



Coordination polymers: Opportunities and challenges for monitoring volatile organic compounds



Pawan Kumar^a, Akash Deep^b, Ki-Hyun Kim^{a,*}, Richard J.C. Brown^c

^a Department of Civil & Environmental Engineering, Hanyang University, 222 Wangsimni-Ro, Seoul 133-791, Republic of Korea

^b Central Scientific Instruments Organisation (CSIR-CSIO), Sector 30 C, Chandigarh 160030, India

^c Analytical Science Division, National Physical Laboratory, Teddington TW11 0LW, UK

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ABSTRACT

Coordination polymers (CPs) are emerging as the next generation of macromolecules for many industrial and technological applications. The highly porous nature of these CPs offers the opportunity to exploit them as very effective adsorbents for gaseous molecules, including volatile organic compounds (VOCs). Release of VOCs into the environment is highly undesirable as they can be extremely harmful to general public health and environmental quality. Lately, a large volume of the scientific literature has pointed toward the potentially important role of CPs in the monitoring and analysis of VOCs, offering unprecedented detection limits. This review discusses the opportunities and challenges for the use of CP materials in such applications, describing their general working principles, analytical performance, advantages, and limitations. Recent progress in the application of CPs in the detection, monitoring, and analysis of VOCs is critically reviewed. The discussion is further extended to cover future applications and current research activities in this emerging analytical field.

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Abbreviations: Al-BDC, aluminum-benzene dicarboxylic acid; Amp, adenosine monophosphate; BDC, benzene dicarboxylic acid; BINOL, 1,10-bi-2-naphthol; BTB, 4,4,4'-benzene-1,3,5-triyl-tribenzoate; CC, colloidal crystals; Cd-MOF, cadmium-metal organic framework; CdTe, cadmium telluride; CNT, carbon nanotube; COF-1, (C₃H₂BO)₆·(C₉H₁₂)₁; COF-5, C₉H₄BO₂; CPO-27, M₂(dhtp) (M = Ni, Co, Mg); CPs, coordination polymer; Cu-BTC, copper-benzene tricarboxylic acid; DMF, N,N-dimethylformamide; EC, Environmental Commission; EPA, Environmental Protection Agency; Fe-BTC, iron based benzene tricarboxylic acid; GCE, glass carbon electrode; H₂ATC, 2-aminoterephthalic acid; H₂BDC, 1,4-benzene dicarboxylic acid; H₄dhtp, 2,5-dihydroxyterephthalic acid; HKUST-1, Cu₃(BTC)₂; HOMO, highest unoccupied molecular orbital; IRMOF, isoreticular metal organic framework; LLCT, ligand-to-ligand charge transfer; LMCT, ligand-to-metal charge transfer; LMOFs, luminescent metal organic frameworks; LSPR, localized surface plasmon resonance; MCL, micro-cantilevers; MIL-125, ZnO₄(bdc)₃·DMF; MIL-53, metal organic frameworks; MOF-101, Cu₂[o-Br-C₆H₃(CO₂)₂]₂(H₂O)₂·DMF₈(H₂O)₂; MOF-177, Zn₄O(BTB)₂; NIOSH, National Institute of Occupational Safety and Health; PBUs, primary building units; PL, photoluminescence; PPM, part per million; QCM, quartz crystal microbalance; RI, refractive index; SAWS, surface acoustic wave sensors; SBU, secondary building units; SERS, surface enhanced resonance spectroscopy; SPR, surface plasmon resonance; TEA, triethyl amine; TGA, thermo gravimetric analysis; UV-Vis, ultraviolet-visible spectroscopy; VOCs, volatile organic compounds; ZIF-8, zeolitic imidazolate framework-8; Zn-MOF, zinc-metal organic framework.

* Corresponding author. Tel.: +82 2220 2325; fax: +82 2 2220 1945.

E-mail address: kkim61@hanyang.ac.kr (K.-H. Kim).

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1. Introduction

Increased emissions of volatile organic compounds (VOCs) and their resulting impact on air quality is now considered of major environmental concern [1,2]. Indeed, some VOCs are identified as highly toxic or carcinogenic in nature and may cause both short- and long-term impacts on human health as well as on the natural ecosystem [3–5]. For example, the well-known carcinogen benzene has a high potential to damage humans in both specific ways (e.g., the liver, kidneys, spleen, and stomach) as well as systematically (e.g., the nervous, circulatory, reproductive, immune, cardiovascular, and respiratory systems) [6,7]. Consequently, a number of major environmental safety agencies (e.g., National Institute of Occupational Safety and Health (NIOSH), Environmental Protection Agency (EPA), and European Agency for Safety and Health at Work (EU-OSHA)) have established guidelines to limit the exposure of humans to VOCs in indoor and workplace air in light of their effect on health, even at low (sub-ppb) concentrations [8–11]. VOCs are also known to be important precursors of tropospheric ozone. For this reason, their emissions (and subsequent presence in outdoor air) are limited by legislation in many regions (for example in Europe [12]).

Emissions of VOCs occur from various diffuse and point sources, such as industrial discharges, solvent use, water treatment, and accidental spills, while contributions are also made from natural sources (such as volcanoes, vegetation, bacteria, fossil fuel deposits including oil, and sands) [13]. Moreover, VOCs can also be emitted from the production and use of many everyday household products (such as paints, fuels, petroleum products, raw materials, and solvents) which makes the control of their emissions particularly difficult. Consequently, control at their source is often attempted (e.g., Directive 2004/42/EC) [14,15]. The measurement infrastructure for the long-term, low resolution detection of VOCs in air is well established; however, currently only a few reliable sensing devices are available commercially to allow effective and continuous monitoring, with high time resolution [16].

Highly sensitive analytical techniques (including chromatography, mass spectrometry, nuclear magnetic resonance, etc.) have commonly been employed for the accurate quantitation of VOCs. These techniques may

display some drawbacks such as high expense, lack of portability, and lower throughput. Moreover, the use of such techniques often requires complex and time consuming pre-treatment steps and highly skilled operators [13,17]. To explore more cost effective alternatives, many sensor-based systems have been developed, using a wide range of detection principles, such as semiconducting metal oxides, conductive polymers, quartz crystal microbalance sensors, and electronic nose devices (Fig. 1). Nonetheless, such sensors generally suffer from limitations in sensitivity, selectivity, reproducibility, interference (from humidity), stability, or false responses due to sensor aging [18,19].

Recently, the combined use of two or three nanomaterials (defined as nanocomposites: such as CNT, Ag, SnO₂, ZnO, TiO₂, gold nanoparticles, and graphene) has been reported for the detection of VOCs [20–30]. However, these novel nanomaterials are not free from the problems commonly experienced in the use of other sensing devices (Table 1). Because of these problems, coordination polymer/metal organic frameworks (CP/MOF) have attracted a great deal of attention in the development of next-generation sensing devices. The use of CP/MOFs offers solutions to the commonly encountered problems discussed above. Basically, a CP/MOF is a crystalline solid made by the self-assembly

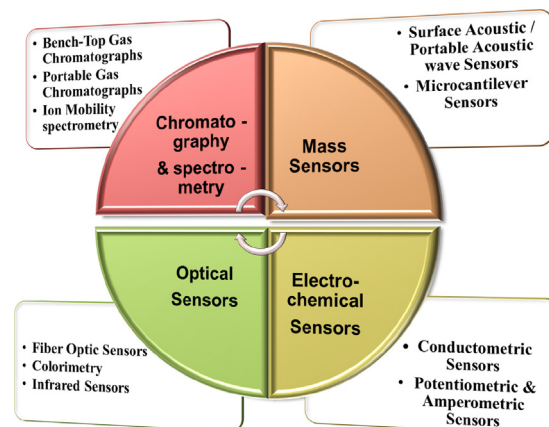


Fig. 1. Classification of different sensor types used for the analysis of VOCs.

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