June 2004
TOC Issues: Part 3 – Blanks for Recovery Studies

This Cleaning Memo will address issues in the proper selection of blanks for TOC in recovery studies. In this situation, the purpose of sampling is to quantitate the organic residues that may be on the coupon (the model surface used for the study), and then compare that value to the amount of organic residues spiked onto the coupon surface.

This situation is slightly different from the situation (blanks for validation samples) discussed last month. (Note: It might be helpful to read last month's Cleaning Memo if you have not already done so.) What is the *same* is that there are still concerns about contributions of TOC from the sampling water, from the swab, and from the container, as well as any possible contribution from the sampling atmosphere. What is *different* is that there are only two sources of organic residues on the sampled surface. One is the residue that is deliberately spiked onto the surface. Second is any organic residue that may be on the cleaned coupon before spiking it. [Some might even argue that there is a third source, namely any organic matter that deposits on the coupon as the spiked material is allowed to dry.]

Another difference is the *consequence* of not adequately controlling for the blank contributions to TOC. As was pointed out last month, if one even ignored the blank value (i.e., did not subtract the blank value from the test sample) in a validation protocol sample, it was not fatal to the protocol because it represented a worst case (i.e., it would report out a value for the organic carbon that was higher than the "true" value for organic carbon). While this may be a significant issue in that it causes the measured values to be above the residue limits, it is not a compliance issue if the measured value (ignoring the blank) is below the acceptance limit value for TOC. For recovery studies, the consequence of not adequately measuring the blank is generally to have measured values for the spiked samples that are higher than the "true" value. However, in this case, a higher value means a *higher percentage recovery*, which is *not a worst-case* (something that causes the recovery percentage to be lower would be considered a worst-case). Therefore, it is extremely important to make sure the blank values are appropriate, and if any approximations are made, they should result in maximum TOC blank values. This would result in either accurate recovery percentages or worst-case (i.e., lower) recovery percentages.

How are blank values for TOC controlled in a recovery study? Several of the items discussed last month are applicable here, namely making sure the blank includes the swab head, the sampling water and the sampling vial. However, a blank comprised of those three sources would *not* capture any organic residues on the cleaned coupons *before* spiking.

Therefore, an appropriate blank for TOC swab sampling would involve swabbing a cleaned coupon in the same manner as the spiked coupon. The results from this swab would add a contribution from the cleaned coupon itself. Of course, the best option is to have coupons that are meticulously cleaned and stored prior to use for recovery studies. If that were the case, then the contribution to the blank from the cleaned coupon would be so minor as to be negligible. But, since it is not practical to insure that the coupon cleaning process is validated to be consistent, it generally is necessary to include a swabbed coupon (or three swabbed coupons) as a blank.

One could conceivably go one step further and spike the blank coupon with a placebo, and dry/handle it in the same way as a coupon spiked with a residue. That is, if spiking of a residue involves application of 0.1 mL of an aqueous solution and drying in a certain manner, then the "blank" coupon should be spiked with 0.1 mL of the same quality water and dried in the same manner. If spiking of the residue involves application of a solvent solution, then the "blank" coupon should be spiked with the same amount of the same quality solvent.

These same issues would apply to blanks and blank coupons for *rinse* recovery testing.

While consideration of these factors is appropriate for recovery studies for TOC, these issues are of much less concern in recovery studies involving specific analytical methods. Exceptions to this include situations where coupons are cleaned and reused for additional studies and situations where the recovery study is for a cleaning agent and the same cleaning agent is used to clean the coupons prior to spiking.

The purpose of this Cleaning Memo is to clarify issues in the use of blanks for recovery studies where the analytical method is TOC. Proper blank selection avoids situations where the calculated recovery percentage is artificially high.