From:	Gilmour, Cindy
To:	William H Orem; Kalla.Peter@epamail.epa.gov
Cc:	Axelrad, Don; David P Krabbenhoft; G. Ronnie Best; scheidt.dan@epamail.epa.gov; wlanding@fsu.edu
Subject:	RE: FW: Sulfide method
Date:	Wednesday, January 07, 2009 2:33:04 PM
Attachments:	Rearick et al ET&C 2005.pdf Rearick THESIS 052504.DOC

All –

We (and many others) have data that suggests that acid-soluble (and SAOB soluble) metal sulfides are almost always an important component of total sulfides in natural waters. Even in filtered samples, there are nano-particulate and colloidal sulfides (See below for some details from a master's thesis where that idea was tested). So I think it is appropriate to call samples measured by either methylene blue/spectrophotometric or ISE/SAOB "total sulfide."

To me, the largest issue in the REMAP surface water sulfide data set (and by the way in little bit of surface water sulfide available from DBHydro) is that surface water samples were unfiltered. Particulates can contain a very large amt of sulfide in the solid phase that can be stripped from particles by acid (or by SAOB). So in using the data, it's critical to define if the samples were filtered, and to what pore size. My bet is that filtered vs. unfiltered is what drives the differences in the EPA and ACME data sets, rather than the method used for analysis. That said, the SOAB/ISE method has a much lower DL (0.1uM on a good day with fresh SAOB and a probe that is clean and working well), and a much higher dynamic range (maybe 6-7 orders of magnitude) than the methylene blue/spectrophotometric method, esp with a Hach kit instead of a long-path spec.

Here's some info on total vs "dissolved" sulfides from Mike Rearick's thesis:

A few years back we developed a DGT method for sulfide in sediments - if you aren't familiar with these, they are something like pore water peepers with sulfide-accumulating gels that you can leave in place in sediments for a while and then retrieve for sulfide analysis. Our intent was to develop a concentration method that could be used for sulfide concentrations well below 0.1 uM, which is roughly the DL for the ISE/SAOB method. It works, but it is a royal PIA, so we haven't used the method much.

As part of that work, the student (Mike Rearick) tested the methylene blue and SAOB/electrode methods against each other and the DGT method. The DGT probes have diffusion membranes on them, and therefore exclude particles.

What he found is that both methods overestimate truly dissolved sulfide in natural waters, by up to about 10X. Both methods strip sulfide from particles and filterable colloids. Methylene blue is acidic; and SAOB is very basic with some strong ligands. The effect of either MB or SAOB is about the same, although SOAB can strip sulfide from thiols, while methylene blue does not appear to.

Mike published the DGT method, but not the methods comparison. Those are in his thesis, which is attached. He tested a variety of anaerobic waters. For a couple of methods comparisons examples,

see fig 9 (p 55). Also, the longer the samples interact with either SAOB or methylene blue, the stronger the effect (Fig 10). I highlighted a few key points in the thesis.

Cindy

From: William H Orem [mailto:borem@usgs.gov]
Sent: Wednesday, January 07, 2009 1:45 PM
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Subject: Re: FW: Sulfide method

Peter:

Thanks. I hope I didn't come across as critical - that was not my intention. Just trying to pass on some issues we had with the methylene blue approach. What you could do for future work if you decide to go electrode is collect the water sample and just fix it with SAOB in the field (this ups the pH and stabilizes the sulfide as S2- for up to about 24 hours). Then the analyses could be done in the hotel room using the electrode with stirring. This has worked pretty well for us and helps make the filed time go faster. Lots of folks use the methylene blue method, so it is a widely accepted approach. We have just had some issues with it in highly colored water. I'm not usually a big proponent of many electrode methods, but the sulfide electrochemical method works really well and is very easy. One possible reason (maybe) your numbers could be higher (apart from the colored water reasons I mentioned earlier) is that maybe you are also seeing metal sulfides from particles in the water using the meth blue method. The electrode approach probably only sees free sulfides.

Bill