_3H_3N)

Vinyl chloride: $CH_2{=}CHCl$ (C_2H_3Cl)

Butyl acetate: $CH_3COO(CH_2)_3CH_3$ ($C_6H_{12}O_2$)

Occupational Health & Safety (OHS) Monitoring

Occupational environment monitoring requires quantitative determination of toxic substances with high accuracy and reliability in accordance with occupational exposure

limits. Benzene, as a proven human carcinogen, has the strictest limits and requires the most sensitive analytical methods. Its determination by SPME-GC/MS in SIM mode enables achievement of the detection limits needed for monitoring eight-hour exposures.

Toluene, with neurotoxic effects upon chronic exposure, is routinely monitored in environments using toluene-based solvents. Its analysis is relatively straightforward due to good sorption on PDMS fiber and the absence of significant interfering substances when using mass spectrometry.

Chloroform and other chlorinated solvents with hepatotoxic effects require special attention due to possible matrix effects in humid environments. n-Hexane, causing peripheral neuropathy upon chronic exposure, is analyzed simultaneously with other aliphatic hydrocarbons, with chromatographic separation being essential for correct quantification. All OHS applications require regular calibration, quality control, and documentation in compliance with accreditation requirements.

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