

FINDING THE FOREVER POLLUTANTS — FAST!

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ABSTRACT: The chemical industry has been a double-edged sword for humanity — offering timely solutions while simultaneously creating long-lasting problems. The often-quoted expression ‘Better Living Through Chemistry’ encompasses how many chemists feel about chemistry, but how will society best use chemistry for a sustainable future? This paper outlines our research into the rapid detection of a widespread, persistent and challenging class of pollutants known as perfluoroalkyl and polyfluoroalkyl substances. These molecules have become ubiquitous through their use in a range of consumer products, industrial manufacturing, and perhaps most significantly in aqueous fire-fighting foams. Perfluorinated and polyfluorinated alkyl substances are known to bioaccumulate, and there are hundreds of known contaminated sites around Australia, and globally. The current methods to identify contaminated sites are very expensive and require specialised analytical instruments, which are often located a long distance from the site of contamination. Our work has developed an instant colour change test for the presence of these pollutants. The goal is for an untrained operator to be able to quickly and accurately identify contamination in their environment.

Keywords: PFAS, perfluorinated alkyl substances, porphyrin, colourimetric

BACKGROUND

Many challenges for humanity have been remedied by using chemistry as part of the solution. But none of the benefits of chemistry are without consequences, and the true consequences are not always quickly evident. Humanity is often painfully slow to respond when chemical issues and challenges do become apparent. By way of example, early combustion engines had a chemical problem. Fuel and oxygen inside the engine must be ignited at a precise moment for the pistons to work together to turn the engine. If the fuel ignites at the wrong time, the consequence is a ‘knock’ which can be inefficient or destructive to the engine. The solution to the problem was a fuel additive sold under the brand name ‘Ethyl’ — short for tetraethyllead (Nickerson 1954). Tetraethyllead was an excellent antiknock agent, a wonderful chemical solution that saved many engines and increased engine power and therefore fuel efficiency. We now know the vast consequences of lead in fuels, and its emission from vehicles all over our world, which include brain damage, hypertension, stroke, intellectual development issues (Angrand et al. 2022), and elevated crime levels (Higney et al. 2022). Lead pollution might seem an issue of the past, but the legacy of lead pollution continues, with an estimated 900,000 deaths per year attributed to environmental lead exposure (World Health Organization 2022).

A modern class of ‘wonder’ molecules are perfluoroalkyl and polyfluoroalkyl substances, collectively

known as PFAS (used as a singular and plural noun). These molecules contain a large number of fluorine atoms bonded to carbon. Carbon–fluorine bonds are some of the strongest and most stable chemical bonds known. The stability of the carbon–fluorine bond make PFAS highly resistant to reactions that would typically break other types of chemical bonds, resulting in them lasting a long time in the environment (Cousins et al. 2020). They have been widely used in industrial and consumer products due to their unique properties, including their chemical stability, heat resistance and repulsion of oil and water. These properties made PFAS ideal for a range of applications, including non-stick cookware, food packaging, water-repellent clothing, cosmetics and fire-fighting foams (Glüge et al. 2020). PFAS are also well known to bioaccumulate (Burkhard 2021), and are implicated in a number of health concerns, such as cancer (Steenland & Winquist 2021), kidney function (Stanifer et al. 2018), cholesterol levels (Andersen et al. 2021), and for pregnant mothers and their babies (Szilagyi et al. 2020).

Testing for PFAS contamination in the environment has become a focus of researchers and regulators, but such testing is complex and expensive (Cordner et al. 2021). Over 5000 PFAS are known, and specialised analytical methods are required to detect and measure their presence in environmental and biological samples. These methods include liquid chromatography — mass spectrometry (LC–MS) and gas chromatography — mass spectrometry (GC–

MS) which are highly sensitive, but costly. The equipment to run these tests are often located many kilometres away from the site of contamination. This can leave people directionless in the field, as they may need to wait multiple days or weeks to know the contamination levels before they can undertake further sampling. The cost of testing can vary widely depending on the type of sample, the number of PFAS compounds being analysed, and the level of detection required, but can range from hundreds to thousands of dollars per sample.

A DIFFERENT APPROACH

Given the time delay and cost of laboratory-based PFAS detection, we have sought to develop a rapid method for the detection of PFAS that could be deployed to the field and be used by an untrained operator for environmental samples. We hope to reduce the cost of identifying PFAS contamination, speeding up the path from identification to remediation. This would ultimately reduce the length of exposure and thus lower the risk of negative health and environmental outcomes. Ideally our test would be similar to a testing kit you might use for a swimming pool, or soil pH, where you take your soil or water, mix it with our molecules, and the colour instantly changes if the sample contains contaminants.

Host–guest chemistry is a branch of supramolecular chemistry that deals with the interactions between host molecules and guest molecules (Steed & Atwood 2022). The host molecules are typically large and can form specific interactions with smaller guest molecules. These interactions are termed ‘non-covalent interactions’ and can include hydrogen bonding, electrostatic interactions, and van der Waals forces. The binding of the guest to the host facilitates a change in properties — in our case colour — which can be measured or detected by the eye, by instrumentation, or by software (Figure 1).

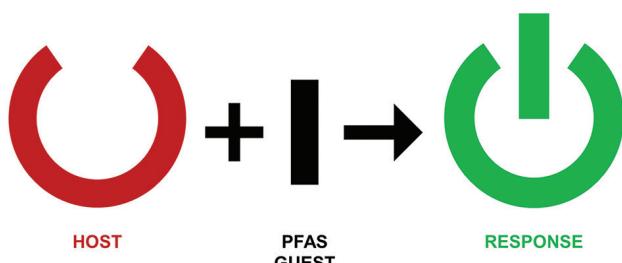
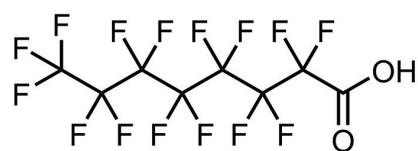
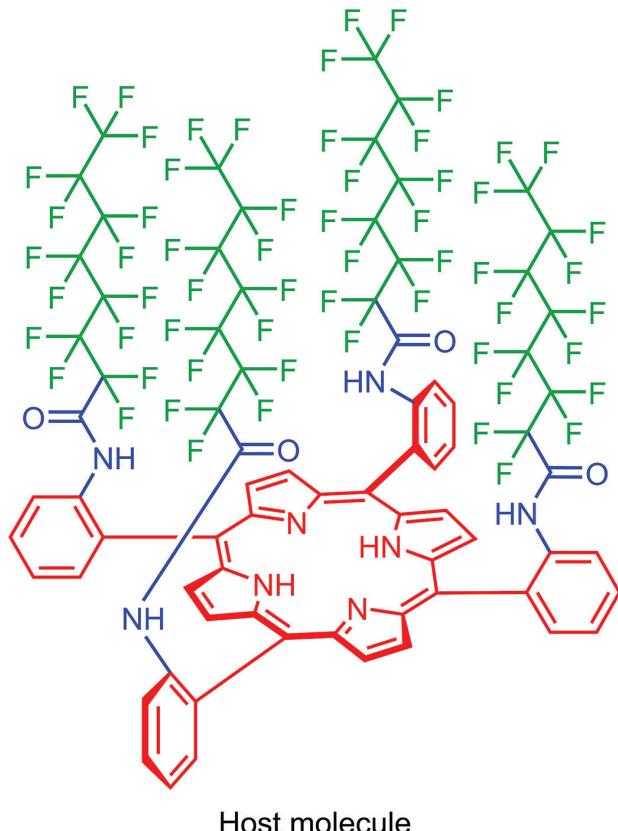


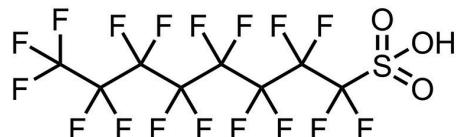
Figure 1: Schematic for Host-Guest Binding and Detection of PFAS.

The host molecules we have prepared are based on porphyrins (Figure 2). These large ring-shaped molecules are highly coloured, and are found widely in nature in blood and in chlorophyll in plants. To this porphyrin we have attached anion binding groups known as amides that are able

to interact with negatively charged groups that are found at the end of common PFAS such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) when they are deprotonated to their anionic forms (Figure 2). The amide groups are further connected to perfluorinated chains which are intended to form interactions with the perfluorinated and polyfluorinated chains of PFAS molecules.



Perfluorooctanoic acid (PFOA)



Perfluorooctanesulfonic acid (PFOS)

Figure 2: Host molecule, with porphyrin (red), amides (blue) and perfluorinated chains (green) highlighted. The common PFAS pollutants PFOA and PFOS are also shown.

The binding of PFOA guest molecules (a commonly found PFAS pollutant) to the host molecule changes the physiochemical properties of the porphyrin, leading to a change in colour. We have explored this molecule in solution (Figure 3a), for extractions from soil (Figure 3b), from biphasic mixtures of water and solvent (Figure 3c), and from water when the host is adsorbed to silica (Figure 3d) (Taylor et al. 2021). The visual response of the porphyrin host molecules can be seen at concentrations as low as 3 ppm from soil, which represents a proof-of-concept experiment for the detection of soil contamination at concentrations relevant to real world samples.

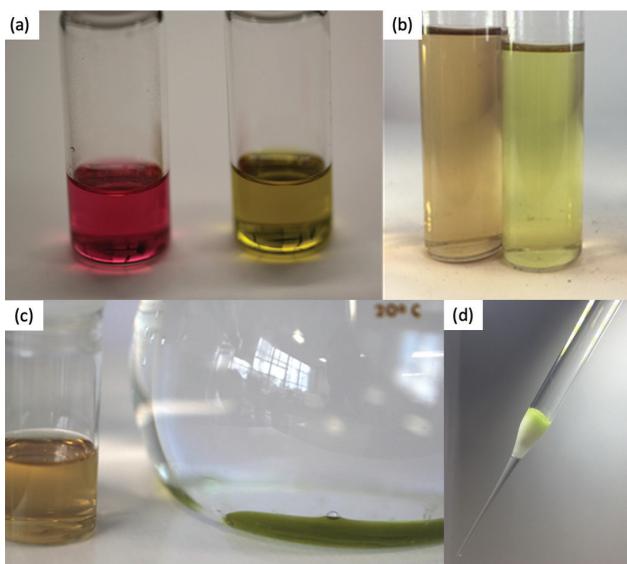


Figure 3: (a) Dichloromethane solutions of host (left) and host with PFOA guest (right) in dichloromethane, (b) Dichloromethane extractions from soil control (left) and doped with 15 ppm PFOA (right), (c) Dichloromethane extraction from water with host solution (right), and biphasic mixture of 3 ppm PFOA water and dichloromethane host solution, (d) Extraction of PFOA from 1 ppm solution in water with host molecule adsorbed to silica gel.

We have further expanded the visual detection of perfluorocarboxylic acids (PFAS molecules similar in chemical structure to PFOA) through colour processing. Taking photos with mobile phones and processing the images with software allowed for the determination of the colour of both the host solution and solutions containing mixtures of host and PFAS guests. We have used the RGB colour information for mixtures of our host porphyrin molecule with known quantities of PFOA to establish the relationship of colour to concentration (Taylor et al. 2023). The colour information obtained from PFOA can then be applied to mixtures of perfluorocarboxylic acids to approximate their concentrations. Our intention is that extracted colour information can be used to develop simple colour chart methods of assessing the concentration of PFAS in environmental samples. An example colour chart

generated from host solutions and solutions with host and PFOA is shown in Figure 4.

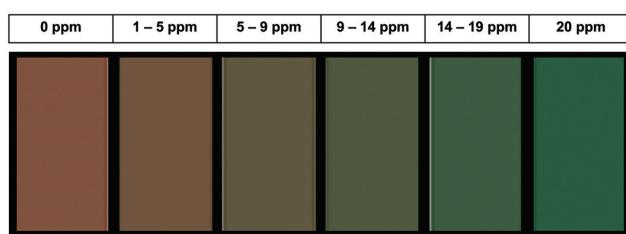


Figure 4: Interpolated colour chart for the estimation of 0–20 ppm perfluorocarboxylic acids using colourimetric techniques.

PFAS IN A SUSTAINABLE WORLD

The methods we are developing are not the real solution to PFAS pollution, and more stringent regulations are required to prevent further PFAS contamination and exposure. In response to regulatory and consumer pressure, some companies have implemented strategies to reduce their use of PFAS, such as reformulating their products to eliminate the use of banned molecules. While this complies with the regulations, similar (and less well studied) PFAS are often used instead. This approach can be seen as a way to avoid the immediate costs and disruption associated with switching to alternative materials, while also enabling companies to maintain the performance and functionality of their products. So although a small number of PFAS have been banned, almost 5000 ‘forever chemicals’ remain in use. Suggestions have been made to ban PFAS as a class of chemicals so that innovative chemists and their employers do not dodge regulations through clever chemistry. We hope that our colour-based technique can make PFAS testing more accessible, especially in remote or resource-limited areas, and can help to increase the frequency of testing. Our methods are still under development and require further research to be validated, standardised and turned into a viable product.

Acknowledgements

The authors acknowledge the muwinina people, the traditional owners of the land on which the research was conducted. Funding for this research was provided by the University of Tasmania.

Conflict of interest

The authors have submitted a provisional patent related to this work (IP Australia application number 2021900529).

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