



Stabilization of Contaminants in Field Samples in the Presence of Persulfate

One advantage of using activated persulfate for *in situ* chemical oxidation of contaminants of concern is its relative stability within the subsurface groundwater environment. Persulfate, in the presence of certain activators, has been observed for up to three to four months following injection. As a result, extended periods of contact between the persulfate and the contaminants are achievable, thus allowing for increased zones of oxidant influence. This persulfate longevity is due to the relatively slow formation of sulfate radicals under several of the activation methods, such as chelated iron or high pH activation. In comparison, hydroxyl radical formation under standard and modified Fenton's reactions is extremely fast, resulting in very short hydrogen peroxide lifetimes in the subsurface. For activated persulfate, this can be considered a "time release" of strong oxidant radicals, resulting in radical production over a period of months rather than hours or days. The progress of persulfate consumption within the subsurface can be monitored using Klozur® Persulfate Field Test Kits or through secondary parameters such as sulfate production.

While the stability of persulfate within the groundwater is advantageous in terms of increasing the probability of success in remediating a contaminated site, it has recently been reported that residual, high concentrations of persulfate within a groundwater monitoring sample may lead to inaccuracy in the laboratory measurement of contaminant concentrations (1). This may arise due to either reaction of the persulfate with the contaminants during transportation to the lab at a different rate than reaction within the groundwater or due to enhanced heat activation of the persulfate during analytical analyses such as headspace gas chromatography (GC) / mass spectrometry (MS), where samples are heated in excess of 30 degrees Celsius to volatilize the VOC contaminants.

Effects of residual persulfate on contaminant concentrations within samples during transport to the laboratory may be minimized by placing the groundwater samples within amber vials to reduce impacts from ultraviolet light which can induce sulfate radical formation, shipping the samples on ice to reduce the persulfate – contaminant reaction kinetics and / or reducing the shipment time from field to lab to analysis. As a result, loss of contaminant due to shipping can be controlled and minimized.

Huling et al (1) report that the loss of contaminant due to heat activation of persulfate during GC / MS or purge – and – trap GC can be quite significant, with contaminant losses of 50% to 100%, depending on contaminant type and initial contaminant concentration under moderate persulfate concentration (2.5 g / L). One method to reduce or eliminate the interaction between residual persulfate and contaminant is through extraction of the target contaminants from the groundwater samples via standard EPA extraction methods, thereby effectively separating the contaminant and the persulfate prior to injection of the contaminant into the GC. Alternatively, Huling et al (1) proposed adding a "stabilizer" to the groundwater samples, thus reducing the reaction between the persulfate and contaminant. They demonstrated that the addition of ascorbic acid can significantly reduce the impact the persulfate has on contaminant loss during analysis. Under similar conditions where contaminant losses were high due to persulfate oxidation, they have shown that the addition of ascorbic acid can reduce these losses to less than 5% for both the GC / MS and purge-and-trap GC methods described in their paper. They have attributed this stabilization to the rapid reaction kinetics between sulfate radical and ascorbic acid as compared to the reaction rate between persulfate and contaminant ($k(\text{persulfate} - \text{ascorbic acid}) \gg k(\text{persulfate} - \text{contaminant})$). In essence, the ascorbic acid is providing a sacrificial reaction pathway for generated sulfate radicals, thereby reducing the concentration of radicals available to react with the contaminants of concern.

The impact of residual persulfate upon contaminant concentration analysis is dependent upon the concentration of the persulfate in the groundwater sample. Huling et al (1) ran their studies at a persulfate concentration of 2.5 g/L. However, these effects are expected to drop off as the persulfate concentration is reduced, and the relative impact becomes minimal as the persulfate concentration becomes less than 0.5 g/L (2). As a result, for groundwater samples that measure low to no residual persulfate (as an example the Klozur Field



Test Kit can measure persulfate concentrations down to 0.5 g/L of persulfate), stabilization may not required. Such conditions should be expected within two to three months of persulfate injection, depending on initial concentration and activation method.

1. Huling, S.G., S. Ko and B. Pivetz. "Groundwater Sampling at ISOC Sites: Binary Mixtures of Volatile Organic Compounds and Peruslfate". **Ground Water Monitoring & Remediation** 31, 2011, p 72 – 79.
2. S.G. Huling, private communication.

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