

Methylene blue active substances (MBAS)

Surfactants and Their Significance in the Environment

Detergents contain synthetic or organic surface-active agents called surfactants, which are derived from petroleum product precursors. They have the common property of lowering the surface tensions of water thus allowing dirt or grease adhered to various articles to be washed off. Industrial facilities use detergents to clean machinery. Soap manufacturers and households will also discharge anionic detergents into the surface water. The problem with these types of discharges is that surfactants can present significant environmental pollution problems. In aquatic environments, surfactants may form a surface film and reduce oxygen transfer at the water surface. Some surfactants may be acutely toxic to aquatic organisms. Detergents can damage fish gills by stripping them of their natural oils, thus interrupting oxygen transfer. Surfactants and detergents may also cause suds or foam to form on surface waters, which is aesthetically displeasing. Furthermore, this foam often contains nutrients such as nitrogen and phosphorous which can; in turn, provoke algae blooms. Surfactants can also alter the hydraulic characteristics of soils, affecting the movement of contaminants through soils and into groundwater. Surfactants are very slow to biodegrade and have carcinogenic and reproductively toxic by-products such as nonylphenol, which is currently regarded as a potent endocrine disrupter.

Testing and Reporting

Commercial mixtures of surfactants consist of several tens to hundreds of homologues, oligomers and isomers of anionic, nonionic, cationic and amphoteric compounds. Therefore, their identification and quantification in the environment is complicated and cumbersome. Anionic surfactants are the most prominent surfactants. The list of the producers of anionic surfactants and trade names of products is very extensive. According to Arthur T. Hubbard in *Biodegradable and Chemically Degradable Anionic Surfactants* published in the Encyclopedia of Surface and Colloid Science (2002), anionic surfactants account for 63% of synthetic surfactant production, with LAS on top of the “big six” surfactant list. It is for these reasons, the industry standard is to analyze for Methylene blue active substances (referred to as MBAS) using LAS as the equivalent standard. There is currently only a single determinative analytical technique approved for NPDES reporting – colorimetric, methylene blue. This method is useful for estimating the anionic surfactant content of waters and wastewaters, but the possible presence of other types of MBAS always must be kept in mind.

The Water Quality Standard for Class C water in North Carolina is currently 500 µg MBAS/L. There are three EPA-approved methods for methylene blue active substances determination: EPA Method 425.1, Standard Methods 5540 C and ASTM D2330-88.

Standard Methods for the Examination of Water and Wastewater describes the procedure as follows: *Methylene blue active substances bring about the transfer of methylene blue, a cationic dye, from an aqueous solution into an immiscible organic liquid upon equilibration. This occurs through ion pair formation by the MBAS anion and the methylene blue cation. The intensity of the resulting blue color in the organic phase is a measure of MBAS.*

The reported results from the MBAS test are always directly linked to the material used as a standard. *For example, “0.72 mg MBAS/L (calculated as LAS, mol wt 318).”*

Summary

So how does all of this impact data interpretation? The data user must first consider that compounds such as organic sulfates, sulfonates, carboxylates, phenols, and even simple inorganic anions such as cyanide, nitrate, thiocyanate, and chloride can be methylene blue-reactive and will result in a positive bias in the reported MBAS concentration. Interference removal steps are included in the analytical method but they have variable effectiveness at removing these positive interferences. In general, MBAS results should be viewed as an acceptable overestimate of the anionic surfactants present in domestic wastewaters, with the understanding that surfactants may comprise only a small proportion of the total substances exhibiting a methylene blue reactivity in surface waters. According to Berna, et al, LAS may contribute as much as 75% of the MBAS in integrated sewage and 50% in treated water. Direct methylene blue analysis of extracts derived from sludge, sediment, and soil invariably leads to highly inflated estimates of LAS. (Berna JL, Moreno A, & Ferrer J (1991) *The behaviour of LAS in the environment*. J Chem Technol Biotechnol, 50: 387-398.)

To end with, it may also be prudent to consider that the quantified anionic surfactants may be significantly less toxic than LAS (the surfactant used as the quantitative standard in the MBAS analysis). The bottom line is that although the MBAS method is an acceptable industry standard, when it comes to environmental impact assessments, the data user can not place too much reliance upon the exact number obtained from the MBAS test.