

Development of USEPA Method 1650 for the Analysis of Adsorbable Organic Halides in Wastewater Matrices

William A. Telliard¹, Harry B. McCarty², and James R. King²

¹U. S. Environmental Protection Agency, Office of Science and Technology, Washington, DC 20460

²Viar and Company, Alexandria, VA 22314

Since the determination in the mid 1980's that polychlorinated dibenzodioxins and dibenzofurans (PCDDs/PCDFs) were associated with effluent discharges from pulp and paper mills, the majority of the United States Environmental Protection Agency's (EPA) efforts to regulate these discharges under the Clean Water Act (CWA) have focused on these highly toxic compounds. However, in response to a civil suit filed against the Agency by U.S. environmental groups, EPA has expanded the scope of its investigations. In addition to monitoring the concentrations of PCDDs and PCDFs in mill effluents and in-process waste streams, EPA is developing monitoring methods for other chlorinated organic compounds associated with the pulp and paper industry.

While measurements of specific compounds will continue to be an important part of EPA's strategy to reduce emissions from these facilities, the Agency is investigating the use of an aggregate measure of the organic halide content of the waste streams. This aggregate measure is termed adsorbable organic halides (AOX). The method under development is based on the ISO/DIS method¹ and other methods for organic halides²⁻⁵, utilizing adsorption onto activated carbon, combustion, and coulometric titration.

The basic analytical technique is not new, but its application to the regulatory control of effluents and compliance monitoring under the CWA places additional requirements on the process. However, the existing methodologies required the addition of significantly more rigid quality assurance and quality control measures to ensure the applicability and defensibility of the AOX measurement as a compliance monitoring tool.

The resulting method produced by the Office of Science and Technology is Method 1650. The method requires the analysis of all samples in duplicate, with a limit of 20% relative percent difference between the duplicate measurements. Blanks, spiked sample analyses, calibration, daily performance testing, and carbon adsorption capacity testing were included. In addition, a limit of 10% was placed on the amount of organic halide associated with the second of the two adsorption columns used in series to process the wastewater sample. The first draft Method 1650 also allowed the use of a "batch" adsorption procedure in place of the column procedure for the analysis of treated effluents.

Single laboratory testing using real world samples demonstrated the applicability of the method to wastewater effluents, and was used to develop preliminary method performance specifications. The first draft of the method was then applied to a large study of the pulp and paper industry that began in mid 1991. Approximately 220 samples were analyzed in the first phase of that study. The samples of final effluents, untreated wastewaters, and in-process waste streams were taken from eight pulp and paper mills each week over a nine week period. As that study is still underway at this time, our intent is to discuss the successes and failures of the draft method in general terms and to illustrate the steps being taken to develop a rugged reliable test procedure.

One of the biggest problems noted in organic halide determinations is background contamination. As these methods use blank subtraction to determine the results for a sample, it is imperative that the level of organic halides found in the activated carbon adsorbent be kept as low as practical. The primary source of carbon contamination in a production laboratory is the presence of chlorinated organic vapors from solvent extraction of environmental samples. While Method 1650 and other methods specify limits on the level of organic halides in the carbon blank, experience indicates that these levels are often exceeded, leading to considerable loss of laboratory time spent reanalyzing samples or to data of limited utility. Therefore, EPA was enthusiastic about the commercial availability of adsorption columns that were packed at the factory, rather than at the laboratory, sealed, and only exposed to the laboratory atmosphere for moments prior to use. Commercial laboratories embraced these columns as a significant time saving device from the standpoint of the labor required to pack the columns and the time spent reanalyzing samples due to blank contamination problems. However, the use of these columns may be related to other difficulties encountered during the pulp and paper study.

Another significant problem associated with the procedure is that of breakthrough of organic halides from the first of the carbon columns to the second column in the series. Each carbon column contains only 40 mg of adsorbent material. The adsorption capacity of this material is tested with a specific organochlorine compound, 2,4,6-trichlorophenol in Method 1650. The procedure measures the aggregate of organic halides in the sample, and the result is a method-defined parameter in that it is strictly dependent on the adsorption procedure used. In recognition of this dependence, Method 1650 uses the term "Adsorbable Organic Halides" rather than "Total Organic Halides" to describe the material, as some halogenated organic compounds in the sample may never be adequately adsorbed on carbon and thus not reliably measured by the procedure. For instance, compounds such as chloroethanol and chloroacetic acid are known to be poorly adsorbed.

The presence of organic halides on the second carbon column in the series may be indicative of several different processes. First, the packing of the column may lead to voids in the carbon which allow the sample to pass too quickly through the column with minimal contact with the adsorbent. This effect is often referred to as channeling. A second possible process is related to the size and shape of the column itself. Longer narrower columns will increase the time of contact of the sample with the adsorbent, whereas shorter wider columns will decrease the contact time. This difference may manifest itself as a difference in flow rates between the two types of columns.

Third, a hundred or more halogenated compounds may be present in a wastewater sample, and each may have different adsorption kinetics on activated carbon. Thus, some will be easily adsorbed on the first column while other compounds will pass through to the second column, and some may not be adsorbed at all. Fourth, the amount of organic halides in the sample may simply exceed the adsorption capacity of the carbon column.

Other organic halide methods have specified a limit of 10% on the breakthrough of halides from the first to the second carbon columns. While this limit is typically specified without an explanation or rationale, two possible derivations are likely. First, 10% is a straight-forward round number derived from a consensus of knowledgeable parties. Alternatively, it may be derived from calculations similar to those performed for solvent extraction efficiencies. Thus, if 90% of the material is retained on the first column, and 90% of the remaining material retained on the second column, then approximately 99% of the actual amount of organic halides in a sample will be captured on the two columns. The 1% "loss" is insignificant relative to other sources of error in the measurement. In keeping with these other organic halide methods, the draft Method 1650 incorporated this 10% breakthrough limit as well.

When the breakthrough limit is exceeded, the method specifies that the sample be diluted further and reanalyzed in an attempt to minimize breakthrough that is due to overloading the absorption capacity of the carbon itself. Assuming that voids and channeling are random occurrences, reanalysis of the diluted sample will likely appear to "cure" the breakthrough problem identified in the original analysis. The diluted sample may also meet the breakthrough limit if the problem in the original analysis was due to too high a flow rate or short contact time as a result of column geometry.

During the first phase of the pulp and paper industry study, an unexpectedly large number of sample analyses were observed to have exceeded the 10% breakthrough limit. This led to concern that the results have contain a low bias due to material that was not adsorbed on the two columns. EPA has identified a variety of causes for this observation. They include: laboratory errors in calculating or reporting the breakthrough value; failure to follow the method as written; and lack of a specification for flow rate through the columns. In addition, because all four laboratories involved in the study were utilizing the prepacked carbon columns, it is possible that something inherent in the prepacked columns may be involved in the breakthrough problems.

In response to the breakthrough problems encountered, EPA obtained reanalyses of the affected samples using three carbon columns in series. The purpose of these reanalyses was to determine what percentage of the organic halides might be passing through the first two columns. In many of these reanalyses, the addition of the third column yielded an AOX concentration in the sample that was within 20% relative percent difference of results of the original analysis. Since the method requires that the results of duplicate analyses agree within no more than 20% relative percent difference, the observed breakthrough above 10% may not have significantly affected the results when compared to the addition of a third adsorption column, and low bias may not be a concern for these samples. For other samples, the results were not comparable between the two procedures. Given that in some

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cases these analyses were conducted months apart, these data may indicate that there is a maximum holding time associated with this analysis.

As a result, EPA is currently performing studies to determine the effects of column geometry, column type (prepacked versus laboratory-packed), flow rates, and holding time. In the meantime, the draft method has been revised for use in the second phase of the pulp and paper study. The revised method requires that the flow rate of the method blank be monitored and limited to 3 mL/minute for a 100 mL sample volume. Since the blank is composed of reagent water and contains no particulate matter that would slow the flow of the sample through the carbon columns, the blank should have a higher flow rate than the samples. Therefore, regulation of the flow for the blank will be a cost-effective means of limiting the flow rate for the samples.

The revised method clarifies the blank subtraction and breakthrough calculations. It also requires that the "duplicate" analyses of each sample be performed at two different levels of dilution. This will minimize the likelihood that the breakthrough will be due to overloading of the carbon adsorption capacity. The revised method also requires that the most dilute analysis contain at least 3 times as much halide as the method blank. The ongoing studies of the breakthrough problem should allow EPA to determine an appropriate upper limit for breakthrough that guards against low bias in the data while still providing a cost-effective monitoring tool. The results of these studies will be used to prepare a final method for promulgation under the authority of the Clean Water Act.

In summary, EPA has learned that what it, the pulp and paper industry, and the environmental groups thought was a relatively simple and cost-effective tool for monitoring and regulating the release of halogenated organic compounds from pulp and paper mills is not so simple after all. Given the fact that AOX is a method-defined measurement, the use of literature values for organic halide emissions generated by various methods must be carefully evaluated before use. When promulgated by EPA, Method 1650 will be the result of extensive interlaboratory testing on real world samples, and should be the most carefully described, rugged, and reliable method for the organic halides yet developed.

References

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