

Novel Chemiluminescence-based Method for the Quantification of the Total N-nitrosamines Concentration in Water

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N-nitrosamines (NOAs) are potent carcinogenic and mutagenic compounds that can be present in water, biological fluids, foodstuffs and cigarette smoke. For instance, NOAs can be formed during oxidative treatment of wastewater and drinking water. Several studies have shown that the formation of NOAs in water can arise from the reactions of amine precursors with chemical oxidants such as chloramines, chlorine or ozone. So far most of the studies published on NOAs in water have focused on only nine specific NOAs selected by the US-Environmental Protection Agency (EPA). However several recent studies have shown that the NOAs selected by the US-EPA might account only for ~5-15% of the total NOAs concentration (TONO) in water.¹ Therefore, quantifying the TONO is necessary to assess the overall risk associated with the presence of NOAs in water. To determine whether N-nitrosodimethylamine and other specific NOAs of current interest are dominant or minor components of the total NOAs pool, several chemiluminescence-based methods using chemical denitrosation agents such as HI₃, HBr or CuCl have been developed.^{2,3} However, denitrosation agents used in chemiluminescence based-methods are very unstable and may form potent nitrosating agents such nitrosyliodide (NOI) that might (re)form NOAs during the analytical process.⁴ Alternatively, NOAs can be photolysed by UV light yielding NO[•] that can be detected by a nitric oxide chemiluminescence analyser. Photochemical reactions are usually easier to control since no chemical reagents are involved and the reaction is controlled by the UV dose. Based on the issues related to chemical denitrosation of NOAs and the promising features of UV photolysis, we have developed and evaluated a photolysis chemiluminescence-based system for the analysis of TONO concentrations in aqueous samples.⁵ The analyses of pre-concentrated water samples have shown that the TONO concentrations in two wastewater effluent samples were 49.8 ± 5.1 nM and 50.2 ± 4.9 nM, whereas in greywater the TONO concentration ranged between 9.3 and 18.3 nM. These TONO concentrations are in the same range as previously reported in the literature and suggest that N-nitrosodimethylamine likely constitutes only of small fraction of the total NOAs pool. By utilizing a capillary microphotochemical reactor to reduce the sample cross-section and volume, irradiation and resulting NOAs photo-decomposition to NO[•] were optimal to reach a sensitivity level comparable to chemical denitrosation (LOD=0.1 mM; LOQ=0.3 mM). Moreover, the reproducibility was enhanced compared to other methods. Because UV-photolysis is more convenient and more reliable to work with, this method simplifies the determination of total NOAs concentration in water.

[1] Zeng, T.; Mitch, W. A. Contribution of N-Nitrosamines and Their Precursors to Domestic Sewage by Greywaters and Blackwaters. *Environ. Sci. Technol.* **2015**.

[2] Wang, J.; Chan, W. G.; Haut, S. A.; Krauss, M. R.; Izac, R. R.; Hempfling, W. P. Determination of Total N-Nitroso Compounds by Chemical Denitrosation Using CuCl. *J. Agric. Food Chem.* **2005**, *53* (12), 4686-4691.

[3] Kulshrestha, P.; McKinstry, K. C.; Fernandez, B. O.; Feelisch, M.; Mitch, W. A. Application of an Optimized Total N-Nitrosamine (TONO) Assay to Pools: Placing N-Nitrosodimethylamine (NDMA) Determinations into Perspective. *Environ. Sci. Technol.* **2010**, *44* (9), 3369-3375.

[4] Hausladen, A.; Rafikov, R.; Angelo, M.; Singel, D. J.; Nudler, E.; Stamler, J. S. Assessment of nitric oxide signals by triiodide chemiluminescence. *Proc. Natl. Acad. Sci.* **2007**, *104* (7), 2157-2162.

[5] Breider, F.; von Gunten, U. Quantification of Total N-Nitrosamine Concentrations in Aqueous Samples via UV-Photolysis and Chemiluminescence Detection of Nitric Oxide. *Anal. Chem.* **2017**, *89* (3), 1574-1582.5