# An Executive Summary

Evolving with Changes in Environmental Analysis Part 2 – Meeting Evolving Regulatory Requirements of EPA Methods for Monitoring Volatile Compounds



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#### Introduction

Environmental sample analysis is a constantly evolving field. Changes in the environment and the contaminants present are mirrored by updates to regulatory guidelines and methodologies. For environmental labs, the challenge of staying up to date with regulatory requirements and maintaining productivity is a balancing act. This manuscript discusses the evolution of regulatory requirements for volatile organic compounds (VOCs) focusing on recently proposed updates and some of the typical challenges experienced in VOC analysis. The discussion also provided guidance for navigating these challenges using solutions that can be incorporated into plans for updating instrumentation. Also featured in this article is a review of the available solutions that can help improve current lab practices and offer additional opportunities to lower operating costs and optimize capabilities for VOC analysis.

### Volatile Organic Contaminants Analysis Background

Volatile organic contaminants are organic contaminants that have low molecular weights, low boiling points, and high vapor pressures. Because of these properties, VOCs tend to readily evaporate and equilibrate with earth's atmosphere at ambient temperature, hence, the label "volatile". Common sources of these compounds include industrial solvents, paints, adhesives, and petroleum products. Another major source of VOCs are emissions from automotive and industrial activity, which has been the recent focus of EPA activity. Because of their assortment of chemical properties and the volatile nature of these compounds, analysis of VOCs is accompanied by frequently occuring challenges. VOC analysis is particularly challenging because the properties of the target compounds constantly drive their migration out of sample extract or matrix prior-to or during analysis.

Among other considerations volatility challenges are dealt with in two ways: airtight sample containers with limited headspace must be used to capture samples and analysis methods require capabilities that efficiently drive vaporization, capture and transfer of the analytes out of matrix and into instrumentation without diffusive loss. To sample the evolved vapors or gases from environmental samples, either headspace or purge and trap techniques are used. Since in the environment these compounds are constantly equilibrating into the atmosphere, samples tend to be at lower concentrations. Consequently, purge and trap is the preferred technique for quantitative analysis due to its ability to concentrate low concentration analytes, while headspace is primarily used as a screening methodology. With purge and trap (Figure 1), a gas is used to purge VOCs out

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of the sample and concentrate them onto an analytical trap column. Note: This is, separate from the analytical GC column used to resolve the components. The trap column is then heated to elute the VOCs from the trap column. Carrier gas flow then sweeps the unbound VOCs into the GC or GC-MS system for analysis. In addition to providing a tool to concentrate low concentration VOCs the purge and trap concentrator (analytical trap) provides an avenue to limit introduction of water to instrumentation. Typically, large amounts of



water sample must be concentrated to meet VOC detection limits which can produce challenges to operation and functioning of the GC and GC-MS systems. Another key function of purge and trap technique is that filters out the volatile portions of the sample, leaving behind the heavier sample artifacts and potential matrix interferences.

#### **Environmental VOC Regulations**

In the US, the EPA sets regulations for monitoring the presence of VOCs in environmental matrices like water, soil, and air including the analytical methods that detail how to extract, identify, and quantitate these contaminants. There are many different considerations for method groupings. Generally, the method series for VOCs are broken up by sample type (or office that the regulation emanated from) and the type of contaminants to be analyzed. The common VOC methods include the 500, 600, and 8000 series methods, as well as the toxic organic air methods. These methods are the current regulatory standards for VOC analysis and typically include some type of GC or GC-MS analysis.

Gas chromatography methods for VOC analysis can include BTEX/MTBE, gasoline range organics or total petroleum hydrocarbons. These methods are usually configured for a single compound analysis or small compound groups. In contrast the GC-MS methods include an assortment of VOC compound types where spectra is used to differentiate between various compounds. Regulatory GC-MS specific methods include EPA Methods 524, 624, 8260, and their associated versions.

Regulators update these methods periodically to manage new risks and/or revamp outdated methods with new requirements. For example method 524 for VOC content in drinking water using GC-MS was updated in 2009 and again in 2011. In 2015, updates were also proposed, via the Method update rule, for US EPA method 624 for VOCs in waste water. Additionally, the SW-846 version 6 update, still in its comment review and feedback period, included updates for EPA Method 8260 for the determination of VOCs in hazardous waste, soil, semi-solids and ground water.

Overall it seems the EPA is optimizing method performance by providing more flexibility in analytical procedures and taking steps to harmonize similar methods between offices. Specific updates include the addition of new technology, use of hydrogen as a carrier gas, and additional analytes.

A specific benchmark for EPA updates to VOC methods where these efforts are demonstrated are the 2009 update for 524.3 and the 2011 update for 524.4. Changes to these methods included the addition of nitrogen as a purge gas, edits to instrument method parameters including data collection, shorter purge and desorb times for purge and trap sample introduction, edits to data processing and adjustments to Lowest Concentration Minimum Reporting Level (LCMRL) calculations.

Despite these updates, many challenges remain, including the addition of new compounds, purge efficiency issues, carryover considerations, moisture management, trapping efficiency, and data interpretation. Without the proper technology and tools, these challenges can lead to inaccurate quantitation, the presence of false positives, reanalysis requirements, difficulty with sample availability, and an overall decrease in lab productivity.

## Answering Challenges with Tools That Evolve with Regulations

Moisture effects are a challenge that can cause a ripple effect in purge and trap GC-MS analyses resulting in a water "front" in the chromatography and internal standard inconsistencies, both of which can cause calibration problems. **Figure 2** illustrates the effects of a raised baseline due to a water "front" caused by moisture present in the GC-MS. If internal standard recovery is variable due to moisture contributions, compound recoveries may fail the acceptance criteria. There are four ways to avoid moisture effects: smaller sample volumes, shorter desorption times, a moisture trap in the concentrator, and higher GC inlet split ratios.

Modern GC-MS instruments, with improved sensitivity, can achieve the desired detection limits using a reduced sample volume (5mL) as opposed to the 25 mL volume traditionally used, introducing less moisture. Shorter desorption times are also helpful in reducing moisture effects. While method 524.2 required a four-minute desorption, 524.3 requires only 0.5 to one minute. A half-minute desorption results in a substantial decrease in the amount of moisture introduced to the instrument. Another way to reduce moisture is by using a blank tube that does not contain any adsorbents, called a moisture retention trap (MORT). The MORT accumulates water, allowing the analytes of interest to pass through and adsorb to the analytical trap, as shown schematically in **Figures 3** and **4** for the purge and desorption steps respectively. By using an 8-port valve, the sample pathway

avoids the moisture trap completely during the desorption step, resulting in better moisture control.

Moisture control can also be managed by using higher split ratios. Traditionally, split ratios up to 100:1 have been recommended, which is great for controlling moisture. However, a side effect of a 100:1 split is higher helium consumption. Using moderate split ratios, like 40:1, is a good compromise between helium use and moisture control, and as presented in **Figure 5**, better sensitivity is obtained.

Methanol creates yet another challenge; excess methanol can cause linearity problems and compound response suppression, particularly in the more sensitive modern GC-MS instruments. In addition, other compounds commonly analyzed can be problematic for example; ethanol and 1,4-dioxane, both of which are becoming more common in VOC analyses. These compounds are miscible in water and are difficult to purge and remove from the sparging vessel after a sample is run. Furthermore, USEPA Method 8260 requires System Performance Check Compounds (SPCCs). SPCC compounds are used to determine if there is a problem



with the operation of the purge and trap concentrator. The minimum average response factors for SPCC compounds are determined for to chloromethane (0.100- low response if purge is too fast), 1,1-dichloroethane (0.100-low response if transfer line is degraded or contaminated), bromoform (0.100-low

response if there is poor purging), chlorobenzene (0.300) and 1,1,2,2-tetrachloroethane (0.300-low response if transfer line is degraded or contaminated) to ensure compound stability and to assess degradation caused by contaminated lines or active sites within the system.



Figure 4: 8 port valve - enhance chromatography



Finally, compound carryover can also create difficulty for VOC analysis. Carryover after high-concentration sample runs can result in sample re-runs and a corresponding loss of productivity. There are multiple solutions for preventing carryover including higher bake temperatures, higher bake flows, hot water and/or methanol sparge vessel rinses. However, the most effective technique of controlling carryover is to heat the sparge vessel during bake to baking-off any remaining analytes in the glassware.

#### Workflow Solutions for VOC Analysis

From VOC sample receipt to data analysis, the Thermo Fisher Scientific environmental analysis portfolio integrates a broad selection of instrumentation and solutions to support this workflow. For screening samples, headspace capabilities include both syringe and loop-type configurations featured in the TriPlus RSH™ and TriPlus™ 300 Headspace Autosamplers (Thermo Scientific™) Autosamplers. In Purge and Trap applications, Thermo Fisher Scientific's GC and GC-MS products integrate with most manufacturers' concentrator instrumentation. In addition to a complete selection of GC and GC-MS capabilities, Thermo Fisher also provides chromatography consumables like inlet liners, septa and ferrules and last but not least they also supply specific environmental data analysis tools in Chromeleon<sup>™</sup> Chromatography Data System (CDS) Software and TraceFinder™ Software (Thermo Scientific<sup>™</sup>) software options.

When updating or choosing new instruments, it is important to keep our analysis goals in mind. For VOC analysis, the required sensitivity often dictates the choice of technology. As illustrated in Figure 6, sensitivity for benzene is greatly increased by moving from headspace to purge and trap instrumentation. Consequently, the detection limits and required reporting limits of the analysis need to be considered while also taking instrument capabilities into account. The TriPlus RSH system includes a dedicated gas syringe tool and heating block for headspace vials as well as auto dilution functionality with the added available option of solid phase micro extraction (SPME) configuration. By adding the SPME feature, a drinking water lab could analyze Geosmin and 2-Methylisoborneol compounds along with headspace samples, providing a dual-purpose instrument that could replace two older systems. Along with the autosampler capability, the Thermo Scientific<sup>™</sup> TRACE<sup>™</sup> 1300 Gas Chromatograph series includes dual detectors and dual injector modularity that can be configured to run simultaneous methods further improving productivity.

In addition to its configurable instrument features, the additional options of the Trace1300 series GC provide the opportunity to reduce laboratory operating costs. Because environmental labs have experienced increases in helium costs and decreases in availability helium conservation has become a key focus for reducing analysis costs. When using purge and trap for the extraction of VOCs, a large amount of helium is consumed. By using nitrogen as a carrier gas for purge and trap





Figure 7: Helium saver module for the lifetime of the instrument

1310 Gas Chromatograph in **Figure 7**, nitrogen blankets the inlet during injection and periods of downtime. Helium use is reserved for use only as a carrier gas to transfer VOC analytes through the column. When used in combination with nitrogen on purge and trap instrumentation, as allowed in EPA method 524.4, overall helium volumes can be drastically reduced to as little as a single cylinder of helium over 15 years.

Another effort to help conserve helium is proposed in edits to EPA method 8260 that includes the option for hydrogen as a carrier gas. In our evaluations using hydrogen as a carrier gas caused catalytic compound conversions and reduced overall sensitivity of the system over time. Along with the need for revalidation which can be expensive and time-consuming hydrogen carrier gas also comes with significant safety concerns. By using nitrogen as a purge and trap gas only, and helium as a carrier gas in conjunction with the Helium Saver Module for GC analysis concerns for hydrogen carrier gas are eliminated allowing maintained productivity and reducing operating costs.

## Conclusion

extraction labs can significantly reduce the amount of helium consumed in a single run. In addition the modularity of the TRACE 1300 GC system delivers a solution for reducing Helium usage during GC sample analysis. Using the Helium Saver Inlet Module, shown installed on a Thermo Scientific<sup>™</sup> TRACE<sup>™</sup> The regulatory landscape of VOC analysis is constantly changing, and while there are many challenges for laboratories to overcome there are many tools and workflow solutions that can help reduce errors, improve productivity, and reduce operating costs.