Comparison of extraction techniques for the analysis of *N*-nitrosamines in South African waters

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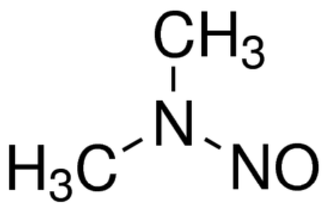
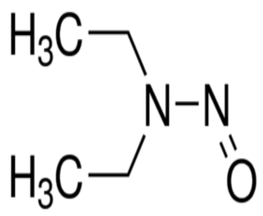
Introduction



N-nitrosodimethylamine



N-nitrosodiethylamine

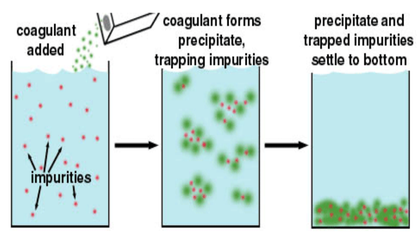
Water treatment plants (WTPs) exploit natural sources of water such as rivers, lakes, springs, groundwater, and municipal wastewater effluents to provide potable drinking water to consumers [1]. These sources of water may contain high levels of contaminants that are of terrestrial and anthropogenic origin that can serve as precursors of disinfection by-products (DBPs). Chlorination and chloramination are the most widely used water disinfection treatments. Some WTPs employ chloramination due to it being able to reduce levels of ubiquitous DBPs such as trihalomethanes and haloacetic acids. Chloramination is the process of adding chloramines, usually monochloramine, to untreated water to destroy pathogenic microbes. However, this disinfection treatment may produce high levels of nitrogenous DBPs, in particular, nitrosamines such as *N*-nitrosodimethylamine (NDMA) [2].

Sampling

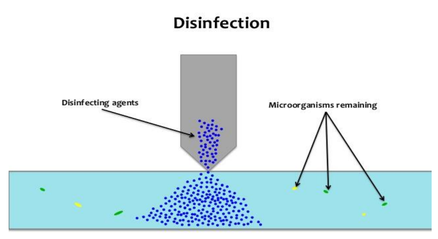
Tap water samples will be collected at sites around Pretoria and water samples will be collected at Rand Water treatment plants before and after the disinfection processes. Samples will be collected in amber glass bottles (500 mL) with PTFE-lined caps. The bottles will be filled to the top to avoid the formation of headspace and either ascorbic acid or sodium thiosulfate (3 %) will be added to the samples to stop any further nitrosamine formation in the samples. The samples will then be transported to the laboratory in a cooler box and stored at 4 ^{o}C prior to analysis. Trip blanks consisting of deionized water and ascorbic acid or sodium thiosulfate will be included for each sampling batch. The analysis will be conducted within one week of collection [2,3].

Typical water treatment process

Rand water abstracts its raw water predominantly from the Vaal dam



Coagulation, flocculation, sedimentation and filtration. Slaked lime is added as the main coagulant to destabilize electrostatic charges of suspended particles. Ferric chloride is added to promote flocculation.



Disinfection done by chlorination and chloramination to kill pathogenic microbes.

Distribution of the water via long pipe networks. The water finally reaches people in their households.

Analytical techniques

Two extraction methods will be explored, and their efficacies will be compared, namely solid phase extraction (SPE) and extraction using molecularly imprinted polymers (MIP). For this research, water samples will be scanned first using SPE LC-MS/MS to check for occurrences of nitrosamines, and suitable MIP templates for nitrosamines that are found to be prevalent in the samples will thus be established.

Fig.1. SPE setup with glass vacuum manifold

A non-imprinted polymer (NIP) will be synthesized using methacrylic acid (MAA) as a functional monomer, ethylene glycol dimethacrylate (EDGMA) as a crosslinker, and toluene as a porogenic solvent. NIP synthesis will be conducted to optimize the conditions of the polymerization reaction. When the optimal conditions for the polymerization reaction are established, a multi-template MIP that has affinity for all templates will be synthesized [5].

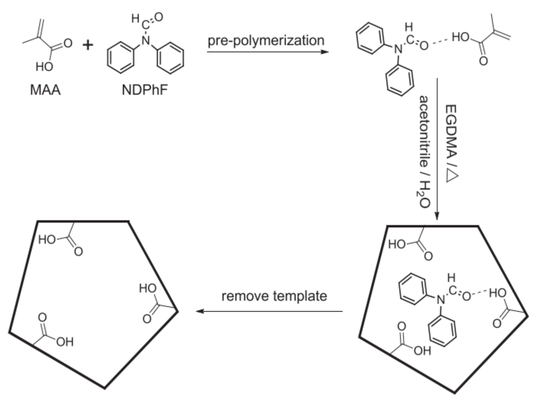


Fig. 2. Molecular structures of N-Nitrsodiphenylamine (NDPhA) and the template molecule N, N-Diphenylformamide (NDPhF). And the schematic representation of the MIPs synthesis, suggesting its molecular structure.

Characterization of NIP and MIPs

Images of each MIP and NIP will be taken using scanning electron microscopy (SEM), whilst thermogravimetric analysis (TGA) will be employed to determine the polymers' thermal stability and the fractions of their volatile components. Fourier transform infrared spectroscopy (FT-IR) of all polymers will be done within a scan range of 4000 to 400 cm^{-1} and their adsorption capacities will be calculated by the following equation:

$Adsorption\ capacity(\frac{mg}{g}) = \frac{(C_i - C_f)V}{W}$, where C_i (mg/L) is the initial concentration of the analyte before adsorption, C_f (mg/L) is the final concentration after adsorption. V is the volume of the solution in litres and W is the mass of the polymer in grams [4].

Green chemistry considerations

During the monitoring of environmental pollutants, it is always of paramount importance that green analytical chemistry principles are adhered to, such as waste prevention, use of safer and renewable solvents, atom economy, use of less hazardous chemicals, energy efficient reactions and cost effective synthesis [6]. For this study, the techniques being employed will always be adjusted accordingly to ensure they abide by the principles of green chemistry as far as possible.

References

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