May 10, 2024

David Berkowitz
Environmental Protection Agency
109 T.W. Alexander Drive
Research Triangle Park, NC 27711

Attention: Stakeholder Input for Method 325B Revisions
*Submitted via (*meetingadmin@scainc.com*)*

Re: Comments on revisions to Method 325B, Volatile Organic Compounds From Fugitive and Area Sources: Sampler Preparation and Analysis

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Dear Mr. Berkowitz,

The American Chemistry Council (ACC), the American Fuel & Petrochemical Manufacturers (AFPM), and the American Petroleum Institute (API) (collectively The Associations) appreciate the opportunity to comment on the U.S. Environmental Protection Agency's (EPA or Agency) to provide input for revisions to Method 325B, Volatile Organic Compounds From Fugitive and Area Sources: Sampler Preparation and Analysis.

ACC represents the leading companies engaged in the business of chemistry and energy. Its' members apply the science of chemistry to make innovative products and services that make people's lives better, healthier, and safer. ACC's members also engage in all aspects of the petroleum industry, including production, refining, transportation, and storage. We are committed to improved environmental, health and safety performance through Responsible Care®, common sense advocacy designed to address major public policy issues, and health and environmental research and product testing.

AFPM is a national trade association representing nearly all U.S. refining and petrochemical manufacturing capacity. AFPM members support more than three million quality jobs, contribute to our nation's economic and national security, and enable the production of thousands of vital products used by families and businesses throughout the United States. AFPM members are committed to filling these roles in a way that is responsible and sustainable for the long term.

API is the national trade association representing America's oil and natural gas industry. API's members are producers, refiners, suppliers, retailers, pipeline operators, and marine transporters, as well as service and supply companies, providing much of our nation's energy. API was formed in 1919 as a standards-setting organization and is the global leader in convening subject matter experts across the industry to establish, maintain, and distribute consensus

standards for the oil and natural gas industry. API has developed more than 800 standards to enhance operational safety, environmental protection, and sustainability in the industry.

On February 28, 2024, EPA established a stakeholder's group to review and provide input on revisions to Method 325B, Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis. This letter contains the Associations' suggestions to improve the Method, including:

- Adding additional tube media types to the Method,
- Adding new uptake rates focusing on 7-day and 14-day durations,
- Updating acceptable tube life/usage criteria, and
- Adding procedures and QA/QC for sample recollection/reanalysis.

The current version of EPA Method 325B was published in 2019. The Associations note that methodologies, materials, and instrumentation change at different rates, and the changes are very likely to outpace revision cycles for a standing method. To that end, many of the specific comments below are focused on method flexibility and ensuring that reliable data are generated over time and in a changing landscape. The Associations look forward to engaging with EPA on the items below.

1. **Sorbent Amount Needed**

   API requests EPA reduce the amount of absorbent required in the passive tubes by 50%, which decreases the amount of sorbent facilities are required to purchase without compromising results. From the required Refinery Sector Rule (RSR) fenceline monitoring, facilities learned that the 60 mm sorbent bed length specified in EPA Method 325B was based on active, pumped sampling applications, presenting an opportunity to reduce the bed length for passive diffusive sampling. The 60 mm sorbent bed length is excessive for passive diffusive collection because adsorption of target compounds is focused on the leading edge of the sorbent bed with negligible migration through the sorbent bed during sample collection. A technical benefit of using less sorbent is that any background artifacts inherent in Carbopack X (or other sorbent) are reduced when using less sorbent.

   Passive tubes themselves are essentially the same as the active tubes, as they are the same size and can contain the same amount of sorbent. Yet the mass collected on a passive tube is much less than the mass collected on an active tube The mass collected on a tube with a shorter sorbent bed will still be well below the collection capacity of the sorbent. The use of a shorter bed should have no impact on the uptake rate of the passive tube. This is driven only by the configuration of the inlet of the passive sampling tube. This same topic can be addressed within the language of the Method: Section 7.1.5 specifies breakthrough volumes of at least 20 and preferably 100 liters. The breakthrough volume for Carbopack X for benzene is approximately 3,000 liters.[1] Using half as much Carbopack X will yield a breakthrough volume that is still well above the Method specification. Of course, this could be easily confirmed by a simple set of parallel experiments using tubes with both full-size and smaller sorbent beds.

[1] ASTM D6196-15

2. **Tube Life: Number of Acceptable Field Uses, Indicators or Tube Quality**
API requests that EPA change the tube replacement interval from "2 years or 50 uses, whichever comes first", to a use-cycle interval only. This change will prevent tubes that are still serviceable from being discarded as waste. The typical rule of thumb for adsorbent (porous polymer) replacement is 100 thermal cycles. To clarify, in this discussion and proposal, the "use-cycle" is a trip to the field followed by analysis and tube re-preparation. This use cycle is easily tracked using the bar-code system already in place for tracking sampling, analysis, and results.

The graphitic carbon sorbents being used are more robust than that and can have much longer use-cycles. The Associations note that most sites utilize a 3 to 4 sample set to accommodate the 2-week sampling periods (e.g., one tube is sent off for analysis and another is put in its place, such that the first tube is not used again for weeks). In this scenario, most tubes are used less than 20 times in the two-year window stated in Section 7.1.6. Conversations with technical staff at EPA suggested that the option to re-pack the tubes after the 2-year interval was intended to address physical breakdown of the friable sorbent, and not degradation in the sorbent properties. As it is not practical or cost-effective to repack tubes, tube vendors are not offering this service to laboratories. As a result, tubes past their 2-year limit are disposed of with limited options for recycling. The 2-year limit creates waste at an unnecessary rate.

The Associations recommend a replacement cycle based on a series of measurable criteria. In current practice, before initial use, each tube is conditioned, and checked for background (clean blank). After use, each tube is conditioned. This is done in batches, usually 20 at a time, and two of the conditioned/recycled tubes are passed through analysis again to demonstrate cleanliness. Internal standards are added to the tube, and the tube is desorbed and analyzed to demonstrate both desorption (by standard recovery) and cleanliness (by the blank result). The Associations propose the following additional quality checks to ensure the efficacy of tubes in service:

- After each 20 use cycles a recovery check is performed. Target analyte is spiked onto the tube and a minimum of 20 liters of gas is passed through the tube. Internal standards are applied, and the tube is analyzed to demonstrate recovery of the target analyte.
- After 100 use cycles, the tubes would be treated as if they were new. That is, each tube will be spiked with internal standards and desorbed to demonstrate cleanliness.

Although not specified in the Method currently, there are several conditions under which a tube should be removed from service.

- High mass loading. A tube that had a very high mass loading is difficult to clean. These tubes undergo individual identification for blank assessment, and if necessary, should be disposed of.
- Poor gas flow. The pressure drop across each tube is checked each time the tube comes into the laboratory. If the pressure drop gets too high, this is indicative of flow issues within the tube, the presence of sorbent fines, and/or general sorbent breakdown. Tubes with this issue should be removed from service and disposed of.

- Poor analytical performance. If the previous analysis showed tube-related issues with desorption, bad peak shape, or poor recoveries, the tube should be removed from service and disposed of.
- Physical integrity. If there are visible sorbent fines outside of the sorbent bed, or if sorbent fines are observed in the instrument or preparation instrumentation, or if the tube itself is showing cracks or nicks, the tube should be removed from service and disposed of.

3. Media Type

As currently laid out, the Method essentially specifies use of Carbopack X as the required sorbent. Sorbent selection is discussed in Section 7.1 of the Method, with a reference to Table 12.1. Carbopack X is cited by name in both locations. There is currently only one domestic supplier of Carbopack X. To alleviate supply chain and pricing concerns, the Associations request EPA remove references to specific sorbents in the Method and instead add criteria that a sorbent manufacturer must meet for a different sorbent to be used. The Associations note that EPA, in the stationary source audit program[2], has tied the requirement to the audit samples being "commercially available" and defined "commercially available" as the presence of two or more suppliers of audit samples. The logic behind the need for multiple suppliers of an item required by an EPA program applies in this instance as well.

A more robust "performance specification" for acceptable sorbents should be included in the Method. Any manufacturer that produces an appropriate sorbent would certify to a facility that their sorbent meets the criteria in the Method for use. A performance specification for an acceptable sorbent could include the following criteria:

- Appropriate adsorption properties (retention volume)
- Stability of target analyte on the sorbent (ability to retain the analyte)
- Appropriate desorption properties for reliable recovery
- Physical robustness (i.e., not forming fines or breaking down)
- Moderate insensitivity to ambient conditions (i.e., temperature, humidity, etc.)

Neither the sorbent manufacturers nor the facilities should have to petition EPA for use of a new sorbent. This approach would make the Method more evergreen and could encourage U.S. suppliers to develop a sorbent for use, reducing the sorbent cost and mitigating supply chain concerns. Including or adding criteria in the Method for use of sorbents other than Carbopack X will allow for faster adoption than waiting for manufacturers to petition EPA for inclusion of their sorbent in a revised Method.

The Associations would like to note that Table 12.1 lists compounds to be sampled using Carbopack X for which Carbopack X does not perform well. These compounds include 1,2-dichlorethane, trichloroethene, and carbon tetrachloride. Carbopack X may also be problematic for the chlorinated hydrocarbons.[3]

[2] §60.8(g)(1) and §63.7(c)(2)(iii)(A))

[3] Markes International Ltd. Uptake Rate Tests: Tests for a range of compounds onto four sorbent types over periods of 1 and 2 weeks. September 27, 2022

4. **Uptake Rates**

Specifications for demonstration of sorbent performance are included in Method 325B (Addendum A) as written; however, there is also a very specific table (12.1) that presents validated sorbents and uptake rates. EPA should allow the use of any credible, published uptake rate study that follows the methodology in Addendum A or the Method-included alternatives:

- ISO 16017-2:2003(E),
- ASTM D6196-03 (Reapproved 2009),
- BS EN 14662-4:2005, or
- Reported in peer-reviewed open literature.

The use of these alternatives should not require any submission for acceptability as Method compliant.

Technology moves faster than Method revisions. The intent of any method should be the collection of acceptable and meaningful data relative to a regulatory standard or permit requirement. Therefore, EPA should provide enough flexibility in the Method in terms of sorbent and material criteria to justify a facility's selected methodology as the marketplace changes and the technology evolves. The Associations note that EPA has, in many of the source testing methods, put in language that allows use of a certain material or its "equivalent." Such an approach should be taken here – EPA should provide an example for facilities that are content to use the current approach but should provide a pathway to allow use of an equivalent approach for those that wish to use other appropriate published data to design their sampling and analysis programs.

Further, EPA could develop and maintain a clearinghouse where acceptable data (those developed using an accredited lab and the methodology in Addendum A) are posted and available for use. This approach would mitigate any concern about using inappropriate data and could serve to improve data quality (consistency, comparability) across all measurement activities.

5. **Recollection: Setup and Validation Techniques**

The Associations request that EPA include and clarify procedures in the Method that allow for duplicate analysis of a sample to confirm an anomalous result. Sample recollection is an appropriate and useful tool to mitigate the "one-shot" nature of a sorbent trap that is thermally desorbed completely before analysis. This approach allows the "recollection" of the sample, so it can be analyzed in the case of any kind of problem with the initial analysis. The methodology is robust and is demonstrated as part of routine laboratory method operations.

Recollection is a bit of a misnomer. Facilities are not recollecting the sample, rather the lab is preserving a portion of the sample for subsequent analysis if necessary. Recollection in this application is just analysis of the preserved portion of the sample. Lab practice and the Method specify that the initial tube (the one sampled in the field) be spiked with internal standards and then be thermally desorbed and collected (cold or not) onto a second tube (called a secondary trap or focusing trap). The second tube can be (according to the

Method) and generally is (according to laboratory practice) thermally desorbed with a portion (~10%) being sent to the detector and the remaining ~90% returned to the initial tube. If everything goes right up to this point, the analysis is finished, and there is no recollection. But, if there is any kind of problem with the analysis or if there is a questionable result, the remaining sample can and will be analyzed. In this case, the initial tube (which now has internal standards and about 90% of the initial sample) is thermally desorbed to a focusing trap (without any additional internal standards). The analysis of the focusing trap proceeds as normal.

Of course, there are additional details associated with this additional manipulation and the extended activities:

- Is this ever done automatically? Yes. Depending on the project and client, second runs can be required whenever the action level is exceeded.
- Is there a parallel sample where the first analysis was valid and the second analysis was done to demonstrate overall performance of this activity? There could be; however, routine laboratory quality includes demonstration of the recollection with acceptable agreement with the primary result on the daily batch quality checks for the continuing calibration verification (CCV).
- Is there a possibility of varying the split to the detector to address very high results? Yes. This is of course done with enough quality checks to ensure that the split value and level of internal spike material is appropriate.

Desorption and analysis are described in Sections 11.3.1.4 and 11.3.1.5 of the Method. The Associations recommend that these sections be enhanced to provide guidance, clarification and limitations for these sequential desorption and splitting activities. In specific, the Associations recommend the following:

- There are a maximum of three analyses performed for each sample.
- If a sample analysis results in a replacement analysis, the second, replacement, analysis is reported.
- If a sample is analyzed in duplicate, and both results meet Method quality criteria, the first result is reported.

6. Overall Quality: Laboratory Certification

The Associations support laboratory certification. Laboratory certification is important and is extremely valuable to the end consumer. Certification at the laboratory level is a holistic evaluation of overall performance. Certification at the method level is a detailed evaluation and demonstration of laboratory performance, both independently (i.e., within the laboratory) and collaboratively (i.e., in comparison to other laboratories).

7. Shipping Temperature Effects

There is no specific requirement for a “cold pack” within Method 325B as promulgated. However, the Method is a bit inconsistent on the topic of transport and storage temperatures:

- Section 6.4.2 addresses extreme temperatures and uses a parked vehicle as an example. This section goes on to suggest the use of a cooler without ice for storage.

- Section 8.2.2 addresses how tubes are to be kept for storage and transportation and states that these should be done at ambient temperatures.
- Section 8.5.4 addresses hold time but goes on to specify that the tester "ensure ambient temperatures stay below 23°C" (73°F). Ignoring how a tester is supposed to manage the weather, for many parts of the country, for portions of the year, 23°C is not ambient temperature.

These requirements have been read to require the use of a cold pack for shipping tubes. However, this is not necessary, as the sampling tube was operating in ambient air while it was collecting sorbent, is capped when it is removed for shipment, and will not release any of the analyte if shipped warm. EPA should remove the requirement to ship the samples below 23°C.

It may be desirable to avoid temperature extremes to avoid damage to the tubes, or any loss of analyte from the sorbent. However, once those extremes are avoided, there is no reason to believe there are temperature-based stability issues associated with these tubes, and the sorbent and analytes within. EPA or industry could perform a one-time demonstration in a controlled environment that there is acceptable Method performance (for example, by preparing a traveling spike or two that is deployed in the field and returned for analysis without temperature control). This issue was addressed in a presentation at an industry conference that we can make available upon request.[4]

Thank you for the opportunity to submit these comments. We look forward to working with the Agency to finalize changes to Method 325B. Please do not hesitate to contact Derek Reese at ReeseD@api.org if you have questions or need more information.

Respectfully submitted,

The American Chemistry Council
American Fuel & Petrochemical Manufacturers
American Petroleum Institute

[4] *Sensitivity of EPA 325 to Field Handling Protocols,* D Reese & H Hayes; 2016 AFPM Environmental Conference.