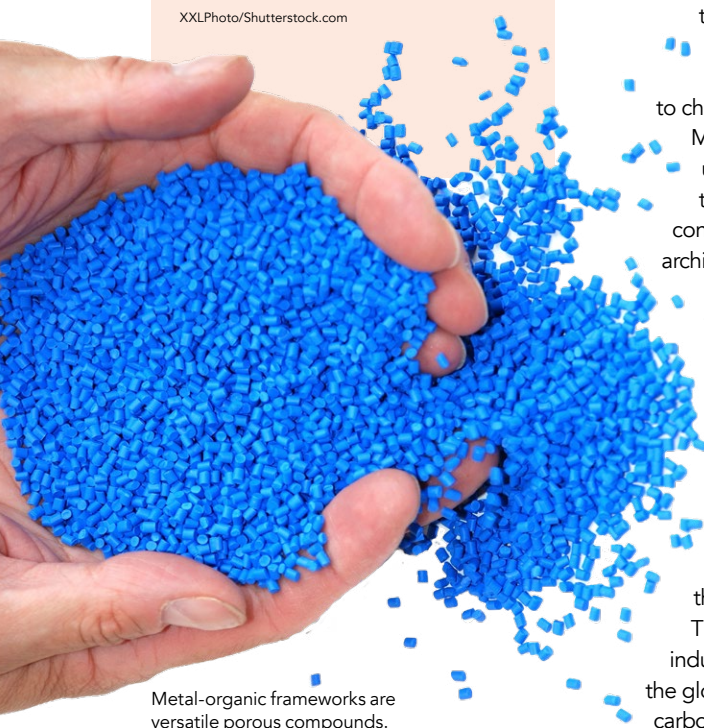


Metal–Organic Frameworks for chromatography and vice versa

Porous materials have a multitude of applications including catalysis, filtration, separation, energy storage, and sensors. To optimise the performance of porous materials within such diverse applications it is important to characterise their chemical properties. Dr Kareem Yusuf and his team, in collaboration with Professor Eddaoudi's group at King Saud University, Saudi Arabia, use inverse gas chromatography (IGC) to research the unique properties and applications of frameworks, an innovative class of porous materials with unique metal-organic properties.

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Metal-organic frameworks are versatile porous compounds.

Metal-organic frameworks (MOFs) are versatile porous crystalline materials that emerged less than 30 years ago. The MOF crystal structure consists of two main components: a positively charged metal-containing building unit that holds a single ion or clusters of ions, and a carbon-based part that links to the metal nodes in a highly ordered framework. The MOF metal nodes, as well as the organic linkers, can be chemically modified in order to alter the shape and size of channels and cages in the porous inner structure, allowing scientists to design materials with tunable properties.

Dr Kareem Yusuf and his team at King Saud University, Saudi Arabia, focus their research on the unique properties and applications of MOFs. The team uses an analytical technique known as inverse gas chromatography (IGC) to characterise the properties of MOFs. IGC is a powerful and user-friendly analytical tool that allows researchers to gain control over the chemical and architectural structure of porous surfaces. This enables them to design and customise the properties and performance of the materials, finely tuned for specific applications. One of the most promising uses of MOFs and other porous materials is the separation of compounds from complex mixtures using the minimum amount of heat. The approach could enable industrial chemists to lower the global energy consumption, carbon dioxide emissions, and

pollution associated with relevant industrial processes.

INVERSE GAS CHROMATOGRAPHY

IGC, also known as inverse pulse gas chromatography, is recognised as an effective tool for studying the surface properties of porous solids. In comparison with other analytical techniques, IGC is relatively simple and requires minimal sample preparation. For this reason, many researchers use IGC for the characterisation of various crystalline, composite, amorphous, or even fibrous solids. In IGC, the explored materials are the stationary phase, while standard analytical probes with different function groups representing different interactions are introduced at constant pressure and over a temperature range. This is a role reversal from the traditional gas chromatography technique, where the unknown mixtures are injected in the gaseous state and are adsorbed to a well-defined stationary surface, then eluted at different retention times for qualitative and/or quantitative analysis.

IGC experiments can be conducted by either a pulse or frontal technique. In pulse IGC a portion of a specific sample containing a molecule that acts as the probe is injected into the experimental column. With the help of carrier gas, the probing substance is transferred through a column that is packed with the material under study. With frontal IGC, the molecular probe is injected continuously into the system, with the advantage that a chemical equilibrium can be achieved between the material and the probe. Most IGC studies employ pulse instead of frontal approaches because they are quicker, more convenient, and provide higher accuracy in those cases where



Inverse gas chromatography has played a very important role in a variety of applications, such as medicinal industry improvements.

MOFs and other porous materials can be used for non-thermal driven separation, lowering global energy consumption and carbon dioxide emissions.

poor interactions are established with the probe. IGC has played a very important role in a variety of applications, such as medicinal industry improvements, the study of chemical and structural properties of carbon nanotubes, and the characterisation of polymers, minerals, and surfactants. However, only a few studies have used IGC for the characterisation of MOFs to investigate their different properties.

SEPARATION SCIENCE

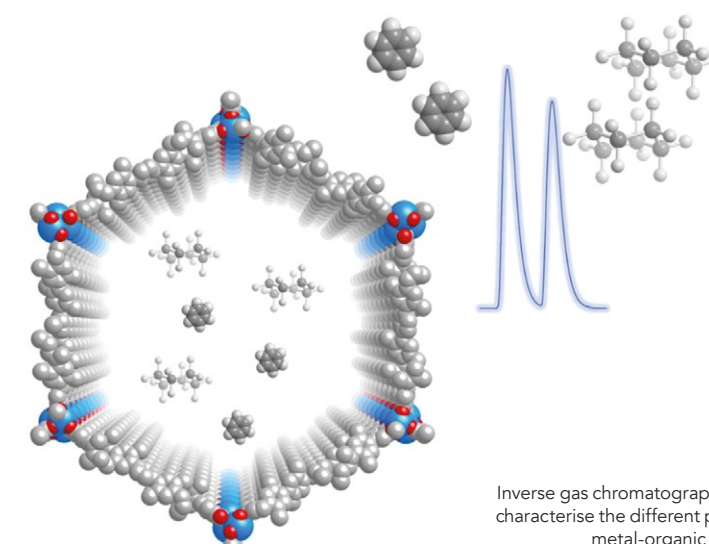
In a recently published study, Yusuf and his colleagues show the many advantages of using IGC as a characterisation tool to investigate the properties of MOFs and to predict how MOF architecture determines its chemical interactions with other molecules. Their research covers the procedural aspects of IGC in-depth, and how the technique can be optimised specifically for the study of MOFs. The porous materials are usually packed either as a dry powder or as suspensions into metallic or glass columns 2–80cm long. High-purity hydrogen or helium were used as inert carrier gases to move the probing molecules, which were in a vapour phase, along the

column. Different molecules would have a different affinity for the packed MOF material. Those with the most affinity for the MOFs will be retained for longer, and the different retention times provide valuable information about the different chemical properties of MOFs. According to Eddaoudi, 'there are hundreds of MOF materials that could be studied for separation science. The precise control of MOF pore size and shape, through the choice of both the metals

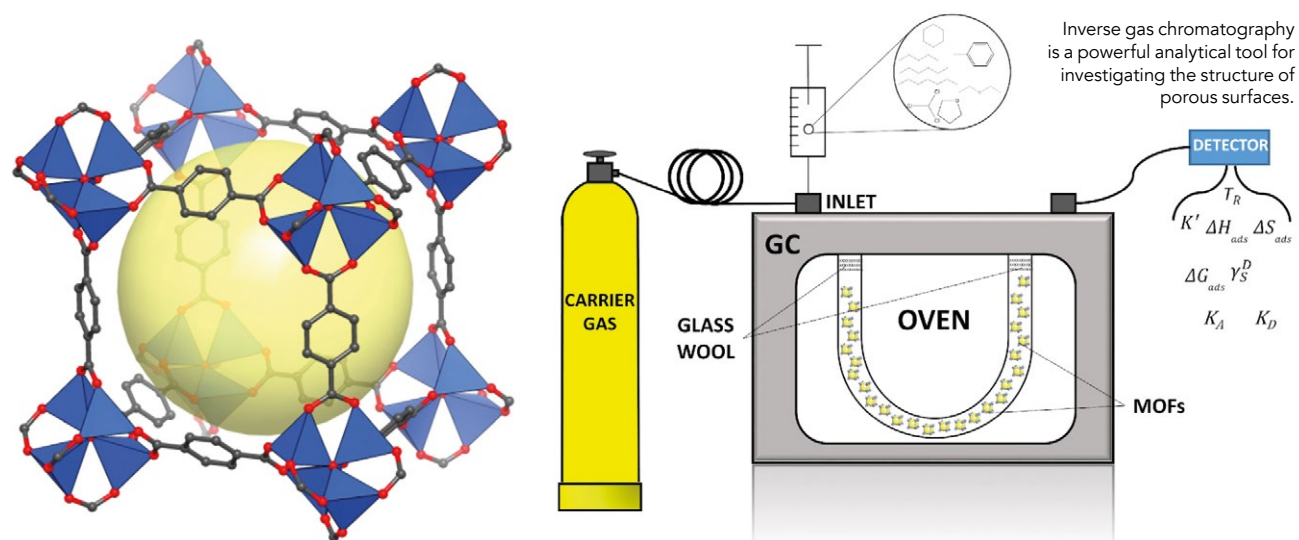
and organic ligands, provides scientists with new routes to explore for exploiting new materials'.

ENERGY-CONSERVING SEPARATION TECHNIQUES

Many industrial processes, especially fuel production, rely heavily on the separation of hydrocarbons from crude oil. It is possible in principle to separate hydrocarbons according to their molecular properties rather than relying on thermal methods such as distillation. Porous materials and in particular MOFs can be exploited for the development of eco-friendly and energy-conserving separation techniques to purify hydrocarbons and other industrial compounds. It is estimated that distillation and other conventional purification



Inverse gas chromatography is used to characterise the different properties of metal-organic frameworks.



techniques account for 10–15% of the world's energy consumption. Unlike distillation, which relies on heat, porous materials could allow industrial chemists to separate molecules according to their chemical properties or size, providing a cheaper and greener alternative.

MOF structures can also be optimised for important applications, such as carbon dioxide sequestration, which is envisaged as one of the possible

lamps contain europium and terbium, while cerium is used in catalytic converters and in white-emitting LEDs. Producing these rare-earth elements economically is a problem of separation, not availability. The separation of lanthanides from ores requires energy-intensive and inefficient extraction processes that use large volumes of chemicals and produce lots of waste and radioactive by-products. Research into the development of porous, cage-like surfaces, including MOFs,

their potential for a wide range of applications. Depending on the shape and size of their pores, MOFs can be designed to serve as gas sequestration and storage systems, catalysts to speed up chemical reactions, or sensors in analytical applications.

Yusuf's work highlights the use of IGC as an effective surface-analysis tool for the characterisation of porous materials, and is perfectly suited to predict the ability of MOF surfaces to interact with a variety of gases, hydrocarbons, solvents, and other compounds. Since many applications of MOFs, from separation chemistry to green energy production and storage, depend on the physical-chemical properties of their surfaces, IGC is poised to become an essential asset for many researchers who are committed to the design and development of efficient, eco-friendly materials and technologies of the future.

The rare-earth element, cerium, is used in white-emitting LEDs.



IGC is poised to become an essential asset for scientists who are committed to develop eco-friendly materials and technologies of the future.

strategies in tackling climate change due to increasing greenhouse gas emissions. Traditionally, liquids such as monoethanolamine are used for carbon sequestration; these liquids react readily with carbon dioxide (CO₂) but considerable amounts of energy, in the form of heat, must be applied to remove CO₂ from the resulting liquid. This makes the process impractical economically and cheaper methods for capturing CO₂ and hydrocarbon emissions must be developed.

FUTURE PERSPECTIVES FOR SEPARATION SCIENCE

Few realise the importance of the 15 'rare-earth elements' of the lanthanide series, which are used in magnets, renewable-energy technologies, and as catalysts in the refining of crude oil. Fluorescent

capable of binding to and extracting lanthanides, would greatly reduce the ecological impact associated with these sought-after resources.

Materials that can capture uranium, such as porous MOFs, could act as molecular 'cages' with the ability to capture other metals (including vanadium, cobalt, and nickel) at the same time. These materials could be incorporated within MOF to create separation membranes that have the potential to greatly reduce the economic and environmental cost involved in the extraction of uranium and other metals from diverse sources, including seawater.

Through their work to better characterise the properties of porous MOF structures, Yusuf and his team hope to unlock

Behind the Research



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Bio

Kareem Yusuf completed his PhD in analytical chemistry at the College of Science, King Saud University in 2016. In 2018, he became assistant professor of analytical chemistry, College of Science, King Saud University, and senior researcher at the Advanced Materials Research Chair (AMRC) since 2008.

Osama Shekhah received his PhD from Freie Universität Berlin and Fritz-Haber institute MPG under the supervision of Professor R Schlögl. He worked with Professor C Wöll (physical chemistry) at Ruhr-Universität Bochum Karlsruhe Institute of Technology as a group leader. Since 2011 he has worked in Professor Eddaoudi's group at KAUST as a group leader.

Zeid ALOthman is Professor of Chemistry, College of Science, King Saud University, KSA. He obtained his PhD in chemistry at Oklahoma State University in 2006. He is the group leader of the Advanced Materials in Chromatography Group, supervisor of the Advanced Materials Research Chair, chairman of Saudi Chemical Society since 2016 and Dean of College of Science, KSU since 2021. He has been selected as a Thomson Reuters Highly Cited Researcher since 2020.

Mohamed Eddaoudi is Distinguished Professor of Chemical Science and Director of the AMPM Center, KAUST, KSA. He received his PhD in chemistry from Université Denis Diderot (Paris VII), France. He was a professor at the University of South Florida (2002–2010). He has been selected as a Thomson Reuters Highly Cited Researcher since 2014.

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Research Objectives

Kareem Yusuf develops analytical methods and investigates the preparation of separation materials.

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Personal Response

What will be the next venture in your research journey?

Hundreds of MOFs and covalent organic frameworks (COFs) emerged during the last decade representing the most versatile porous materials ever created. They constantly develop and find their way into various adsorption applications including separation, among others. The next venture in our research journey is to develop new parameters using IGC technique to cover more MOFs and COFs, toward an integrated characterisation technique that could either become a stand-alone route or an essential piece of the characterisation and development puzzle.

