



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

Judith R. Morgan
VP, Chief Compliance Officer
PACE Analytical Services, LLC
1800 Elm Street SE
Minneapolis, MN 55414

SUBJECT: Review of Pace Analytical Method PAM-16130-SSI,
Determination of 2,3,7,8-Substituted Tetra- through Octa-Chlorinated Dibenzo-*p*-Dioxins
and Dibenzofurans (CDDs/CDFs) Using Shimadzu Gas Chromatography Mass
Spectrometry (GC-MS/MS)
(ATP Case No. N21-0001)

DATE: June 28, 2022

I have reviewed Pace Analytical Method PAM-16130-SSI (ATP Case No. N21-0001), "Determination of 2,3,7,8-Substituted Tetra- through Octa-Chlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (CDDs/CDFs) Using Shimadzu Gas Chromatography Mass Spectrometry (GC-MS/MS), Revision 1.1" and the supporting validation data in ATP Case No. N21-0001. I determined that this method meets all requirements for measurement of 2,3,7,8-substituted tetra- through octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) in wastewater. That is, the performance of this method is substantially similar to methods listed at 40 CFR Part 136 for measurement of PCDDs/PCDFs in wastewater.

I will recommend that this method be included in future regulatory actions in which EPA adds to the list of approved methods at 40 CFR Part 136. However, this ATP review does not replace this notice and comment rulemaking process. In the interim, a user may, on a facility-by-facility basis, seek approval from their regional authority for use of this method in measuring PCDDs/PCDFs in wastewater in Clean Water Act (CWA) programs.

If I can be of any additional assistance on this matter or others, please contact me at walker.lemuel@epa.gov.

Sincerely,

A handwritten signature in black ink that reads "Lemuel Walker, Jr." in a cursive script.

Lemuel Walker, Jr.
CWA ATP Coordinator
Technology and Analytical Support Branch
Engineering and Analysis Division
Office of Science and Technology

cc: William C. Lipps, Shimadzu Scientific Instruments, Inc.
Quality Assurance Managers (all Regions)
ATP Coordinators (all Regions)

Justification

Development of EPA Method 1613 for the analysis of polychlorinated dioxins and furans (PCDDs/PCDFs) began in 1988, in response to reports of very low, but measurable concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in finished paper products and wastewater effluents from the pulp and paper industry. The method utilizes gas chromatography and high-resolution mass spectrometry (GC/HRMS) to identify the target analytes in the presence of other organic contaminants, at concentrations in the picogram per liter (pg/L) range. The success of GC/HRMS is due to its ability to differentiate masses that differ in the 4th decimal place (e.g., 303.9016 for 2,3,7,8-TCDD versus 303.9020 for a potential interference), where a low-resolution mass spectrometer with unit mass resolution (e.g., 1 atomic mass unit) would see them both at mass 304 and report the combined response as the concentration of 2,3,7,8-TDD. At that time, GC/HRMS instrumentation was roughly ten times as expensive as the more common low-resolution instrumentation, and there were fewer instrument vendors who manufactured GC/HRMS units.

Method 1613B was promulgated at 40 CFR 136 in 1995 and remains the only approved method for dioxins and furans at NPDES permit levels (Methods 613 and 625.1 may only be used for screening). Method 1613B is also the only method approved at 40 CFR Part 136 that relies on GC/HRMS as the determinative technique.

As a result, the need for HRMS instruments is somewhat limited, and market forces have lead some instrument vendors to move away from supporting new GC/HRMS instrumentation. In addition, in the last 30 years, there has been substantial consolidation of manufacturers, with the disappearance of many of the vendors whose instruments were used to develop and validate Method 1613B.

GC/MS/MS, in which two mass spectrometers are assembled in series, allowing the instrument to distinguish analytes of interest by additional fragmentation of the parent compound, offers many of the advantages of GC/HRMS without the need to employ such high mass resolution. Approval of a GC/MS/MS method for measurement of PCDDs/PCDFs would take advantage of this newer technology and has the potential to lower laboratory costs and expand the pool of available laboratories, while not compromising method performance.

This ATP application is the result of effort a collaborative effort between Pace Analytical Services LLC, and Shimadzu Scientific Instruments, Inc. The final method, Pace Analytical Method PAM-16130-SSI, is heavily adapted from Method 1613B. No changes have been made to the extraction or cleanup procedures specified in Method 1613B. All required quality control tests (or analogous tests) and associated acceptance criteria have been included in Method PAM-16130-SSI as well.

In an effort to minimize costs to both the applicants and the Agency where possible, Pace Analytical and Shimadzu Scientific Instruments, Inc. who collaborated on this method, worked closely with EPA's CWA ATP Coordinator to design the single-laboratory validation study of this method. The goal of the validation study was to demonstrate that all of the performance criteria specified in Method 1613B could be met and that comparable performance could be achieved when using GC-MS/MS instrumentation for determination of PCDDs/PCDFs in extracts from real-world samples.

The attached validation study report and final method are the results of this effort and form the basis for the Office of Water's determination that the performance of Pace Analytical Method PAM-16130-SSI is substantially similar to methods listed at 40 CFR Part 136 for measurement of PCDDs/PCDFs in wastewater.