

Evaluation of Tris Base and Temperature as Preservatives for the Analysis of Per- and Polyfluoroalkyl Substances in a Variety of Aqueous Matrices

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Background/Objectives. EPA Method 537 remains the only promulgated EPA method for the analysis of per- and polyfluorinated alkyl substances (PFAS). While the 2009 EPA 537 method focuses specifically on drinking water, the determination of PFAS has seen a substantial growth in non-drinking water aqueous matrices. One of the mandates in EPA 537 is the addition of the preservative Tris base, a blend of Tris [Tris(hydroxymethyl)aminomethane] and Tris-HCL [Tris(hydroxymethyl)aminomethane hydrochloride] to act as a buffer near pH 7 and to neutralize free chlorine. This preservative is added during sampling to the polypropylene vessels at the rate of 5.0g/L to all samples and samples are held at $\leq 6^{\circ}\text{C}$ for a maximum of 14 days until extraction. While there has been some validation for the modification of the EPA 537 method, the effect of the omission of TRIZMA and holding temperatures has yet to be studied to our knowledge. This study aims to identify the temporal differences of spiked PFAS recoveries in HPLC, surface, and municipal tap water with and without the addition of TRIZMA and refrigerated temperatures as preservatives.

Approach/Activities. HPLC, tap, and surface water from the Northern California Sierra Foothills were first analyzed for background PFAS and then spiked with known concentrations of 27 PFAS varying in chain length and functional group. The different matrices were divided by the addition or absence of TRIZMA preservative and the second variable of storing samples at a temperature of either $\leq 4^{\circ}\text{C}$ or at $20\pm 5^{\circ}\text{C}$. Weekly extractions were completed in duplicate for each of these control groups. The experiment was processed for eight weeks. The extraction consists of ion-exchange SPE until samples are exhausted. Compounds are separated on a 2.1x100mm C18 column via UHPLC and detected on an MS/MS using scheduled MRM. Quantification by internal standard and isotope dilution techniques are performed using a linear or second order regression.

Results/Lessons Learned. Although early in the study, initial results indicate that the presence of TRIZMA does not have an impact on the PFAS recoveries. No indication of concentration effects based on holding temperature have been observed to date across all chain lengths of PFAS. If the data suggest a dependency on chain length for recovery over time, the composition of the storage vessel should be evaluated. Also, if the presence of tris base does not have an impact on the data, field operations might explore the feasibility of drop-shipping of bottles directly to the field. Although additional testing needs to be performed, the possibility of storing samples at room temperature until extraction would free up valuable temperature-controlled storage.