



## Measurement of Persulfate in Solution

The determination of persulfate concentration in groundwater post *in situ* application is critical in determining parameters such as the persulfate radius of influence (ROI) achieved and the residence time of the persulfate in the contaminated zone. In general, measurement of persulfate concentration in the field is problematic. Metals, either native to the soil or added for persulfate activation, may interfere with various persulfate analytical methods, yielding variable, inaccurate or misleading results. In addition, some methods, which may be suitable for the laboratory, may not be suitable for field application due to the need of sensitive or expensive detection equipment. In this edition of *Peroxygen Talk*, the measurement of persulfate in ground water is explored. A more detailed review, including comparisons between various persulfate analytical methods, can be found in Reference 1.

### Analytical Methods Involving Persulfate – Iron Reactions

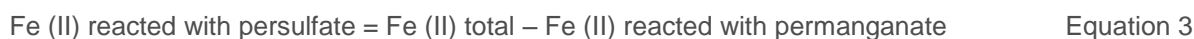
Persulfate anion will oxidize divalent iron [Fe(II)] to form trivalent iron [Fe(III)] in the reaction:



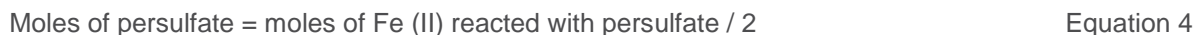
Quantitative determination of persulfate concentration can be achieved by first adding in excess a known amount of Fe (II) to the persulfate solution. A portion of the Fe(II) is then converted to Fe(III) via Equation 1. The remaining Fe (II) is then titrated with either a known concentration of potassium permanganate [KMnO<sub>4</sub>] to a pink end-point or ceric sulfate [Ce(SO<sub>4</sub>)<sub>2</sub>] to a Ferroin indicator end-point (a color change from orange to clear or light blue). As an example, for permanganate:



Using the volume of permanganate or ceric sulfate needed to reach the endpoint (which occurs when all of the remaining Fe (II) is oxidized), allows for the determination of how much persulfate was originally present :



then:



As this method is dependent upon a known quantity of Fe (II) in the test solution, naturally occurring iron and other reduced metals and residual contaminant that may react with the permanganate or ceric sulfate, in the groundwater can significantly impact the quantification of the persulfate concentration. Also, additives such as chelates, as when using chelated metal activation for persulfate, may cause interference with the titration. For example, Fe(III)-EDTA will interfere with the permanganate titration, but not so with the ceric sulfate titration. Addition of other oxidants, such as hydrogen peroxide likewise will impact the accuracy of the method, as additional oxidant will also oxidize the Fe(II), making it difficult to determine the persulfate contribution. For hydrogen peroxide – persulfate combinations, it is possible to react the peroxide with ceric sulfate first, to a Ferroin end-point, as the ceric sulfate will preferentially react with hydrogen peroxide over persulfate. When the end-point is reached, the hydrogen peroxide will have been consumed (which will also give a quantifiable measurement of the peroxide in solution). Then the permanganate or ceric sulfate back-titration of Fe (II) can be utilized to quantify the remaining



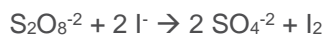
persulfate. The above titration method can provide a very accurate measurement of persulfate in solution. But typically it is only applicable in a laboratory, due to the instrumentation and chemicals required.

#### *Application in the field*

We have developed an easy-to-use, onsite titration kit for the measurement of persulfate in groundwater that addresses the limitations mentioned above, the new Klozur® Persulfate Field Test Kits. Two kits are currently available, one for use when activating Klozur persulfate with either high pH or with iron sulfate, and a second kit for use when activating Klozur persulfate with chelated iron. If hydrogen peroxide is being used as the activator, please contact us for additional support.

### **Iodometric Methods**

Persulfate anion will react with potassium iodide as:



Equation 5

I<sub>2</sub> forms a brown color. In the laboratory, this method can be made quantitative by titrating the resulting solution with thiosulfate, reducing the I<sub>2</sub> back to I<sup>-</sup>, the end-point identified by the disappearance of the brown color. This can be enhanced by the addition of starch, which will form an intense blue complex with I<sub>2</sub> in the presence of I<sup>-</sup>. Disappearance of the blue color indicates the end-point when I<sup>-</sup> has been consumed. This method will have less interference from native metals as compared to the persulfate - iron method described above. However, accuracy will be affected by the instability of I<sub>2</sub> and the sensitivity of the reaction to the timing of the addition of the starch indicator.

#### *Application in the field*

The presence of persulfate can be qualitatively assessed by looking for a color change when starch is added to a solution of the groundwater and potassium iodide. If persulfate is present, a blue color will appear. However, instability of thiosulfate solutions, oxidation of I<sup>-</sup> by air and sunlight and the sensitivity of the end-point on the addition timing of the starch limit the use of this method as a *quantitative* assessment tool in the field for persulfate concentration.

### **Spectroscopic Methods**

Huang, et al<sup>2</sup> developed a laboratory spectroscopic method for the quantification of persulfate. The method is based on the oxidation of Fe(II) by persulfate to Fe(III). The Fe (III) is then complexed with thiocyanate (SCN<sup>-</sup>), which forms an intense red color. A spectrophotometer is then used to determine the concentration of the iron - thiocyanate complex as a function of absorbance at a wavelength of 450 nm. As this method is dependent upon Equation 1, it is subject to the same interferences from background iron concentrations and chelating agents as described for the persulfate – iron methods.

Several other spectroscopic methods have been developed for persulfate as well. These have been reported in reference 1 and by Williams<sup>3</sup>. In general, spectroscopic methods can obtain a high degree of quantification in a laboratory setting. However, the applicability to use in the field is somewhat limited due to the need of spectrophotometers. These methods may be suitable to mobile field labs equipped with the appropriate devices.



## Novel Techniques for Future Development

Gillian<sup>1</sup>, in work supported by Arcadis, developed a couple of new spectroscopic methods for the analytical determination of persulfate concentration. One of these includes the use of indole as a reactant with persulfate, forming a distinctive blue-colored compound. A second method utilizes the reaction of persulfate with promethazine-HCL, which forms a red-colored compound. Gillian<sup>1</sup> reports that in particular, the promethazine-HCL procedure has potential to be developed into a field test method, provided that iron concentrations in the groundwater are not high. Rossabi<sup>4</sup> et al described a novel approach to using ion chromatography to measure aqueous persulfate concentrations, and reported a measurement range of 0 – 500 mg persulfate / liter.

## Other Field Measurement Methods

There are commercially available persulfate test kits on the market. These are predominately based on the permanganate back-titration of Fe (II), Equation 1, which relies on matching a shade of purple to a subsequent persulfate concentration. Such kits can have significant interference from native groundwater iron or residual contaminant. In addition, these kits can be too sensitive in that they may indicate the presence of persulfate into the mg / L range, far below the effective persulfate dosing for most contaminated sites.

Secondary parameters, such as conductivity and sulfate concentration can be used to monitor the effective movement of persulfate in the subsurface. Persulfate injection will significantly increase the conductance of groundwater due to the increase in ion concentrations. Down-well conductivity probes and direct-push rod probes have been used successfully to determine the presence of persulfate in groundwater. Commercially available sulfate concentration kits have also been used to determine the presence of persulfate in down-gradient monitoring wells, as persulfate is consumed through reaction, it generates sulfate. Dissolved oxygen, ORP and pH measurement can also be used to track persulfate in the subsurface through its impact on groundwater parameters.

1. Lai, Gillian. "Development of Analytical Methods for Estimation of Oxidants Concentrations". Master's thesis, Imperial College, London, September, 2007.
2. Huang, K.C., Couttenye, R.A. and Hoag, G.E. "Kinetics of heat-assisted persulfate oxidation of methyl terty-butyl ether (MTEBE)". **Chemosphere** 49, p 413-420, 2002.
3. Williams, W. J. **Handbook of Anion Determination**. 1979, London, Butterworths.
4. Rossabi, J. and B. Fassolt. "Ion Chromotography for Persulfate and Total Oxidant Demand Analysis". 1<sup>st</sup> Annual Southeastern *In Situ* Soil and Groundwater Remediation Conference, Raleigh, NC 2007.

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