https://chemclassjournal.com/
ChemClass Journal Vol. 9 Issue 4 (2025); 340 - 355
e-ISSN:3092-8214 p-ISSN:3092-8206
doi.org/10.33003/chemclass-2025-0904/26

Metal-Organic Frameworks in Analytical Chemistry: Emerging Platforms for Sensing, Separation, and Sample Preparation -- A Mini Review

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Abstract

Metal-organic frameworks (MOFs) have emerged as versatile porous materials with exceptional tunability and high surface area, enabling advanced analytical applications in sensing, separation, and sample preparation. This review provides a concise yet comprehensive synthesis of recent progress while identifying critical gaps in stability, scalability, and analytical protocol standardization. By linking structure to performance, the review highlights how pore engineering, surface functionality, and composite design enhance analytical precision. Remaining challenges—including hydrolytic instability, pore blocking, and synthetic variations—are discussed alongside emerging opportunities in AI-assisted MOF discovery and sustainable analytical method development.

Keywords: Analytical chemistry, Chromatographic separation, Chemical sensing, Functional materials, Metal-organic frameworks (MOFs), Sample preparation

Introduction

Analytical chemistry continues to evolve toward miniaturized, rapid, and environmentally sustainable workflows [1], [2]. These developments require materials that combine high selectivity, large surface area, tuneable functionality, and compatibility with diverse detection platforms. Metal-organic frameworks (MOFs), composed of metal clusters linked by organic ligands, offer precisely adjustable pore environments and chemical functionalities that support selective adsorption, molecular recognition, and efficient sample manipulation [3], [4]. Since their early applications in gas adsorption and luminescent sensing, MOFs have expanded into a wide range of analytical roles, including MOF-coated chromatographic phases, mixed-matrix membranes, magnetic sorbents, electrochemical sensors, and MOF-based microextraction materials [5]. Rapid growth in

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MOF design—from mixed-linker strategies to post-synthetic modification—has further enabled tailored performance for specific analytes [6], [7]. Despite this progress, existing reviews often provide broad overviews rather than analytical-chemistry-focused discussions that link structural features to measurement performance [8]. This article addresses that gap by integrating fundamental MOF characteristics with their roles in sensing, separation science, and sample preparation [5]. The review concludes with challenges and future opportunities relating to stability, scalability, and green analytical chemistry. MOF research between 2020 and 2025 has expanded rapidly, particularly in analytical chemistry, where the ability to tune pore size, metal identity, and surface chemistry plays a central role in optimizing selectivity and sensitivity [9], [11]. However, the field faces challenges including hydrolytic degradation, inconsistent synthetic reproducibility, and difficulties integrating MOFs into commercial analytical instruments [1], [12], [14].

To guide both new and experienced researchers, this review is structured to move from foundational structure-performance relationships to analytical applications: sensing, separation science, and sample preparation. The final section highlights emerging research directions and unresolved challenges.

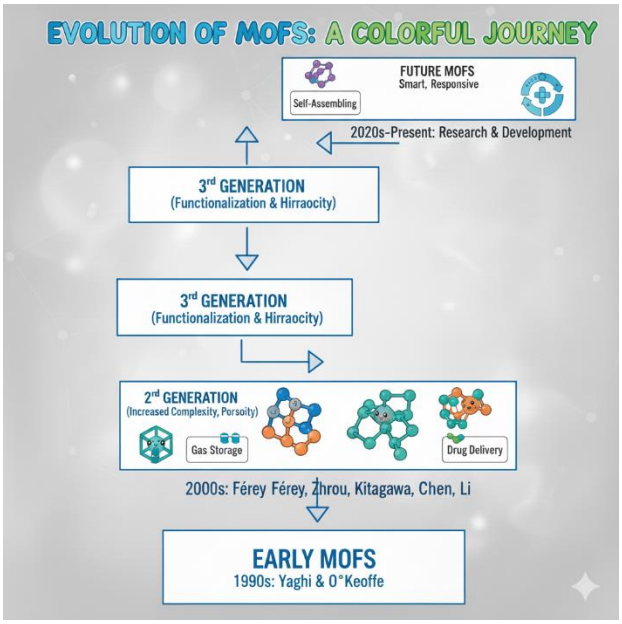


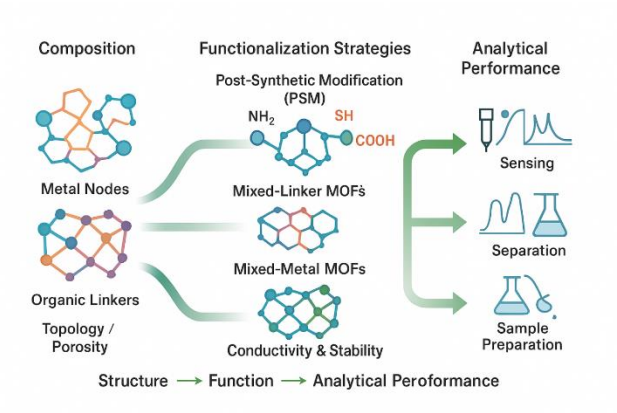
Figure 1: Flowchart showing the Evolution of MOFs

2.0 Structural and Functional Fundamentals of MOFs

Metal-organic frameworks are crystalline porous materials assembled from metal ions or secondary building units (SBUs) bridged by organic linkers [15][20]. Their high structural diversity arises from the range of available linkers, coordination geometries, and framework topologies, enabling micro-, meso-, and hierarchical porosity [16], [21], [22]. In analytical chemistry, MOF performance is influenced primarily by: Pore size and accessibility—controlling diffusion and adsorption [12], [23], [24]; surface functionality—influencing selectivity and binding strength [25], [26]; framework stability—especially under aqueous or biological conditions

[22], [27], [29]; electronic properties—important for optical and electrochemical sensing [30], [32].

Robust metal clusters such as Zr_6, Ti_8, and Al_3 promote high hydrolytic and thermal stability, making them suitable for sensing and extraction in aqueous systems [3], [9], [29], [33], [36]. Functionalization strategies—including mixed-linker synthesis, post-synthetic modification, and metal substitution—enable fine control of chemical affinity and signal responsiveness [3], [15], [37], [38]. Although often described separately, many modern MOFs combine multiple strategies to maximize sensitivity, reusability, and structural robustness.



Scheme 1. Structural and Functional Fundamentals of Metal–Organic Frameworks (MOFs)

3.0 MOFs in Chemical Sensing

MOFs have become important sensing materials due to their tuneable porosity, high surface area, and capacity to integrate optically or electrochemically active sites [39], [41]. Their modular structures enable selective interactions with target analytes, supporting applications in gas sensing, ion detection, biomolecule recognition, and environmental monitoring [25], [39], [41].

3.1 Optical Sensing

Luminescent MOFs (LMOFs) operate through mechanisms such as ligand-centred emission, metal-to-ligand charge transfer, and guest-induced quenching or enhancement [30], [42], [43]. Pore engineering—controlling ligand flexibility, linker functionality, and metal-centre identity—improves diffusion and selectivity. Composite systems (e.g., MOF-carbon or MOF-polymer hybrids) enhance signal strength and structural stability [4], [6], [44].

3.2 Electrochemical Sensing

Electrochemical MOF sensors benefit from uniform dispersion of active sites and high analyte uptake. MOFs improve catalytic behaviour through redox-active ligands, mixed-valence metals, or conductive additives. MOF-polymer and MOF-graphene composites address intrinsic low conductivity while maintaining sensitivity and reproducibility [45], [46]. Detection limits generally fall in the nano- to picomolar range, depending on analyte affinity.

3.3 Mass-Sensitive and QCM Sensing

Quartz crystal microbalance (QCM) sensors exploit the low density, high porosity, and strong

adsorption capacity of MOFs. Frequency shifts correlate with analyte uptake; Zr-based MOFs exhibit particularly good cycling stability. Applications include detection of volatile organic compounds (VOCs), environmental pollutants, and industrial gases [47], [50].

4.0 MOFs in Separation Science

Metal-organic frameworks have become increasingly important in separation science due to their high porosity, tuneable pore structures, and ability to introduce specific chemical functionalities. These features enable selective retention, size-based discrimination, and targeted interactions that support modern chromatographic and membrane-based separation platforms [51], [52].

4.1 Chromatographic Applications

4.1.1 MOF-Based Stationary Phases in Liquid Chromatography (LC)

MOFs incorporated into LC stationary phases enhance separation efficiency through: Size-exclusion effects from well-defined pore windows, π-π interactions with aromatic analytes via conjugated linkers, Metal-analyte coordination for selective retention, Hydrogen-bonding sites introduced through functionalized linkers [53], [55]. Common strategies include embedding MOF particles into silica, coating capillary columns with MOF films, or using MOF-polymer composites to improve stability. Zr-based MOFs (e.g., UiO-type structures) are frequently favoured because of their robustness in aqueous mobile phases [56].

4.1.2 Gas Chromatography (GC)

MOFs with high thermal stability have been successfully applied as GC coatings, offering: Strong interactions with small polar molecules, tailorable adsorption strengths for VOCs, Enhanced efficiency compared to traditional polymer-based phases. The precise geometry of MOF channels supports high-resolution separations, especially for isomeric compounds [57], [59].

4.1.3 Membrane-Based Separations

MOFs improve membrane separations by enhancing permeability and selectivity, often overcoming trade-offs in traditional polymer membranes.

4.1.4 MOF-Based Mixed Matrix Membranes (MMMs)

Incorporating MOFs into polymer matrices enhances: Gas permeability through porous frameworks, **Selectivity** via pore size control and chemical affinity, Mechanical strength when rigid MOF fillers are used. Examples include incorporating ZIF-type MOFs for CO_2/N_2 separation and UiO-derived fillers for water purification [60], [61].

4.1.5 MOF Thin-Film Membranes

MOF thin films fabricated on porous supports provide: Uniform pore channels for molecular sieving, fast transport pathways for small molecules, Compatibility with pervaporation, nanofiltration, and organic solvent nanofiltration (OSN). These membranes excel in selective dehydration, VOC recovery, and removal of heavy metal ions [62], [63].

4.2 Mechanistic Insights

- **Size-exclusion:** Separation based on precise pore apertures matching analyte kinetic diameters [64], [65].
- **π-π interactions:** Enhanced retention of aromatic analytes via linker conjugation [66], [67].
- **Coordination binding:** Metal nodes form transient bonds with Lewis basic analytes [11], [68].
- **Electrostatic interactions:** Charged frameworks preferentially attract oppositely charged species [59], [69].

4.3 Comparative Assessment

Across chromatographic and membrane platforms, MOFs exhibit:

Strengths: High selectivity from tailored pore chemistry [70], compatibility with both liquid and gas separations [12], ability to introduce specific interaction sites [63], improved permeability in membranes [60].

Limitations: Potential framework instability under harsh conditions [71], difficulty achieving uniform MOF-polymer dispersion (MMMs) [72], scaling challenges for industrial applications [73].

Table 1: Representative MOF-Based Materials and Their Applications in Separation Science

MOF / Composite	Separation Type	Key Mechanism(s)	Target Analyte(s) or Application	Performance Highlights	Representative References
UiO-66-NH_2	HPLC stationary phase	Hydrogen bonding, π–π interaction	Phenolic and pharmaceutical compounds	Improved selectivity and resolution compared to silica supports	[7], [22], [56]
MIL-101(Cr)	HPLC and GC stationary phase	π–π interaction; pore-size exclusion	Aromatic hydrocarbons, medicinal compounds	Excellent stability and high chromatographic efficiency	[5], [54], [59]
ZIF-8	Gas chromatography and membrane separation	Molecular sieving (size exclusion)	Alcohols, esters, light hydrocarbons	High thermal stability; H_2/CO_2 and propylene/propane selectivity	[60], [61], [72]
Cu-BTC (HKUST-1)	Gas-phase and VOC separation	Open metal-site coordination	Volatile organic compounds	Rapid elution and minimal peak broadening	[24], [48], [70]
UiO-67–NH_2	Capillary electrochromatography (CEC)	Electrostatic and hydrogen-bond interactions	Chiral amino acids, enantiomeric drugs	High enantioselectivity and short migration times	[7], [22], [66]
Zr-MOF/polymer hybrid	Mixed-matrix membrane (MMM)	Electrostatic and pore-diffusion control	Gas mixtures (CO_2/CH_4, H_2/CO_2)	Selectivity up to 95; strong mechanical robustness	[6], [60], [72]
ZIF-8@GO composite	Ion-selective membrane	Size exclusion and electrostatic interactions	Metal ions (Pb^{2+}, UO_2^{2+})	High ion selectivity; reusable over 10 cycles	[53], [69], [80]
Homochiral Zr-MOF	Chiral separation	Hydrogen bonding and π–π stacking	Amino alcohols, racemic drugs	Strong enantioselectivity;	[65], [66], [67]

MOF / Composite	Separation Type	Key Mechanism(s)	Target Analyte(s) or Application	Performance Highlights	Representative References
				reusable framework	
Sulfonated Zr-MOF	Aqueous pollutant adsorption	Metal–ligand coordination	Heavy metals (Pb^{2+}, Cd^{2+})	Adsorption capacity >600 mg g^{-1}; high regeneration ability	[22], [68], [80]
NH_2-MIL-53(Al)/polymer MMM	Gas separation (CO_2 capture)	Hydrogen bonding network and diffusion	CO_2/CH_4 mixtures	Enhanced permeability and stability	[37], [60], [72]

5.0 MOFs in Sample Preparation

Metal-organic frameworks (MOFs) are increasingly applied in sample-preparation workflows due to their high adsorption capacity, tuneable surface chemistry, and ability to selectively extract trace analytes from complex matrices [74]. Their modular structures support various extraction formats, including dispersive solid-phase extraction (dSPE), solid-phase microextraction (SPME), and stir-bar sorptive extraction (SBSE) [75].

5.1 Dispersive Solid-Phase Extraction (dSPE)

MOF-based dSPE sorbents demonstrate strong affinity for organic pollutants, heavy metals, dyes, pharmaceuticals, and emerging contaminants. Their large surface area and tuneable functionality facilitate selective extraction via: π-π stacking, metal-ligand affinity, hydrogen bonding, size-based adsorption [76].

Functionalized MOFs (e.g., amino-, thiol-, or sulfonate-modified frameworks) improve selectivity toward specific analyte classes. Magnetic MOFs (Fe_3O_4@MOF composites) simplify separation by enabling rapid magnetic retrieval without filtration [55], [77]. Some of the advantages include; High extraction efficiency, simple and rapid handling, suitability for environmental, food, and biological samples [78], [79]. Thus, some limitations include potential pore blockage during repeated use, framework degradation in strongly acidic or basic matrices, variability in synthetic reproducibility between batches [71], [80].

5.2 Solid-Phase Microextraction (SPME)

SPME fibres coated with MOFs provide enhanced adsorption capacity relative to polymeric coatings due to their ordered pore networks and strong analyte affinity. MOF-coated fibres improve extraction of: VOCs, phenolic compounds, pesticides, pharmaceutical residues, biological metabolites [75], [81]. Recent improvements incorporate MOF-carbon nanotube or MOF-graphene composites to enhance mechanical durability and heat resistance for headspace SPME. The key benefits are; High sensitivity with minimal sample volume, compatibility with GC, LC, and MS, controlled porosity improving selectivity. Some of the challenges include; Achieving crack-free, uniform coatings, mechanical fragility of pure MOF layers, need for better thermal stability for GC applications [82], [83].

5.3 Stir-Bar Sorptive Extraction (SBSE)

In SBSE, MOFs immobilized on stir bars significantly improve enrichment factors due to their vast porosity and strong adsorption sites [84]. MOF-coated SBSE devices have been evaluated for: PAHs, nitroaromatics, pharmaceutical residues, endocrine-disrupting compounds. Compared to traditional PDMS coatings, MOF-based SBSE provides greater selectivity, faster adsorption kinetics, and higher pre-concentration performance [85]. However, coating adhesion remains a challenge; composite binders or polymer-MOF hybrids often improve stability during repeated extraction cycles [86], [87].

5.4 Comparative Performance and Critical Evaluation

Table 2. A unified comparison of MOF-based extraction formats:

Technique	Strengths	Limitations
dSPE	High surface area; rapid extraction; magnetic recovery (MMOFs) [80]	Pore blockage, possible framework degradation [80]
SPME	High sensitivity; aligns with miniaturized workflows; selective coatings [78]	Fragile coatings; thermal stability issues [88]
SBSE	Excellent enrichment; high analyte loading [89]	Adhesion challenges; less suited for high-throughput workflows [90]

6.0 Future Perspectives and Conclusion

Metal-organic frameworks continue to demonstrate significant potential in analytical chemistry due to their tuneable porosity, high surface area, and ability to incorporate functional groups for selective interactions. Their applications in sensing, separation, and sample preparation illustrate how rational framework design can enhance analytical performance through improved selectivity, sensitivity, and enrichment capacity.

Despite these advantages, several challenges limit widespread adoption. Hydrolytic instability in some MOFs, pore blockage during repeated use, coating adhesion issues (in SPME and SBSE), and inconsistencies in synthetic reproducibility remain ongoing concerns. Additionally, the lack of standardized evaluation protocols makes it difficult to compare sorbent performance across studies.

Future progress will rely on:

- design of more robust and environmentally stable MOFs
- improved integration with polymers, magnetic supports, and conductive additives
- computational and AI-assisted material discovery
- development of scalable, green, and cost-effective synthesis routes
- standardized guidelines for analytical testing and stability assessment

Conclusion

Metal-organic frameworks (MOFs) signify a groundbreaking development within the domain of analytical chemistry, providing adaptable frameworks for applications in sensing, separation, and sample preparation. As elucidated in this review, their distinctive structural properties—particularly their remarkable tunability, expansive surface area, and customizable pore environments—facilitate accurate molecular recognition and effective sample manipulation. By correlating structural attributes with performance metrics, scholars have illustrated that methodologies such as pore engineering and surface functionalization can considerably augment analytical precision and selectivity. Notwithstanding their promise, the incorporation of MOFs into conventional analytical protocols encounters significant challenges. Principal obstacles encompass hydrolytic instability, pore obstruction, and complications related to synthetic reproducibility and scalability. Additionally, the lack of standardization constitutes a crucial impediment to widespread commercial implementation. Moving forward, the prospects for MOF-centric analytics rest on resolving these stability issues

and adopting forthcoming innovations such as AI-driven material discovery. By surmounting these challenges and aligning with the tenets of green analytical chemistry, MOFs are positioned to transition from promising research entities to indispensable instruments for compact, rapid, and sustainable analytical methodologies.

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