The Need for Specific Detectors in Nitrosamine Testing in Water

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Nitrosamines are a group of compounds pertaining to the generalised formula $R^1N(-R^2)-N=O$ where R^1 and R^2 can be a vast array of hydrocarbon based compounds, with over 300 known and investigated. Of these, at least 90% are known or thought to be carcinogenic, with n-nitrosodimethylamine (NDMA) the most widely investigated and thought to be the most dangerous to health. Nitrosamines are formed in a wide range of industrial processes, food and beverage production, as well as formation within the human stomach. Although many different mechanisms for the production of these compounds are known, generally heat combined with an amine and a nitrate/nitrite source is the most common.

Research into the carcinogenic and mutagenic effects of nitrosamines, have been extensively performed with early evidence indicating liver tumour formation in rats. Nitrosamines were further implicated as the cause of a large range of liver disorders, including cancer, in farm animals which had been fed on nitrosamine containing feedstock. N-nitrosodimethylamine (NDMA) is the most widely studied nitrosamine and thought to be the most damaging to human health.

There are various groups or nitrosamines with the most commonly analysed being the volatile nitrosamines. This group consists, as the name implies, of compounds of generally low boiling points, such as NDMA, N-nitrosodipropylamine (NDPA) and n-nitrosomorpholine (NMOR) and are produced in a vast array of processes. These are particularly dangerous as these can be ingested by humans from the surrounding air as well as direct contact. Many nitrosamines are industry specific, for example the tobacco specific nitrosamines (TSNAs) are formed around nicotine and compounds found in the raw material and smoke produced by burning. Another example of industry specific nitrosamines and also commonly classed as a non-volatile nitrosamine, is N-nitrosodiethanolamine (NDELA). This compound is formed in the cosmetic industry due to the use of proteins and triethanolamine as a preserving agent. As well as those mentioned above, nitrosamines are also routinely measured throughout many industries, with the most common being rubber production, beer/malting, food (especially smoked goods) and agrochemical. Due to the suspected dangers through inhalation and/or ingestion of these compounds, many industries and products are strictly monitored for content, as well as, nitrosamine precursors.

During the 1990s and early 2000s, the discovery of alarming levels of nitrosamines in water and wastewater caused an increase in research into the formation pathways and removal [1,2]. This was especially concerning due to the increase of recycling wastewater for drinking purposes. Nitrosamines are now classified as a sub-group within the disinfection by-products (DBPs). The DBPs are formed when the chemical used for disinfecting the drinking water reacts with natural organic matter and/or bromide/iodide in the source water. Popular disinfectants include chlorine, ozone, chlorine dioxide and chloramine. Source waters can include rivers, lakes, streams, groundwater, and sometimes seawater.

The research found the use of chloramines as a sterilising agent for water instigated the formation of nitrosamines, especially NDMA. Chloramines where initially used for the treatment of water to maintain residual chlorine levels without the addition of neat chlorine, as this caused a wide range of DBPs (not known to include nitrosamines). Although a definitive reaction pathway has not yet been proved, many have reported the formation of nitrosamines [3,4], occurs by the oxidation of unsymmetrical dimethylhydrazine (UDMH), which itself is formed from dimethylformamide (DMF) and monochloramine *(Figure 1)*. The research into drinking water sources led to investigations into the presence of nitrosamines in swimming pools and hot tubs [5,6,7]. Permissible levels vary widely dependent on the governing body overseeing the analysis. In England and Wales, permissible levels of 1 ng l^{-1} for NDMA are in place. Whereas in California, 10 ng l^{-1} is the notification level for NDMA and N-nitrosodiethylamine (NDEA), although this level is under evaluation with 3 ng l^{-1} likely to be implemented in the future. In many countries the analysis of nitrosamines in drinking water is not fully regulated with no acceptable levels analysed or in place.

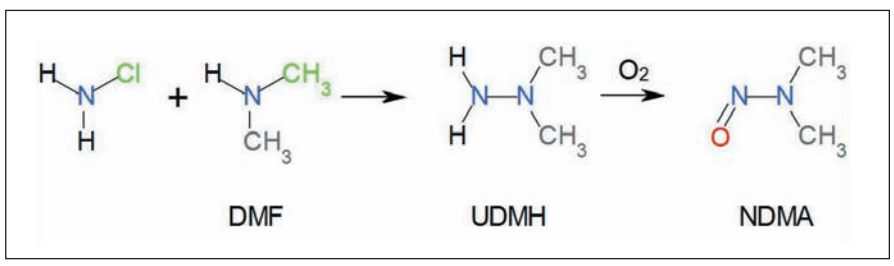

Figure 1. The formation of nitrosamines in water

Jurado-Sanchez et al [8]. found the occurrence of 25 amines including 5 nitrosamines whilst studying a drinking water treatment plant. It was also noted the levels increased by around 10 fold after the chloramination process. A slight increase in concentration was also observed within the distribution system. Seasonal effects were also found with colder temperatures being attributed to an increase of the amines and specifically the nitrosamines.

Swimming pools and hot tubs have been investigated, as increased levels of chloramines are added to stop users becoming ill. However studies have shown the formation of nitrosamines is enhanced due to bodily fluids and excretions, giving far higher levels in swimming pools as opposed to tap water.

It was also observed the water present in outdoor pools was significantly lower than that obtained from indoor pools. This was attributed to breakdown of the nitrosamines by UV light from the sun and increased ventilation due to wind.

Figure 2. Thermal Energy Analyser (TEA) connected to a Gas Chromatograph (GC)

Many different techniques are used to separate and determine the nitrosamines from water. Methods involving solid phase extraction (SPE) and solid phase micro extraction (SPME) are extremely popular, with an extensive range of differing sorbents. For example, the EPA 521 method employs coconut charcoal based SPE to preconcentrate 500 ml of water, down to 1 ml of dichloromethane (DCM) for analysis. Dependent on the method, the eluent is analysed by gas chromatography (GC) [9,10] or liquid chromatography (LC) [11]. GC methods utilise nitrogen specific detectors for nitrosamines, such as the thermal energy analyser (TEA) *(Figure 2)* or the nitrogen phosphorus detector (NPD), with mass spectrometry (MS) especially tandem being employed for GC and LC.

Samples were collected as per the EPA 521 method mentioned above and then extracted using SPE and concentrated down. They were then subsequently analysed using a GC connected to a TEA. The first chromatogram *(Figure 3)* shows a sample spiked with NDMA and NDPA at the UK reporting levels of 1ng l^{-1}.

The second chromatogram *(Figure 4)* shows a tap water sample with levels of NDPA showing at approximately 0.3ng l^{-1} as well as other unidentified peaks. The third chromatogram *(Figure 5)* shows a sample of swimming pool water. This showed levels of NDMA present at around the UK reporting level (1ng l^{-1}) as well as other unidentified peaks at even higher levels.

Although the MS analysis will give identification of the actual compounds, there is still a vital role for the nitrogen specific detectors. The selectivity and sensitivity of such detectors, coupled to the relative ease of use and far less cost per sample, enables fast 'complete' analysis of the whole sample. Many MS systems are routinely used in single ion monitoring mode [to test for NDMA only] to obtain the sufficient sensitivity required.

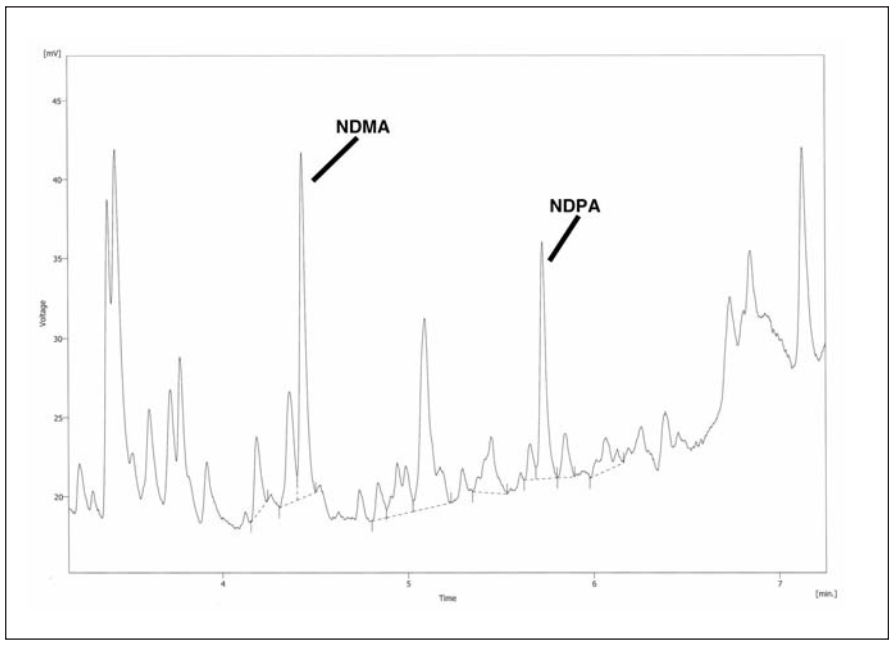

Figure 3. Water sample with 1ng l^{-1} of NDMA and NDPA analysed using a TEA

But as mentioned earlier, a vast amount of other potentially dangerous nitrosamines can be present within the sample, which using this MS mode will ignore. This is not only an issue within the water industry, but is also the case in many others, such as foodstuff and pesticide residues. In essence following standardised methods can in some cases, cause tunnel vision for a single compound leading to bad laboratory practice and missing other hazardous substances.

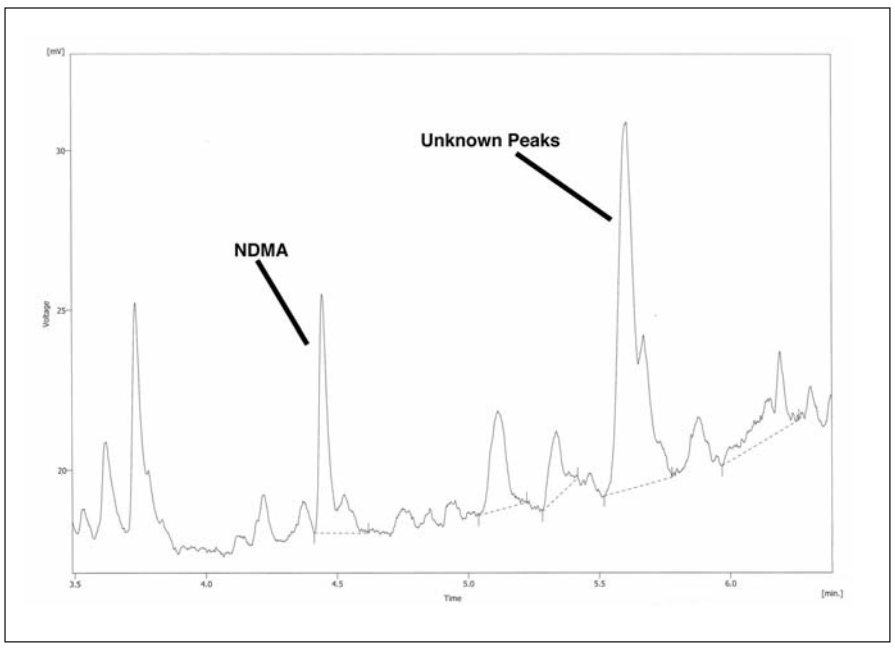

Figure 5. Swimming bath water sample analysed using a TEA

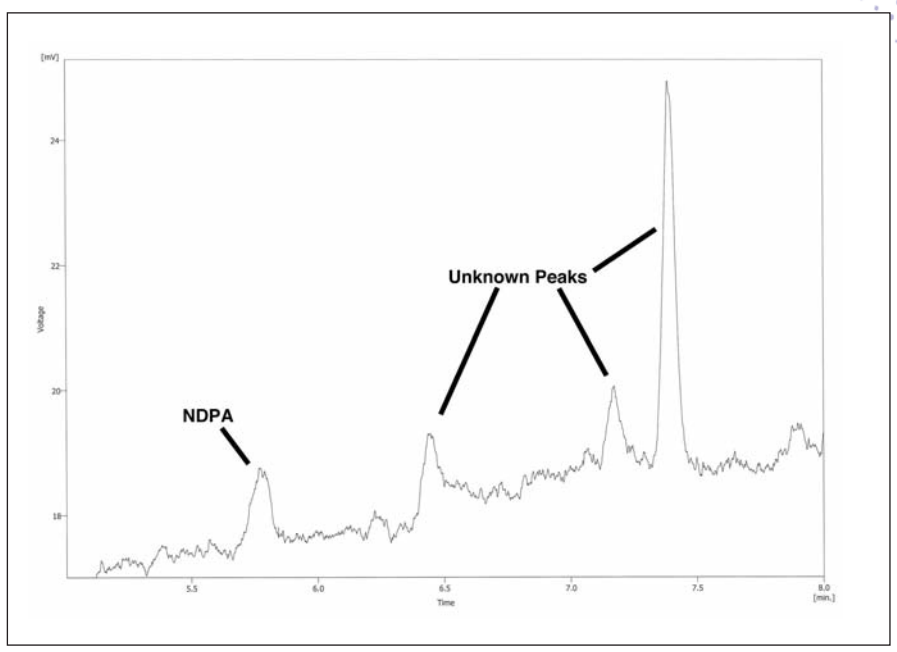

Figure 4. Tap water sample analysed using a TEA

Therefore, having the ability to use these specific detectors for screening purposes can be an extremely useful tool for the modern analytical laboratory. These instruments would highlight samples with large contamination as well as samples containing unexpected peaks that would require further investigation. Modern robotic autosampler's along with intelligent software can perform all of the processes including SPE, injection onto a fast screening GC with thermal energy analyser, full peak identification and subsequent injection onto a GC with mass spec to confirm specific compounds or identify other unknown high peaks.

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Measuring System is Integral to Queen's University's Polymer Characterisation Lab

"The Zetasizer Nano ZS is an integral piece of equipment in our polymer characterisation laboratory," said Daniel Krasznai, Department of Chemical Engineering, Queen's University, Kingston, Canada. "The most important features that the Zetasizer Nano ZS offers are rapidity, reproducibility, and a user-friendly interface."

Daniel Krasznai's supervisor, Dr Michael F. Cunningham, holds the Ontario Research Chair in Green Chemistry and Engineering at Queen's University. His team focuses on the synthesis of polymer colloids using a range of dispersed free-radical polymerisation techniques. Together with Dr Niels M.B. Smeets, and fellow collaborators Dr Pascale Champagne and Dr Timothy F.L. McKenna, they have recently published a paper in which they use the Zetasizer Nano ZS to characterise novel core-shell materials in pure water.

In this publication, Dr Smeets' previous work on the rational design of hyperbranched synthetic polymers from Catalytic Chain Transfer Polymerisation (CCTP) was extended to provide a core-shell copolymer consisting of a synthetic core decorated with a polysaccharide shell, allowing for easy dispersion in water. Resulting data from the Zetasizer Nano ZS was used to support the anticipated core-shell structure. Because these core-shell particles are discrete and covalently linked, there is no need for micellization to create a stable colloidal system in water.

"The Zetasizer Nano ZS is a useful instrument for us since the average particle size, particle size distribution, and zeta potential of our materials are key parameters in terms of understanding the fundamental issues surrounding particle creation and stabilisation, as well as reaction kinetics and macromolecular architecture. A particularly unique application of the Zetasizer Nano ZS is that we can measure the average particle size and zeta potential of some of our samples using undiluted suspensions (of a few wt% in concentration)," continued Dr Smeets.

The published paper; 'Polysaccharide-stabilised core cross-linked polymer micelle analogues' by Krasznai et al, was published in Polymer Chemistry, Issue 4, 2012, and is available online through RSC Publishing.

The Zetasizer Nano ZS measures particle and molecule size from less than one nanometer up to several microns using dynamic light scattering, zeta potential and electrophoretic mobility using electrophoretic light scattering, and molecular weight using static light scattering.

MORE INFO. 34