EDQW 1,4-Dioxane Sampling & Analysis Guidance

Objective/Purpose and Applicability:

The main objective of this document is to provide guidance on selection of sampling and analysis methods for 1,4-dioxane (1, 4-D) in aqueous matrix based on the current state of the science. The guidance in this document apply to actions taken under the Defense Environmental Response Program (DERP) and funded from the Environmental Restoration (ER) and Base Realignment and Closure (BRAC) accounts.

Sampling:

Historically, methods and devices such as grab samplers (e.g., HydrasleeveTM and SnapTM Samplers), low-flow purging, and passive diffusion samplers have been used for sampling 1,4-D. All of these methods and devices have been shown to have comparable results, with the exception of passive diffusion bag (PDB) samplers that use a single low-density polyethylene membrane. 1,4-D does not diffuse across this membrane and therefore should not be used. Other passive diffusion samplers such as rigid porous polyethylene (RPP) passive diffusion samplers and the dual-membrane passive diffusion bag (DMPDB) samplers have been shown to be comparable.

Care must be taken in selecting the detergents used for decontamination processes, as 1,4-D is a common impurity found in detergents. Because of this, when possible, disposable, single-use equipment is recommended. If non-dedicated equipment must be used, the use of equipment blanks is critical, especially when project limits are in the low ppb to ppt range.

The type of sample container, preservation requirements, and applicable holding times vary, depending on the matrix and analytical method to be employed.

Preparation and Analysis:

There are currently multiple methods published by the EPA for the analysis of 1,4-D. The method best suited for a sampling event is dependent on the matrix of interest and criteria to which the data will be evaluated against.

For the analysis of drinking water, the EPA Office of Water (OW) has published EPA Method 522, *Determination of 1, 4-Dioxane in Drinking Water by Solid Phase Extraction (SPE) and Gas Chromatography Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM).* The use of SPE and SIM, coupled with the fact drinking water is a matrix type void of significant matrix interferences, allows for this method to achieve the lowest limit of quantitation (LOQ) of all of the EPA 1,4-D aqueous methods, typically ranging from 50 to 100 ppt.

For all other matrices, EPA has published methods that treat 1,4-D as a volatile compound (SW-846 Method 8260, EPA Method 624, and EPA 1624) and as a semi-volatile compound (SW-846 Method 8270, EPA Method 625, and EPA 1625). There are many sample preparation techniques applicable to the semi-volatile compound method, however; most of the options have the potential to bias low sample results due to 1,4-D's chemical properties. The extraction technique, solid phase extraction (SPE) is not affected by these characteristics. In addition to these options, there are also analytical technique options included in both semi-volatile and volatile methods, including selective ion monitoring

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(SIM) and isotope dilution quantitation. The precision, accuracy, and quantification range of each resulting method (sample preparation/extraction and analytical technique combination) greatly varies. While the appropriate method to be utilized is dependent on your project data quality objectives, some general guidelines should be considered.

Selection of Preparation/Analysis Methods:

Generally, a project should utilize a method with an LOQ that is 3-10 times lower than the project action or screening level. Consider requiring a lower LOQ if the laboratory's recovery data show a low bias, or if matrix interference is expected. When a limit of quantitation of less than 2 ppb is required, volatile methods are not recommended because they typically cannot achieve a LOQ below 2 ppb. In these instances, a semi-volatile method that utilizes SIM with isotope dilution quantification is recommended. When using isotope dilution quantification, the reported 1,4-D concentrations are adjusted for poor extraction efficiencies, however, in cases of extremely poor efficiencies (e.g., <20% recovery), the adjustment made can result in extremely biased high results. If extremely low reporting limits (ppt range) are required and matrix spike quality control criteria indicate extremely poor efficiencies in real world matrices, a method which utilizes SPE for sample preparation (EPA Method 3535), followed by GC/MS SIM for analysis, and isotope dilution for quantitation is recommended. Since SIM and isotope dilution quantitation are presented as options in GC/MS methods, laboratory scope of accreditations may not include this information, therefore the laboratory should be contacted to determine if they offer such a method. Recently, the Interstate Technology Regulatory Council (ITRC) has published a 1,4-D technical regulatory document, the *1,4-Dioxane Guidance Document.* For further information on 1,4-dioxane, this document can be found on the ITRC website at: https://14d-1.itrcweb.org/.