






July 23, 2021

Emily Dominiak
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(submitted via 1-4D.HCPCCproducts@dec.ny.gov)

**Re: Comments on New York State Department of Environmental Conservation (NYSDEC) draft "Method Performance Criteria (MPC)"**

Dear Ms. Dominiak:

I write on behalf of The American Cleaning Institute® (ACI)[1], the Personal Care Products Council (PCPC)[2], Consumer Healthcare Products Association (CHPA)[3], Consumer Brands Association (CBA)[4], and Household & Commercial Products Association (HCPA)[5] regarding the draft "Method Performance Criteria" (draft/MPC).

**General Comments**

ACI, PCPC, CHPA, CBA, HCPA and member companies support the inclusion of minimum performance criteria in determining threshold limits of 1,4-dioxane in regulated products. Our comments draw on extensive experience with

[1]ACI represents the $60 billion U.S. cleaning product supply chain. ACI members include the manufacturers and formulators of soaps, detergents, and general cleaning products used in household, commercial, industrial and institutional settings; companies that supply ingredients and finished packaging for these products; and chemical distributors. ACI serves the growth and innovation of the U.S. cleaning products industry by advancing the health and quality of life of people and protecting our planet. ACI achieves this through a continuous commitment to sound science and being a credible voice for the cleaning products industry.

[2]Based in Washington, D.C., PCPC is the leading national trade association representing the global cosmetic and personal care products industry. Founded in 1894, the Council's more than 600 member companies manufacture, distribute, and supply the vast majority of finished personal care products marketed in the United States. As the makers of a diverse range of products that millions of consumers rely on every day, from sunscreens, toothpaste, and shampoo to moisturizer, lipstick, and fragrance, member companies are global leaders committed to product safety, quality, and innovation.

[3]The Consumer Healthcare Products Association (CHPA), founded in 1881, is the national trade association representing the leading manufacturers and marketers of consumer healthcare products, including over-the-counter (OTC) medicines, dietary supplements, and consumer medical devices. CHPA is committed to empowering self-care by ensuring that Americans have access to products they can count on to be reliable, affordable, and convenient, while also delivering new and better ways to get and stay healthy. Visit www.chpa.org.

[4]The Consumer Brands Association (Consumer Brands) champions the industry whose products Americans depend on every day, representing more than 1,700 iconic brands. From household and personal care products to food and beverage products, the consumer packaged goods industry plays a vital role in powering the U.S. economy, contributing $2 trillion to the U.S. GDP and supporting more than 20 million American jobs.

[5]The Household & Commercial Products Association (HCPA) is the premier trade association representing companies that manufacture and sell $180 billion annually of trusted and familiar products used for cleaning, protecting, maintaining, and disinfecting homes and commercial environments. HCPA member companies employ 200,000 people in the U.S. whose work helps consumers and workers to create cleaner, healthier, and more productive lives. Our mission is to protect, promote, and enhance the household and commercial products industry and the consumers and workers who use our members' products. Products represented by HCPA are divided into seven product divisions: Aerosol, Air Care, Antimicrobial, Cleaning, Floor Care, Industrial & Automotive, and Pest Management products.

analytical methods for measuring concentrations of 1,4-dioxane in both raw materials and finished products. As such, ACI, PCPC, CHPA, CBA, and HCPA strongly encourage NYDEC to include headspace sampling as an additional method principle. Headspace sampling/extraction is a key method utilized by industry and were included in the methods shared by Clarkson University and the California Department of Toxic Substances Control (DTSC) but is not specifically referenced in the draft. We recommend that all qualifying methodologies be considered for this principles document as well as in regulations. For example, through the work by ACI and member companies, we believe headspace sampling is an additional method principle that should be included in trace analysis of 1,4-dioxane in products. Consumer household and personal cleaning products contain considerable amounts of semi-volatile matrix components. Headspace sampling should be leveraged to limit potential for introducing interferences and limit instrument contamination, which will be especially relevant for unknown samples. The in-progress round robin testing by industry laboratories and Clarkson University will provide perspective on the importance of headspace sampling.

We recommend that sample preparation conditions be included in the MPC given the diversity of 1,4- dioxane products. As indicated above, consumer products contain semi-volatile components and other ingredients in a product's matrix. Samples at the very minimum should be well-mixed to ensure homogeneity and dissolution. Guidance should also be provided for sample and standard weighing. More details are in our comments below.

We believe the allowable error range of 30% on measurements is too wide. A narrower range of 15-20% is reasonably achievable by competent laboratories.

We recommend including additional guidance on:

- Review of calibration range to minimize negative or positive bias.
- Ensuring head space conditions are optimized. Experience that extended heating and extreme temperatures may result in positive bias.
- Guidance on column selection – driven by sample matrix.

The MCP should provide guidance on quality control check standards. In addition, DEC should include guidance on confirmatory replicate testing with freshly prepared samples and standards if preliminary results are above regulatory thresholds, or if there are contradictory testing results.

We also recommend DEC include a preamble to give rationales to support each method principle. Such as:

**Method Principles**

*To enable high reliability, reproducibility, sensitivity and accuracy of analytical measurement of 1,4-dioxane testing in finished products should utilize the following*:

- Deuterated Internal Standard – To account for dilution/other sample handling errors and to correct for differences between standard and sample matrices, a deuterated internal standard should be used. The use of deuterated 1,4-dioxane will ensure the internal standard has similar physical-chemical properties as the target analyte.
- Headspace Sample Extraction – Consumer products contain considerable amounts of semi-volatile matrix components. Headspace sampling should be used to limit potential introduction of interferences and limit instrument contamination, especially for unknown samples.
- Gas Chromatography (GC) Separation - GC is necessary to separate 1,4-dioxane from volatile and semi-volatile components in the matrix that may be interferences (e.g. perfume components, solvents).
- Mass Spectrometry (MS) Detection - MS enables sensitive and selective detection of the target analyte. MS detection in Selected/Single Ion Monitoring (SIM) mode will enable the ability to approach low ppm levels.

**Specific Comments:**

The following section is a combination of red-lined edits and highlighted additions and comments and recommendations to the draft MCP.

**~~Method~~ Sample Preparation Criteria**

1. The method must use isotope dilution with 1,4-dioxane-d8 as an internal standard (IS)recommended at the concentration within the calibration range of the target compound.

2. Finished products should be mixed and ensured to be homogenous before sampling.
3. Finished products should be adequately dispersed/dissolved during sample preparation steps to ensure complete 1,4-dioxane extraction and complete mixing with 1,4-dioxane-d8.
4. Samples and standards should be weighed with precision to enable reporting results to the nearest 0.01 ppm.

**GC-MS Instrument Criteria**

1. All study samples must be analyzed on a properly calibrated instrument and meet manufacturer's specifications. If the instrument calibrations or other instrument quality control (QC) (i.e. mass spectrometer tune, mass calibration check, or qualitative identification criteria) are outside the normal criteria, standard measures to correct the problem must be performed prior to analyzing samples.
2. The use of a gas chromatograph/mass spectrometer is necessary for the chromatographic separation of analytes and fragmentation of analytes for identification.
    a. Methods may use full scan, selected ion monitoring (SIM), or multiple reactionmonitoring (MRM) scanning modes to meet the LOQ, depending on available instrumentation.
    b. Methods must incorporate, at a minimum, 1 quantitation and 1 qualifying ion for target and IS identification. The ratios of qualifier ions should be characterized in standards and compared to these ratios from sample analysis to ensure that there are no interfering peaks.
        i. 1,4-dioxane
            1. Parent Ion: 88
            2. Fragmentation Ions: 58, 56
        ii. 1,4-dioxane-d8
            1. Parent Ion: 96
            2. Fragmentation Ions: 64, 61
3. A signal to noise (S/N) ratio of 3:1 must be met for all ions for 1,4-dioxane in all samples,including calibration solutions.
4. The Limit of Quantitation (LOQ) should be at or below 1/10 the regulatory threshold e.g., for products with a regulatory threshold of 1 ppm, the LOQ must be less than or equal to 0.1 ppm.

*Comments*:

2.b. We recommend the removal of the decimal points, and a step to ensure that there are no interfering peaks.
As the signal to noise ratio and the limit of quantitation are to GC/MS, we recommend these criteria be moved to this section.
3. The Limit of Detection (LOD) is traditionally established using a signal to noise ratio of 3. This is a minimum requirement to detect the target analyte and should not be confused with establishing a quantitation limit. For quantitation purposes, a SN of 10:1 or 15:1 is appropriate. Further, S/N ratio alone is not sufficient for establishing a LOQ. Precision performance from multiple preparations of the LOQ should be evaluated.
4. In addition to this, the standards should be prepared at or below this concentration, and the signal to noise ratio for these preparations should be greater than or equal to 10. Building on this, the area precision of the standards should be evaluated at the LOQ preparation, a minimum CV or RSD should be reported (typically 15-20% or less). The LOQ should be incorporated into the calibration curves for all measurements.

*Calibration*

1. The instrument tune check for SIM and MRM must be done prior to calibration. Werecommend using BFB tune for full scan.
2. Retention time (RT) and relative retention time requirements:
    a. internal standard RT plus or minus 0.33 minutes to mid-point of initial calibration(ICAL); and
    b. analyte RT less than 10 seconds to mid-point of ICAL or first Continuing Calibration Verification (CCV).
3. The calibration must utilize at least six non-zero calibration levels. The fitted line must have an average response factor (RF) relative standard deviation (RSD) of less than or equal to 20 percent, or linear with a correlation

coefficient ($r^2$) greater than 0.99. Each point above the lowest calibration level must be within 30 percent of the true value. Thelowest calibration level must be within 50 percent of the true value.

4. An initial calibration verification (ICV), with a concentration at or near mid-point of the calibration curve, must be analyzed immediately following the calibration and be within30 percent of the true value.
5. A continuing calibration verification (CCV) solution must be analyzed before sampleanalysis, after every $10^{th}$ analytical run, and at the end of analysis. The determined concentration must be within 20 percent of the true value.
6. Blanks should be run to eliminate or reduce carryover or cross contamination. Blanksshould be inserted between samples with high concentration analytes to verify no carryover of 1,4-dioxane from one sample to the next.
7. Quality control check standards should be analyzed to ensure calibration accuracy and appropriate recovery criteria established.

*Comments*:
2. a. In our experience, relative percent retention time criterion is used (e.g., <2% RSD for dioxane and istd retention times in calibration standards). We recommend this criterion be included.
2. b. We recommend this section be removed as it is unnecessary.
3. Similarly, relative % retention time criterion is used (e.g., <2% RSD for dioxane and istd retention times in calibration standards). If single point calibration is used, response characteristics should be established over a relevant concentration range (multi-day $r^2$, relative y-intercept, etc.) during method validation. In addition, a +/-30% seems too wide of a window. Bioanalytical assays utilize similar instrumentation and target +/- 15%. For LOQ or lowest calibration standard, bioanalytical validation targets +/- 20%, not 50%. $R^2$ and check standard recovery should be sufficient for calibration.
4. Again, +/- 30% is a much wider range to target. We believe that this step is superfluous and can be deleted.
5. This may not be necessary. If ICV is run after calibration, choosing to do a CCV is unnecessary. In general, ICV criteria should be less or equal to CCV criteria, therefore, we recommend 10% for ICV and retain 20% for CCV.
7. We recommend adding a step to check calibration accuracy.

**Quality Control**

All data must adhere to a quality control protocol and include a duplicate sample preparation and analysis for each product analyzed. An example of such a protocol is outlined below. Alternate protocolsare acceptable assuming they incorporate steps to ensure that method blanks, analytical accuracy, and precision are maintained for each run and can demonstrate a relative percent difference (RPD) less than or equal to 20 percent and an extraction recovery between 70 and 130 percent.

Example protocol

1. A method blank is run with every batch of up to 20 samples. The concentration of 1,4-dioxane in all method blanks must be less than the limit of quantitation.
2. A laboratory control sample and duplicate preparation are analyzed with every batch of20 samples and must be within 30 percent of the true value and RPD less than or equal to 20 percent.
3. A matrix spike and duplicate are analyzed with every batch of 20 samples with a recovery value within 70 and 130 percent and RPD less than or equal to 20 percent. Thelaboratory may establish internal control limits but must not exceed the 70 to 130 percent recovery range.
4. The RT of the analyte of interest in the sample are less than 10 seconds to the mid-pointof ICAL or the first CCV.
5. If preliminary results suggest a sample is above the regulatory threshold, confirmatory testing should be conducted with new, triplicate preparation of the sample in question with appropriate quality control check standards to ensure calibration accuracy.

*Comments*:
Recovery tolerances from cosmetic samples could vary. Targeting a +/- 30% range form any matrix is fine, but these tolerances should not be the same as the tolerance given for working calibration standards. Those tolerances should be more restrictive.
4. As noted above, the inclusion of the step may not be required.
Addition of section 5 is an example of guidance for samples that may be above threshold.

**Points of Clarification**
As a follow-up to the stakeholder discussion held July 16 with NYSDEC staff, DEC notes that it is considering whether to include the draft MCP in the forthcoming 1,4 dioxane regulations. ACI recommends that DEC consider this MCP as general guidance for communicating scientific approaches, methodologies, and best practices to support compliance with the law. This will help ensure that approaches for meeting the performance criteria can continue to be refined and developed, while allowing the MCP document to evolve in accordance with the best available science. We emphasize that a more complete knowledge on how methods and results will be assessed and managed by NYSDEC would assist with these and future comments.

Thank you for your attention to comments and interests of ACI, PCPC, CHPA, CBA, HCPA and members companies. We are interested in working with NYSDEC on clarification and improvements to the draft 1,4-dioxane Method Performance Criteria, use of testing criteria, and scope of the regulation for products being tested.

Sincerely,

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Vice President, Technical & International Affairs

Arielle Brown
Senior Manager, Government Affairs