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**GUIDANCE FOR ANALYSIS  
OF  
INDOOR AIR SAMPLES**

**Colorado Department of  
Public Health and Environment**

**Hazardous Materials and Waste Management Division  
(303) 692-3300**

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### **Purpose of this Guidance**

*This is intended as general guidance for generators of hazardous waste and is meant to assist in compliance with the hazardous waste regulations. The guidance is not meant to modify or replace the promulgated regulations which undergo periodic revisions. In the event of a conflict between this guidance and promulgated regulations, the regulations govern. Some portions of the hazardous waste regulations are complex and this guidance does not go into details of these complex situations. If a regulatory situation is not described in the guidance or clarification is desired, an official interpretation of a specific hazardous waste regulation can be requested by writing to the Hazardous Materials and Waste Management Division at the address on page 7.*

*We would appreciate any comments or suggestions for making improvements in future editions. Suggestions or comments can be sent to the address on page 7.*

**This document was revised to correct the isotope ratios on page one, paragraph three.**

## **GUIDANCE FOR ANALYSIS OF INDOOR AIR SAMPLES**

The Hazardous Materials and Waste Management Division (“HMWMD”) of the Colorado Department of Public Health and Environment, in consultation with US EPA Region VIII, have evaluated analysis protocols being employed to ascertain the inhalation exposure pathway for domiciles impacted by volatile organic compounds (e.g., chlorinated solvents and their degradation products) released to the environment, and specify minimal acceptable requirements.

The impact to residential communities by volatile organic compounds via the respiratory exposure pathway is being assessed by regulated industries with oversight from the agency. The purpose of these investigations is to acquire data to be used as inputs into a risk assessment process employed by agency toxicologists, and to provide a tool with which to establish remediation and response activities. These types of investigations are Category 1 Projects which the agency considers to be the highest priority effort with potentially large negative public health impacts. In order to maximize the usability of these data and minimize the cost of these investigations, the agency is here defining the minimal acceptable technical thresholds and attributes for these data.

### **The minimal acceptable tuning requirements for GC/MS-SIM instruments**

GC/MS instruments operated to meet Compendium Methods TO-14, TO-14a, TO-15, and TO-16 Scan mode, must meet specified tuning requirements for operation. SIM tuning and data acquisition requirements are not specified. Presently, instruments may be tuned in any manner at the discretion of the laboratory, and may include tuning to Scan mode requirements with an accompanying loss in sensitivity. The agency notes that tuning algorithms which are designed to maximize the 69 atomic mass unit (“amu”) ion for the tuning compound perfluorotributylamine (“PFTBA”) inherently produce a better signal to noise ratio, and a lower detection limit. These tuning algorithms are typically referred to as the “Autotune” instrument option. The agency will require that tuning be accomplished by way of Autotune protocols, and the following conditions must be met: (1) The operator must confirm that the 69/70, 219/220, and 502/503 isotope ratios occur at the proper ratios of 1 percent (+/- 50 %), 5 percent (+/-25 %), 10 percent (+/- 10 %) respectively; (2) The peak width at half height for the 502, 219, and 69 PFTBA isotopes be 0.5 amu +/- 0.2 amu; and (3) The operator must confirm the correct mass assignment of these isotopes to a tolerance of 0.1 amu (e.g., 69.0 amu +/- 0.1 amu).

Once tuned, these instruments have acceptable electronic drift; such that, operators must verify that the tuning is stable at a minimum of once per operating day to insure correct mass axis alignment, and eliminate data accumulated with contaminated ion sources. These instrument tuning requirements specify the minimum acceptable performance goals which are easily verified.

### **The minimal acceptable data acquisition requirements for GC/MS-SIM instruments**

GC/MS instruments operated to meet Compendium Methods in the SIM mode must be tuned and operated to acquire data with 1 amu of resolution. Presently, there are no tuning criteria for the SIM mode in these methods. The agency evaluated data produced with low resolution (between 1.4

and 1.8 amu) and high resolution (1 amu) approaches on a linear quadrupole instrument. The data produced with high resolution show a demonstrable improvement in signal to noise ratio, fewer interferences, and a lower detection limit for all compounds of interest. Furthermore, actual data accumulated for an indoor air quality assessment was examined, and all samples analyzed by a low resolution approach exhibited detrimental interferences. Only two samples demonstrated the absence of interference. These samples were found to have been acquired with a high resolution approach (1 amu of resolution). Data acquired with 1 amu of resolution met required detection limits for the compounds of interest.

The agency requires that GC/MS-SIM data be acquired with 1 amu of resolution, and that the following conditions must be met: (1) the operator must demonstrate compliance with the tuning specifications; (2) the operator must confirm that the software method used to collect calibrant and sample data be set to the high resolution option (1 amu); (3) the ion dwell times must have been optimized to obtain a minimum of 10 scans per peak; and (4) the electron multiplier voltages must be set to meet the detection limits of the project (conveniently accomplished by setting EM voltages at +300 volts relative to the tune voltage).

### **The minimal acceptable requirements for ion selection for GC/MS-SIM and GC/MS-Scan**

GC/MS instruments operated to meet Compendium Methods in the SIM and Scan modes report the air concentration of contaminants by using prominent and unique fragmentation ions in the contaminant's mass spectra. The magnitude of these so called "characteristic" ions, operate in both the SIM and Scan modes as the means to measure the concentration of the contaminant present in the sample. In the SIM mode, the characteristic ions function additionally to provide the identity to the contaminant found in the sample. The Compendium Methods are an assemblage of known analytical approaches which are peer reviewed, documented, and made available for general use. These methods are not offered as absolute, or infallible approaches. There is an assumption that knowledgeable and proficient scientists will operate on data resulting from these methods, and will take actions to meet the data quality objectives of specific projects.

The Compendium Methods have tabular attachments which list the contaminant and its characteristic ions. EPA and HMWMD chemists have independently come to the identical conclusion that the chlorinated solvents characteristic ions used in these methods are substantially different from those tabular lists in methods for other EPA programs (water and hazardous waste). For the typical suite of nine solvent contaminants and degradation products accumulated for indoor air samples, four of these targets have different characteristic ions in equivalent methods (EPA method 8260B, EPA method 624, and EPA method 524). The agency is aware that a significant amount of thought and consultation occurred for the adoption of the characteristic ions for these contaminants into these equivalent methods, and there is no discernible distinction for the media sampled for these contaminants because all analytical approaches ultimately utilize a gas phase for analysis. The Agencies believe that the selection of characteristic ions for this analysis is another critical element for the correct application of indoor air sampling. The agency desires to point out that the selection of characteristic ions is not a simple matter of consulting water and waste analytical methodologies, but is driven by the careful consideration of library mass spectra for the

contaminant of interest, and the presence/influence of interference. Absolutely, all available information should be consulted, but sampling and analysis to illuminate environmental impacts must include a minimal iterative performance examination of the data resulting from a particular technique. If early data sets demonstrate intolerable interference on particular ions, then subsequent analysis certainly ought to recognize other more appropriate characteristic ions which eliminate, and minimize the influence of interference.

Interferences occur in Scan and SIM data, and if these interferences occur in conjunction with characteristic ions of target contaminants, the actual concentrations may be overestimated. The agency has detected that characteristic ions used quantitatively in either mode with interference may significantly overestimate the air concentration of contaminants, regardless of the risk assessment objective (chronic or acute exposure). A dogmatic selection of quantitation ions and the presence of coeluting interferants can cause overestimates of the actual risk to impacted populations. Obviously, overestimating the impact involves unnecessarily alarming citizens to the impact of these solvent releases, and the over commitment of resources to dubious problems. More importantly, the agency's toxicologists rely on accurate data to generate a reasonable risk assessment. Funding for these remedial activities rely on private and public money, and the agency prefers to expend resources based upon the best available information to achieve needed remediation, when it is necessary. The agency prefers to use characteristic ions found in equivalent EPA methodology for GC/MS-Scan applications, and has formulated suggested ions for GC/MS-SIM based upon best professional judgment, after accounting for detrimental interferences observed in three projects, as follows:

<u>Contaminant</u>	<u>Compendium Characteristic Ions<sup>(1)</sup></u>	<u>Agency preferred GC/MS-Scan Equivalent Method Characteristic Ions<sup>(2)</sup></u>	<u>GC/MS-SIM Suggested Ions</u>
1,1-DCE	61 <sup>(3)</sup> , 96	96, 61, 63	96, 98 <sup>(5)</sup>
1,2-DCA	62, 64	62, 98	62, 98 <sup>(5)</sup> or 62, 64
Methylene Cl	49 <sup>(3)</sup> , 84 <sup>(4)</sup> , 86	84, 86, 49	84, 86
TCE	130, 95 <sup>(4)</sup>	95, 130, 132	130, 132

- (1) EPA Air Compendium Methods T0-14, T0-14a, T0-15, and TO-16. Primary (quantitation ion) listed first.
- (2) EPA method(s) 8260B (SW-846), 624 (Clean Water), and 524 (Drinking Water). Primary ion listed first.
- (3) Interference detected on the primary (quantitation) ion, evaluation of 3 projects. Data from two laboratories using GC/MS-Scan and GC/MS-SIM.
- (4) Interference detected on the secondary (confirming) ion, evaluation of 3 projects. Data from two laboratories using GC/MS-Scan and GC/MS-SIM.
- (5) The selection of the 98 ion reflects the prominence of this ion for this compound, and observed interferences.

Interferences that have occurred in SIM data tend to obscure the identity of target compounds. The SIM approach uses a combination of retention time for characteristic ions and the characteristic ion abundance ratio to identify a contaminant. If interferences occur with target contaminants, both identification criteria may fail, and have failed. Laboratories operating this technique are reduced to “estimating” the identity and the concentration of the suspect contaminant where interferants occur in these data. This has been accomplished by assigning a “J” qualifier to the reported result. These actions are justified by the chromatographic retention time of a single characteristic ion in a single chromatographic column. The Agencies understand this approach, but are concerned about the potential for misidentification by relying solely upon a one dimensional datum.

Chromatographic behavior is a useful tool in the determination of solvent contaminants because this behavior provides a probability that a particular contaminant is present, but chromatographic behavior also includes a finite probability that the identification is incorrect. The agency is also concerned about the manner in which these qualifications apply to these data. By convention, the “J” qualification applies only to the quantitative result for the contaminant, not the identity of the contaminant. The agency will allow this approach only if such identifications additionally report that the contaminant was detected but not confirmed, along with the reason for this determination (retention time for characteristic ions, or ion ratio out of range). The agency firmly believes that the frequency of occurrence for this problem will become minor when appropriate tuning, data acquisition, and selection of characteristic ions are fully and completely implemented with a timely, iterative performance evaluation on the resulting data.

The agency and regulated facilities should not feel unreasonably constrained by Compendium methods to accomplish prudent and necessary steps to insure the adequacy of data. EPA’s Office of Solid Waste and Emergency Response (“OSWER”), has established a performance based

approach to the collection of data for all of its programs, and HMWMD has likewise announced, in the preamble to the adoption of Update III to SW-846, its commitment to allow, or require analytical methodology with performance which meets the data quality objectives of a project.

The agency is aware that there are ongoing projects affected by this decision. Because of this, the agency will allow data previously accumulated that does not meet these minimal requirements, but will examine these data to determine if the data quality objectives were met. Based on these examinations, the agency may require additional sampling and analysis. Projects which require this type of sampling and analysis, proceed only by approval of the agency, and the agency will only approve of plans which specify those minimum requirements discussed here. Regulated facilities involved in sampling indoor air should amend their sampling and analysis plans immediately to reflect these minimal requirements.

To assist in this endeavor, Attachment 1 to this document specifies in tabular form the minimal acceptable requirements for analysis of indoor air samples.

**Attachment 1**  
**Minimal acceptable requirement for analysis of indoor air samples**

<b><u>Activity</u></b>	<b><u>Specifications</u></b>	<b><u>Documentation needed</u></b>
<b>GC/MS-SIM Tuning</b>	Autotune or equivalent. Acceptable Isotopic ratios (1, 5, 10 %) Peak width at half height (0.5 amu +/- 0.2) Correct mass assignment (+/- 0.1 amu)	Printout of tune report.
<b>GC/MS-SIM Data Acquisition</b>	Meet tune specifications. Optimize ion dwell time.  Set electron multiplier voltage to achieve required detection limits.  Collect calibrant and sample analysis data with the high resolution option. (1 amu)	Printout of instrument method. 10 scans/peak minimum. Printout of Extracted Ion Chromatogram. Data Quality Objectives.  Printout of instrument method. Raw Sample Data
<b>Ion Selection</b>		<b>Reference</b>
<b>GC/MS-SIM</b>	<u>Select primary ions from 8260B tabular data, or at least two ions, justified from Library Spectra, that meet data quality objectives.</u> (Free from interferences)  Consecutively evaluate ion selection. Adjust as necessary.	<u>Method 8260B, Library Spectra</u>  Library Spectra, Raw Sample Data
<b>GC/MS-SCAN</b>	<u>Select primary ions from 8260B tabular data, or at least two ions, justified from Library Spectra that meet data quality objectives.</u> (Free from interferences)  Consecutively evaluate ion selection. Adjust as necessary.	<u>Method 8260B, Library Spectra</u>  Library Spectra, Raw Sample Data

**GC/MS-SIM Reporting Requirements**

Confirmed Positive detections: (REPORT: Concentration, qualify quantitative estimates with a "J")

- ion relative retention time tracks that of standards (+/- 0.10 RRT)
- characteristic ion abundance ratio tracks ratio of standards (+/- 25 %)
- characteristic ions maximize within +/- one scan

Unconfirmed detections: (REPORT: Detected not confirmed, specify reason. Qualify quantitative estimates with a "J")

- ion relative retention time tracks that of standards (+/- 0.10 RRT)
- characteristic ion abundance ratio fails to track ratio of standards (+/- 25 %)
- characteristic ions do not maximize within +/- one scan

## CONTACT INFORMATION

24-hour Emergency Response Line (877) 518-5608

*New state-wide toll-free*

Colorado Department of Public Health and Environment (303) 692-2000

(CDPHE) toll-free (800) 886-7689

Hazardous Materials and Waste Management Division (303) 692-3300

(HMWMD) toll-free (888) 569-1831

HMWMD Technical Assistance Line (303) 692-3320

CDPHE Website

<http://www.cdphe.state.co.us/>

HMWMD Website

<http://www.cdphe.state.co.us/hm/>

Downloadable Regulations

<http://www.cdphe.state.co.us/regulate.asp>

HMWMD Internet e-mail

[comments.hmwmd@state.co.us](mailto:comments.hmwmd@state.co.us)

Other Phone Numbers:

National Response Center (800) 424-8802

RCRA/Superfund Hotline (800) 424-9346

Send questions in writing to:

Colorado Department of Public Health and Environment

Hazardous Materials and Waste Management Division

Technical Assistance

4300 Cherry Creek Drive South

Denver, CO 80246-1530

OR

FAX (303) 759-5355

Please provide as much detail as possible regarding your question and the waste or process to which it applies.