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A REVIEW OF CARBON DISULFIDE-GC/FID VERSUS THERMAL DESORPTION-GC/MS METHODS THROUGH THE LENS OF ANALYTICAL PROFICIENCY AND HUMAN AND ENVIRONMENTAL HEALTH RISK

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by

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Abstract

NIOSH Method 2549 uses a hyphenated thermal desorption-gas chromatography/mass spectrometry instrumental method with thermal desorption tubes as the sample media for assessment of a variety of volatile and semi-volatile compounds. Other methods in the NIOSH Manual of Analytical Methods use solvent extraction methods for analysis. Of note are those methods that require the analysis of coconut charcoal tubes using carbon disulfide extraction and subsequent analysis via gas chromatography-flame ionization detector. Presented here is a comparison of the methodologies with regard to environmental and occupational health ramifications, as well as method sensitivity as evaluated via limits of detection and compound ranges.

Evaluation of the changes of capability in thermal desorption instrumentation over the twenty years following the inception of the NIOSH 2549 Method call for a review of its use as a screening method. Advances suggest that quantitative methods are now appropriate based on said advances. Elimination of prior “one-shot” sample desorption that lead to the favor of solvent extraction for volatile organic compound analysis is no longer applicable. While both methods have certain limitations, benefits such as sensitivity gains related to pre-concentration (thermal desorption) techniques along with the added benefit of control via elimination of solvent support a review of standing methods for many volatile organic compounds in the NIOSH method lexicon. Drawing from updated reference methods and various studies, additional data can be gleaned to further support the advancement of thermal desorption as a trusted and versatile means of quantitation.

Keywords: Thermal desorption; Solvent desorption; Air analysis; Volatile organic compounds; NIOSH 2549; NMAM; EPA TO-17; ISO 16017-1 and 2: 2003

Dedication

Dedicated to Leland Barnes and Edmund Osterman (my dudes); you make me smile. To my Family and Friends: thank you for your unwavering support of my educational goals (even when I disappear for long periods of time to study), for listening (and pretending to care) when I go off on tangents about worker safety, and for generally being awesome – where would I be without you?

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In acknowledgement of Ardith A. Grote and Eugene R. Kennedy, Ph.D., authors of the NIOSH 2549 Method, a key foundational work instigating much additional study and advancement of the field.

In acknowledgement of Elizabeth Woolfenden, co-author of the EPA TO-17 Method, admired scientist, and true innovator in the world of thermal desorption. The advances you and Markes International Ltd. have made have forever changed the face of thermal desorption technology.

Thank you to Markes International Ltd., my employer, for the generous use of photos and reference literature – and to my colleagues who have taught me everything I know about thermal desorption. It was through my work with you that I was introduced to Industrial Hygiene, thus setting me on my next path of learning.

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Glossary of Terms

Term	Definition
CCT	Coconut charcoal tube
CDC	Center for Disease Control
CNS	Central nervous system
CS_2	Carbon disulfide
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
GC	Gas chromatograph
HSE	Health and Safety Executive
IARC	International Agency for Research on Cancer
ISO	International Organization for Standardization
MS	Mass spectrometer (Single Quadrupole unless otherwise specified)
NIOSH	National Institute for Occupational Safety and Health
OSH	Occupational Safety and Health
OSHA	Occupational Safety & Health Administration
PEL	Permissible exposure limit
PID	Photoionization detector
PNS	Peripheral nervous system
REL	Recommended exposure limit
RSD	Relative standard deviation
SIM	Selected-ion monitoring
$\check{S}_r$	Pooled relative standard deviation
SVOC/s	Semi-volatile organic compound/s
TD	Thermal desorption instrument
TD Tube	Thermal desorption tube
TIC	Total ion chromatogram
TPH	Total petroleum hydrocarbons
VOC/s	Volatile organic compound/s

1. Introduction

Within the ever-changing landscape of science, particularly in analytical chemistry, progress is continually made to advance our ability to gather quantitative data at lower and lower limits of quantitation and detection. This stems from advances in analytical instrumentation capabilities and has the dual effect of supporting the analysis of compounds at more stringent limits then may have previously been possible. Collaborative work of multiple enforcement and recommending bodies also act as an impetus to achieve lower detection limits. As new toxicological and epidemiological data becomes available, revised environmental and occupational exposure limits are set in response; complimented by greater analytical sensitivity.

It is through a culmination of the efforts of recommending and enforcement bodies such as the International Agency for Research on Cancer (IARC), the National Institute for Occupational Safety and Health (NIOSH), the Environmental Protection Agency (EPA), and the Occupational Health and Safety Administration (OSHA) that sufficient information can be gathered to support the lowering of occupational exposure limits (OSHA, 2017). While certain enforcement bodies do not directly affect OELs, it is through collaborative information sharing that further justification for OEL amendments can be made. An example of this would be OSHA's proposed beryllium rule, which relied on NIOSH, EPA, and IARC identification of this substance as a carcinogen to justify lowered limits (OSHA, 2017).

Over and above toxicological or epidemiological studies, one might ask what other situations merit review of the methods used to obtain data? Is a direct risk to health and safety professionals performing these analyses enough? Do the environmental ramifications of a particular method also provide the necessary impetus for reassessment? A challenge to methods is the ability to evolve with the ever-advancing world of instrumentation and the various

alternative methods that may offer not only superior quantitation, but added incentives of less risk and/or better protection of the environment. Two Centers for Disease Control and Prevention (CDC) - NIOSH methodologies for analysis of volatile and semi-volatile compounds will be compared in this work with a focus on the improvements that may be seen in one versus the other: in sensitivity; environmental ramifications; and health and safety concerns.

2. Research Question: Solvent Extraction or Thermal Desorption?

Solvent extraction is a method that has become ubiquitous in the study of volatile and semi-volatile organic compounds. Various solvents are used in these extractions, such as isopropyl alcohol, methylene chloride, methanol, hexane, etc. The CDC - NIOSH Manual of Analytical Methods, 4th Edition, has an extensive list of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) which may be quantitated via solvent extraction. As to narrow the scope of this work, an emphasis was made to evaluate methods that use carbon disulfide (CS_2) extraction of VOCs and SVOCs from coconut charcoal tubes followed by separation and quantitation via gas chromatography-flame ionization detector (GC/FID).

This sampling technique involves the adsorption of organic compounds onto a glass tube with a 7 cm x 6-mm OD x 4-mm ID geometry. This contains two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section, henceforth referred to as coconut charcoal tubes (CCT) in this document. Using active (pumped) or passive (diffusive) sampling methods, said tubes are subsequently analyzed using CS_2 extraction of the sorbent material, and liquid injection of the compound containing post-extraction solvent into the GC-FID. The methods evaluated using this methodology were all taken from NIOSH Manual of Analytical Methods (NMAM), 4^{th} Edition: Ketones I, Method

1300 (Grote, 1994), 1,1,2-Trichloro-1,2,2-Trifluoroethane, Method 1020 (Pendergrass, 1994a), hydrocarbons, Halogenated, Method 1003 (Pendergrass, 2003), Hydrocarbons, Aromatic, Method 1501 (Pendergrass, 2003), Methylene Chloride, Method 1005 (Pendergrass, 1998), Ethyl Acetate, Method 1457 (Pendergrass, 1994b), Terpenes, Method 1552 (Pendergrass, 1996), and Hydrocarbons, BP 36°-216°C, Method 1500 (Lunsford, 2003).

An additional method exists in NMAM, 4th Edition, Method 2549 (Grote & Kennedy, 1996), which may be used for a multitude of VOCs. This method instead utilizes "standard" (3.5" length x ¼" O.D. geometry) thermal desorption tubes for sampling, which may utilize a variety of different sorbents, most typically porous polymers, graphitized carbon blacks, and/or carbonized molecular sieves, based on the compounds of interest one wishes to capture. This is then followed by hyphenated thermal desorption, gas chromatograph, and mass spectrometer analysis. The method is currently listed as a screening method.

This review will focus on a number of important concerns raised when one compares solvent extraction versus thermal desorption methods, as well as the appropriateness of thermal desorption being limited to a screening method. Important environmental and occupational safety and health concerns are raised in the use of solvent extraction methods, which will be considered. In addition, the review assesses the historic precedent favoring solvent extraction and said precedent's accuracy in light of thermal desorption instrumentation advancements over the course of the last twenty years.

3. Background

3.1. Environmental Ramifications and Physical Hazards of Solvent Extraction

The hazards associated with solvents and solvent disposal have been well documented. While CS_2 is not persistent in water and soil and dissipates quickly due to the high vapor

pressure of the compound (352.6 mm Hg at 25 °C) once in the atmosphere, photochemical smog is generated via a reaction with other volatile organic compounds in the air matrix, such as carbonyl sulfide and sulfur dioxide. The persistence in water is limited with an approximate 2 day half-life (National Pollutant Inventory, 2014).

In terms of toxicity to animals, acute and chronic toxic effects are noted with particularly deleterious effects on aquatic life. In the case of acute exposures, death of animals (LD50: = 1200 mg/kg (Rat), birds, fish (LC50: = 4 mg/L, 96h static (*Poecilia reticulata*)), and plants (EC50: = 21 mg/L, 96h (*Chlorella pyrenoidosa*)) may occur (Fisher Scientific, 2016). Due to the fact that exposure effects may be delayed, this can be a particular hazard to offspring (National Pollutant Inventory, 2014). In terms of chronic effects, reduced lifespan, embryotoxicity, and fetotoxicity in animal studies have been shown (Kushwaha, 2015).

Physical hazards associated with the use of CS_2 include its flammability and explosive potential. As a result, adequate ventilation must be assured. One of the primary controls used is closed system ventilation. In addition, reactions of CS_2 can occur with air, alkali metals, aluminum, azides, many oxidants, and phenyl copper-triphenylphosphine complexes (ATSDR, 2013) so the ability to maintain the atmospheric integrity in storage and work areas is imperative to preventing resultant violent and/or explosive reactions that might occur through lack of proper ventilation. This also indicates a requirement to avoid friction and shock and to ensure electrostatic charges do not occur (CDC NIOSH, 2014).

A review of the OSHA's "accident search" site lists multiple incidents related to use of CS_2. Of note were two events caused by carbon disulfide within a period of 5 months of one another in 1987. On July 23, 1987 at the Research Triangle Institute, an employee was using a separatory funnel to purify carbon disulfide when the chemical exploded, causing a fire. Seven

employees were injured, 6 due to asphyxia from smoke, while the employee performing the separation suffered burns. In February of that same year, at Teepak, Inc., a semi-continuous monitoring device was to be installed to check carbon disulfide levels, but was not yet operational. It is believed that the CS_2 vapor buildup in one of the tanks of the process machines was ignited by a heat exchanger at the tank. This resulted in a fire and explosion causing injury to 6 employees. Thankfully, there were no fatalities. Unfortunately, in a 2006 explosion at Ops Contracting Services LLC, a fatality resulted from a worker's attempt to clean sludge from a tank containing residual CS_2. Burns and gas inhalation were thought to be the cause of death 6 days later when the worker perished (OSHA, 2017).

3.2. Human Health Hazards

The more conservative occupational exposure limits, Recommended Exposure Limits set by NIOSH and Threshold Limit values, set by the American Conference of Governmental Industrial Hygienists, list a NIOSH 10 hour and ACGIH 8 hour TWA of 1 ppm (3 mg/m^3) (OSHA, 2017). NIOSH goes on to also list a 10 ppm (30mg/m^3) STEL [skin] with an IDLH of 500 ppm. ACGIH also lists a 0.5 mg/g creatinine Biological Exposure Indices (BEI) with the determinant being 2-Thioxothiazolidine- 4-carboxylic acid (TTCA) in urine (OSHA, 2015). Even the less stringent OSHA permissible exposure limit is set at a 20 ppm TWA; 30 ppm Ceiling for 30 min; and 100 ppm Peak. The primary exposure route is inhalation, but dermal and ingestion secondary exposure routes are also noted (CDC NIOSH, 2014).

Toxicological evidence has indicated that one of the primary concerns of CS_2 exposure is developmental risks resulting from fetal exposure. This in conjunction with risk for fetal reabsorption make avoiding exposure of pregnant women vital. Aside from fetotoxicity, the

health effects ascribed to acute exposures are many and varied. ATSDR (2014) reports additional acute health effects including:

> Central nervous system (CNS) related issues such as nausea, dizziness, headache, delusions, hallucinations, delirium, mania, psychosis, blurred vision, convulsions, and coma…respiratory tract irritation… ocular manifestation such as corneal burns and conjunctivitis; dermal irritation ranging from pain, redness, and blisters of the mucosa to more advanced second and third degree burns with higher exposures; cardiovascular (angina); and gastric (nausea and abdominal pain) issues.

In chronic exposures, carcinogenicity has not been established, but action as a genotoxin and reprotoxicant are well documented. Not only can fetal development be affected, additionally CS_2 can cause menstrual abnormalities in female subjects while male subjects experience changes in spermatogenesis stemming from testicular damage and decreased libido (ATSDR, 2014). Similar central nervous system and peripheral nervous system issues result with chronic and acute exposures, and can cause permanent damage. The cardiovascular abnormalities manifest in electrocardiogram (ECG) readings and atherosclerosis. Systemic issues are far reaching with involvement of liver, gastrointestinal, kidney, blood and optic pathogenesis also reported (ATSDR, 2014).

There seems to be a dearth of information on the risks of chronic exposure directly relating to laboratory professionals and the type of low dose, chronic exposures they might experience over a lifetime of lab work. That being said, Ruijten et al (1990) offered work that provided some parallels to what might be seen as a result of lab work's chronic, low dose exposures. A group of workers in a viscose rayon plant with chronic exposures (mean 20 yrs.),

even below the current 10 ppm REL, showed a decrease in conduction velocity of slow motor fibers, indicative of CS_2 neuropathy (Ruijten, 1990). Chronic low dose exposures over a period of only 2 or 3 years have already shown deleterious effect on reproductive function. One study noted that in a three year period, exposure to 9.63 ppm levels resulted in depressed blood progesterone levels, increased estriol, and irregular menstruation in women. In men, 12.84 to 25.69 ppm exposures resulted in Asthenospermia, hypospermia, and teratospermia in just two years (World Health Organization, 2000).

3.3. Common Exposure Groups

Carbon disulfide is commonly applied in industrial processes, the manufacture of viscose rayon fibers being the most conspicuous. Other frequent areas of use include as a solvent, in production, as a fumigant, and insecticide. In coal and oil production, carbon disulfide is often seen as an emitted byproduct (State of California, n.d.). Workers performing these tasks require monitoring and appropriate control measures to be in place to ensure their safety throughout the course of their job.

As listed in the above examples of CS_2 usage, Carbon disulfide is often used as a solvent in organic extraction techniques. Chemists must be made aware of the necessary control measures to prevent exposure. While ventilation systems such as fume hoods are often used to keep levels under OELs, PPE is also required. PPE, however, is the lowest in the hierarchy of controls that should be employed in mitigating exposure, having no direct effect on the chemical in use or its concentration. The NIOSH methods for assessment of VOCs and SVOCs using carbon disulfide extraction of coconut charcoal tubes, ironically, put the very health and safety professionals trying to prevent exposures at risk of potential exposure themselves.

3.4. Historical Use of GC/FID and GC/MS

Carbon disulfide solvent extraction was historically used with GC/FID because the solvent was nearly invisible to the detector. This is a destructive technique of analysis, and once the sample was run, said sample was consumed during ionization by the FID. That being said, it was widely considered preferable as the extracted solvent could then be reprocessed if needed, meaning this was not a "one-shot" technology.

In years to follow, with advancement in GC/MS, the efficacy of this hyphenated instrumental set-up has been called into question for some applications. In the spring of 2001, in a presentation by Actlabs to the National Centre for Forensic Science and the International Institute for Forensic Sciences (Sutherland & Almirall, 2001), a review of ASTM E1387-01; *Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography*, cited the insufficiency of GC/FID methods for the analysis of ignitable liquids. Not only was there a high risk of false negative results, the data were indefensible for all but the simplest of profiles. The ASTM 2001 Committee E30 Chairman agreed that the technique raised concerns, with Lentini (2001) stating:

> A calculation of error rates among over 200 laboratories participating in the last three CTS (Round Robin) tests revealed that users of E-1618 (GC/MS) had an error rate roughly half that of users of E-1387 (GC/FID). As a consequence, (ASTM committee) E30 is considering the withdrawal of E-1387.

GC/FID was subsequently withdrawn as of 2010. The E-1618 remains an active standard for the complex identification of ignitable liquids. Even the standing solvent extraction method to identify ignitable liquid residues in fire debris (ASTM, 2010) uses GC/MS. A very effective

method in the case of samples where low concentrations of the ignitable residues are present is ASTM E-1412, *Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Activated Charcoal*. This uses thermal desorption tubes to take an aliquot of headspace sample for pre-concentration and analyzes with a GC/MS backend (ASTM, 2016).

Without a doubt, FID has good sensitivity (10^7) and linearity, as well as low relative standard deviations (RSDs). It has been used with great success for applications involving *n*-alkanes. One major benefit of FID is that the initial cost of the detector is less than MS. Although, when one considers cost of solvent use and disposal as well as ventilation costs, it would seem FID and MS are on par. The benefits mentioned support FID still often being used and written into standard methods. In a recent evaluation study for Photochemical Assessment Monitoring Stations, eight different vendors used various hyphenated instrumental setups to determine the most effective for study of ozone precursors (Cavender, 2014). The two most highly rated, with many rating factors including precision and bias, used GC/MS and GC/FID/Photoionization detector (PID). A joining thread between them was the use of an online monitoring system using Thermal Desorption/pre-concentration technology as the sample introduction method.

As FID is essentially a "carbon counter" it is invaluable for hydrocarbons in that it breaks the C-H bonds to form ions (Ettre, 2008). It is this very same advantage that explains why CS_2 is nearly invisible in the context of GC/FID analysis. Unfortunately, this also translates into far less usefulness for other functional groups, such as halogenated groups, those with N_2, etc. as the sensitivity is effected by the lack of burn. Another primary benefit of mass spectrometry that

cannot be understated is the ability to determine unknown compounds via library search e.g. NIST library, whereas FID requires foreknowledge of compound to be analyzed.

MS detectors, more specifically the most commonly used quadrupole mass spectrometer, have the ability to quantitate regardless of the element, albeit with slightly diminished linear range (10^5). Sensitivity of the total ion chromatogram (TIC) is equivalent to that of FID, and even greater still when run in SIM (selected-ion monitoring) mode (Shimadzu, 2017). In additional work, Haddad and MacMurphey (1997) showed that there was no statistically significant difference in total petroleum hydrocarbon (TPH) values quantified using GC/MS and GC/FID methods, supporting use of GC/MS methods for offering quantitation of all varieties of organic compound classes, including hydrocarbons.

3.5. Solvent Extraction

Solvent extraction allows for a compound in a gas to then be transferred to a solid (sorbent, CCT, etc.), and then from that solid to then be extracted into a liquid (solvent). In the methods discussed, the compounds are absorbed onto CCT, and subsequently extracted using a solvent in which the compounds will be soluble, in this case CS_2.

The use of carbon disulfide in solvent extraction with FID has additional limitations even with the low detector response that was anticipated. The repeatability that is a prominent boon to FID use is lost in the variability generated by use of solvent extraction. In the prior section, the discussion of solvent extraction's favor based on the ability to maintain a portion of the extracted sample for further evaluation is frankly unwarranted. This point of logic has since been called into question due to the variable results seen due to the evaporation of CS_2 from sample, as well as absorption of the sample onto the GC septa (Woolfenden & Poole, 2012).

Other issues of solvent extraction, particularly in the context of use with GC/MS though not relegated to said detector, are solvent impurities and baseline irregularities of the chromatogram that interfere with reproducible data, and even can mask compounds of interest in solvent fronts (Woolfenden & Poole, 2012). One of the most disadvantageous issues that may be raised with solvent extraction is the severe reduction it causes in method sensitivity and the ability to see low concentrations. The limits of detection (LODs) typically start at a 0.1 to 1 ppm range. This is in part due to lessened desorption efficiency seen in CS_2 extraction methods, where it is not unusual to see 75% efficiencies as standard (ISO16200, 2014).

3.6. Thermal Desorption

Thermal desorption takes advantage of the same theory one sees used in gas chromatography. In essence, the thermal desorption tube acts as a packed column, capturing compounds based on their volatility range. Then, when a heating ramp is applied with carrier gas flow through the tube, the compounds are released from the sorbent to be analyzed in their gaseous form through the remaining GC and detector steps. In this instrumental technology's infancy, the "one shot" threat that pushed favor of solvent extraction methods was accurate; once a tube was run through the system, the sample no longer remained. This is no longer the case; thermal desorption has come a long way since the "Coker cooker" of the 1970s (Woolfenden & Poole, 2012).

Once a tube is sampled, not only can a split be applied for high concentration samples to avoid overload of the detector, additionally, that split effluent can be quantitatively recollected onto a clean tube and re-run at various alternative split ratios or stored for method validation. In situations where low concentrations are encountered, the TD instrument can be run in splitless mode to gain the most sensitivity from the pre-concentration technique. Where solvent extraction

is diluting the sample and then taking a small amount of that diluted eluent, TD performs the opposite function, as illustrated in Figure 1:

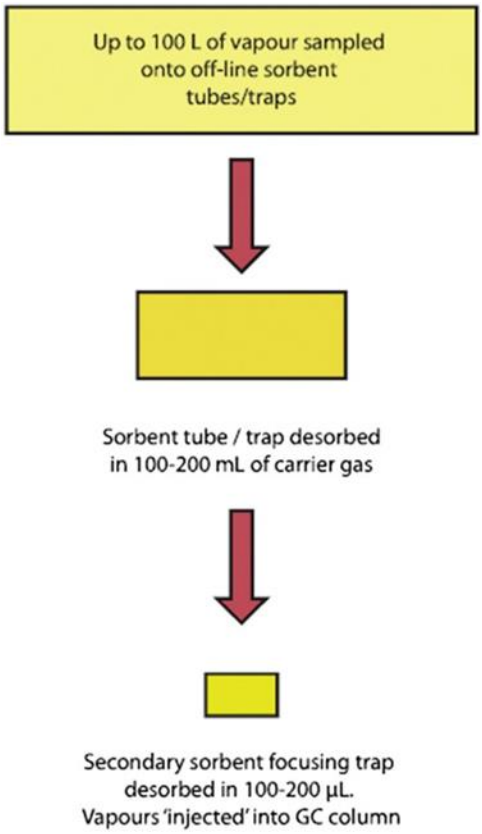

Figure 1. Thermal desorption pre-concentration of multi-stage units.[1]

This particular concentrating effect is the result of a number of factors and is related to the improved desorption efficiency seen. By its nature, TD is a dynamic process with the flow of carrier gas removing compounds from the tube as it heats, transferring them onto a focusing trap for the secondary stage of the two step desorption process. This is not the case of the static solvent extraction processes, which lead to partitioning between sorbent, solvent, and vapor phases (Woolfenden & Poole, 2012).

[1] Source: Courtesy of and use granted by Elizabeth Woolfenden, 2016

Another effect of the sensitivity gains in pre-concentration via TD is the ability to take far lower sample volumes than are required for solvent extraction. Ramírez, Cuadras, Rovira, Borrull, and Marcé (2010) reported the requirement for 720 L sample volumes for solvent extraction methods in order to achieve the same LODs as a 2.64 L sample volumes for the thermal desorption method on all of the 90 compounds assessed.

While there are a number of thermal desorption units available on the market, the following explanation is specific to the engineering design of Markes International, Ltd's thermal desorption units. To better understand the process by which two-stage desorption and recollection take place, the following Figures 2 and 3 are utilized:

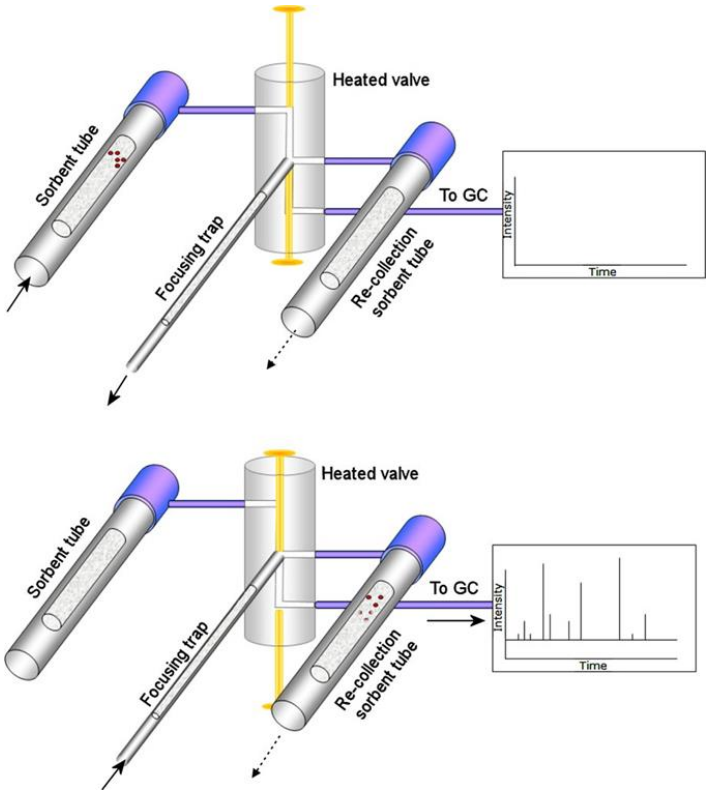

Figure 2. Quantitative recollection of thermal desorption tube split effluent[2]

[2] Source: Courtesy of and use granted by Woolfenden, 2016

Note that the split can be recollected at both points in the two-stage desorption; split from tube to trap and again when split from trap to GC column. The ability to split at two different times in the desorption process allow for 125,000:1 split. While it is not usual that one would require such a high split ratio, this ability to do high splits and splitless injection permit analysis of varied concentration ranges from percent to sub-part per trillion (ppt).

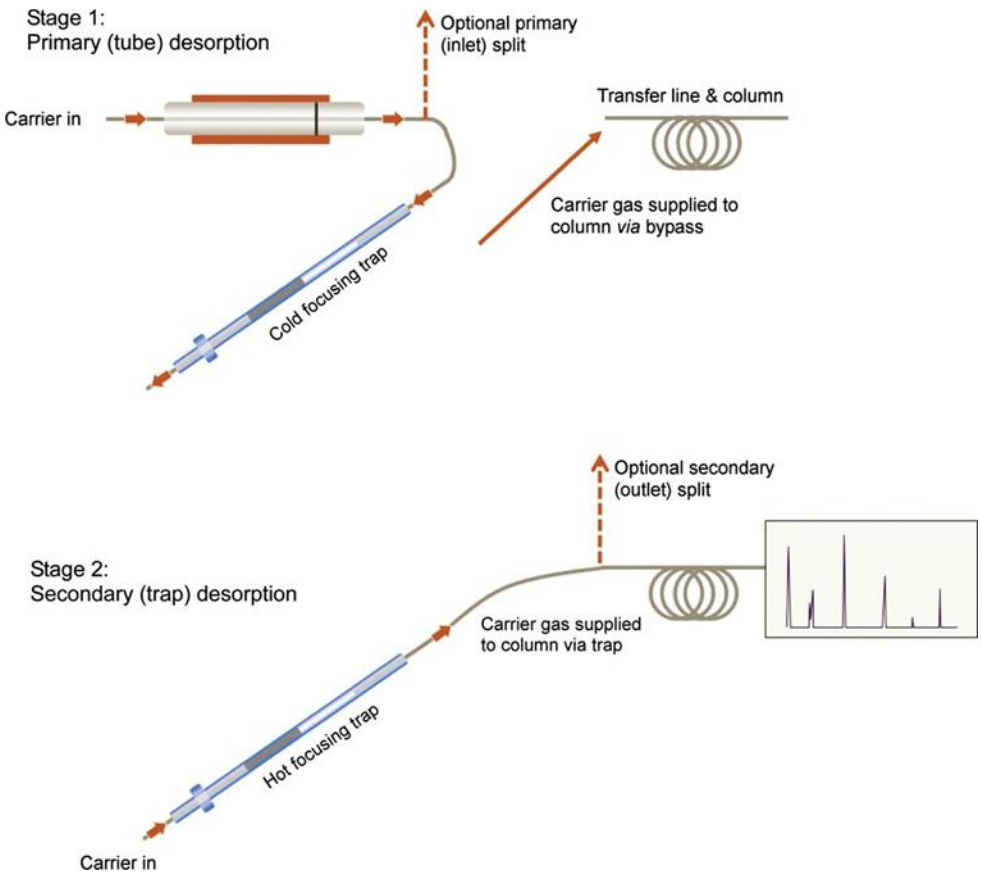

Figure 3. Illustration of two-stage thermal desorption.[3]

The thermal desorption tube onto which the sample has been collected is desorbed using a carrier gas, most commonly helium. The carrier gas runs through the tube during the designated heating period, defined by type of compounds to be assessed, as well as the sorbents

[3] Source: Courtesy of and use granted by Woolfenden, 2016

chosen onto which the sample has been collected. These are then recollected and concentrated onto the focusing trap.

The focusing trap is also sometimes referred to as a “cold trap” although this is somewhat a misnomer as many applications only require ambient temperatures to capture compounds on the trap. In instances of highly volatile compounds, one would then see sub-ambient temperature use. Once the compounds are on the trap, it is then heated at 100°C/sec to form a plug at the head of the GC column. It is this two-stage process that allows for sharp chromatographic peaks. If single-stage desorption is used, one sees broad peaks occurring (Figure 4).

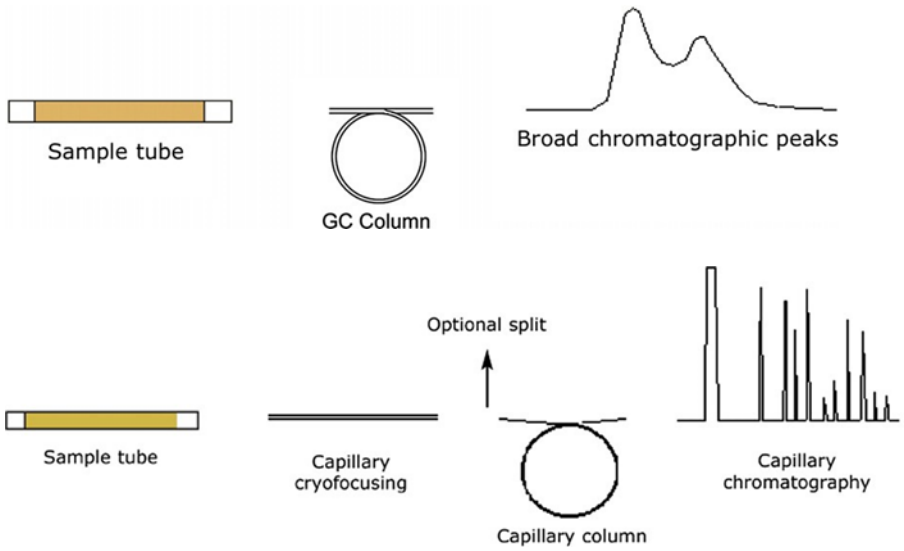

Figure 4. Illustration of chromatography with (top) single-stage desorption units, and (bottom) two-stage desorption units.[4]

This technique allows for desorption efficiencies in the range of 95% up to 100% as standard.

[4] Source: Courtesy of and use granted by Woolfenden, 2016

Another interesting aspect of thermal desorption is the ability to selectively reduce matrix interferences. One prime example is dry purging of a tube prior to analytical run to reduce water or solvent. The caveat being that the solvent or water must have a volatility different enough from the compound of interest as not to risk removal of said compound. Additionally, TD methods allow for use of multiple sorbent beds, some of which are hydrophobic, such as porous polymers like Tenax TA. By using these in conjunction with stronger sorbents also inline, there is the dual effect of better water management via lesser mass of the hydrophilic bed, and thus less water mass retention, as well as extended volatility range that may be captured on tube (Woolfenden, 2010a).

The extension of the range of compounds that may be captured onto tube is primarily a product of two functions: a system that can backflush with carrier gas in the opposite direction in which the sample was taken, and the use of suitable sorbents for collection of sample. The TD tube and trap both have strong to weak sorbents in the direction of sampling, so heavier SVOC compounds are retained on the weaker sorbents while the VOCs continue to and are retained by the stronger sorbents (Woolfenden, 2010b). It is in this way that loss of compounds and permanent contamination of the strong sorbent are avoided. When the carrier gas is then backflushed through the tube and then trap, the compounds are released in the opposite direction from which they were sampled. One of the better known instances of extended volatility range using multi-bed sorbent tubes is the EPA TO-17 method. By using a porous polymer, graphitized carbon black, and carbonized molecular sieve 3-bed TD tube, the full range of volatility of all compounds required in the method are able to be quantitatively retained, as seen in the chromatogram in Figure 5.

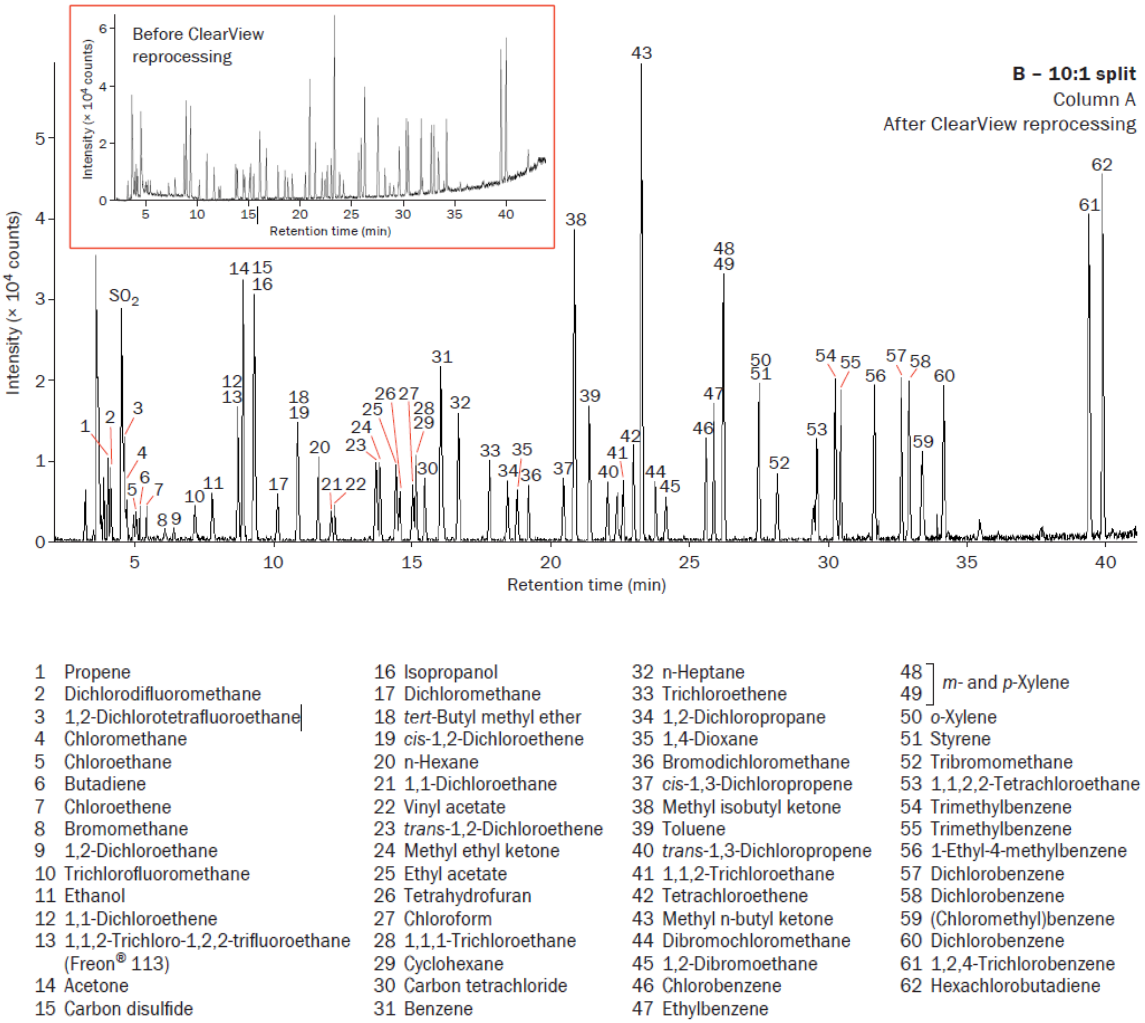

Figure 5. Chromatogram of EPA TO-17 performed using a multi-bed sorbent tube, using a sample equivalent to 1 L of a 1 ppb standard on a Markes Unity thermal desorption unit and subsequently having undergone Post-run data processing with ClearView dynamic baseline compensation software.[5]

3.7. Green Chemistry Perspective

Thermal desorption tubes can be used in excess of 100 times or more, where CCT tubes are destroyed in the sample preparation process. TD tubes, at the end of their sorbent life, can also then be repacked and used again. The move toward sustainability, reuse, and greener living is

[5] Source: Courtesy of and use granted by Markes International, Application Note 086 *Monitoring 'air toxics' in ambient air using sorbent tubes by automated, cryogen-free thermal desorption in accordance with US EPA Method TO-17*, www.markes.com

seen advancing not just as a cultural norm, but also in the science community. In the case of green chemistry, an early definition was given Anastas and Warner (1998) that outlined 12 principles of green chemistry, listed verbatim as follows:

1. Prevention - It is better to prevent waste than to treat or clean up waste after it has been created.
2. Atom Economy - Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less Hazardous Chemical Syntheses - Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Designing Safer Chemicals- Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. Safer Solvents and Auxiliaries - The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Design for Energy Efficiency - Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. Use of Renewable Feedstocks - A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives - Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. Catalysis - Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Design for Degradation - Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. Real-time analysis for Pollution Prevention - Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Inherently Safer Chemistry for Accident Prevention - Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

In relation to thermal desorption, it meets a number of these criteria. It is inherently safer (#12), prevents waste being formed from solvent (#1), by eliminating the need for their use (#5). This is not the case of CS_2 solvent extraction methods, which do not meet any of the qualifications on the list for green chemistry.

3.8. Additional Sample Introduction Methods

Thermal desorption in the context of this paper deals mainly with use of thermal desorption tubes as the sampling media and subsequent sample introduction method into the

hyphenated analytical system. While it is beyond the scope of this work to provide in-depth analysis of the various applications that may also be performed using thermal desorption, it must be noted that this versatile technique offers a variety of sample introduction methods that may then take advantage of the two-stage pre-concentrating capability, offering up to 10^6 sensitivity gains (Woolfenden, 2010b).

One common method is the collection of a volatile sample into canisters or tedlar bags, most notably EPA TO-15. Using a TD canister accessory, one can then concentrate this sample onto the focusing trap. Another popular introduction method is via on-line monitoring system (Markes Ltd., Unity-xr,/ Airserver-xr) for very volatile compounds that are, in fact, so volatile as to require immediate extraction from the air and onto trap and cannot be retained on tube. Ozone precursors and greenhouse gases are prime examples of this application of thermal desorption technology. In the chemical weapons arena, one would want to have continuous near-real time monitoring of the air. Utilizing a dual trap system, a near real time measurement can be performed where one sample is trap loaded as the other is being run, and then these processes reverse to provide full coverage (Markes Ltd., TT24-7-xr). With a large variety of accessories and sampling equipment, thermal desorption exceeds just the primary tube running capability associated with the technique.

4. Methodology Comparison

There are already standing methods that are well established for CS_2 solvent extraction of coconut charcoal as well as thermal desorption methods. A comparison of these two methodologies can be made by reviewing existing standard methods. These methods show the utility and the quality of the result of each methodology in terms of limits of detection and concentration range.

NIOSH methods for solvent extraction are used, where-as in the case of thermal desorption, the breadth of existing knowledge is more greatly encompassed in using additional, well established, and more recent methods for illustrative purposes. There are a number of relevant methods that illustrate the efficacy of pumped sampling and diffusive methods that enable the collection of VOCs onto thermal desorption tube. While many are for environmental applications, the fundamental principles remain the same throughout.

Initial research of NIOSH methods identified a number of compounds that had shared availability of both TD/GC-MS and CS2/CCT/GC-FID methods. This more limited data set was then compared to validated methods from other enforcement and recommending bodies, such as EPA, Health and Safety Executive (HSE), and the International Organization for Standardization (ISO). In cases where data on the compound did not exist within the methods cited, outside studies and application work were sought to verify compound data.

This limited list shows only a small portion of the compounds that have been validated by these bodies, and even as part of the NIOSH methods themselves. For example, as mentioned prior, the list of solvents used for extraction are quite varied. In many of these in the organic compound family, they can all be run using thermal desorption sample introduction technologies rather than solvent extraction. A rule of thumb for thermal desorption is that if a standing GC method for the compound exists, it will be compatible. The different sample introduction methods allow for assessment of compounds with carbons *n*-C_2 and freons, all the way up to *n*-$C_{40\text{-}44}$ and polycyclic aromatic hydrocarbons (PAHs) (Woolfenden & Poole, 2012).

In Appendix B, one can see an application note compiled by Markes International showing an extensive list of relevant validations and compounds of interest. Note that many of the same compounds can also be found on the NIOSH 2549 method as well. The list of

additional compounds that are germane in TD use are wide and varied, far reaching beyond even the scope of these documents. However, the focus on standing NIOSH methods that have comparable compounds analyzed with TD methods is again chosen to show the differences in the efficacy of these methods based on analytical parameters.

In Table 1, for reference a comparison is made of volumes and flow rates listed in the cited NIOSH methods. Note that the table shows the compounds of interest compared in the NIOSH methods, as well as being illustrative of the flow rates that were considered apropos to TD tube sampling at the time of the 2549 Method's inception. In cases where the compound was listed on the method but not studied, no flow rate has been listed.

Table 1 . Comparison of NIOSH TD/GC-MS and CS2 /CCT/GC-FID method sampling volumes and flow rates.

Chemical	Method No. TD/GC-MS	Method No. CS2/CCT/GC-FID	Vol. (L) min max TD/GC-MS	Flow Rate TD/GC-MS (L/min)	Vol. (L) min max CS2/CCT/GC-FID	Flow rate CS2/CCT/GC-FID (L/Min)
1,1,1 -Trichloroethane	2549	1003	1 - 6	0.01 - 0.05	0.1 - 8	0.01 - 0.2
1,1,2 -Trichloro- 1,2,2 -trifluoroethane	2549	1020	1 - 6	0.01 - 0.05	0.1 - 3	0.01 - 0.05
Acetone	2549	1300	1 - 6	0.01 - 0.05	0.5 - 3	0.01 - 0.2
Benzene	2549	1501	1 - 6	0.01 - 0.05	5 - 30	0.01 - 0.2
Cyclohexanone	2549	1300	1 - 6	0.01 - 0.05	1 - 10	0.01 - 0.2
Dichloromethane	2549	1005	1 - 6	0.01 - 0.05	0.5 - 2.5	0.01 - 0.2
Ethyl acetate	2549	1457	1 - 6	0.01 - 0.05	0.1 - 10	0.01 - 0.2
Limonene	2549	1552	1 - 6	0.01 - 0.05	2 - 30	0.01 - 0.2
Methyl isobutyl ketone	2549	1300	1 - 6	0.01 - 0.05	1 - 10	0.01 - 0.2
n-Decane	2549	1500	1 - 6	0.01 - 0.05		
n-Heptane	2549	1500	1 - 6	0.01 - 0.05		
n-Hexane	2549	1500	1 - 6	0.01 - 0.05	4 - 4	0.01 - 0.2
n-Octane	2549	1500	1 - 6	0.01 - 0.05	4 - 4	0.01 - 0.2
n-Pentane	2549	1500	1 - 6	0.01 - 0.05	4 - 4	0.01 - 0.2
Pinene	2549	1552	1 - 6	0.01 - 0.05	2 - 30	0.01 - 0.2
Toluene	2549	1501	1 - 6	0.01 - 0.05	1 - 8	0.01 - 0.2
Xylene	2549	1501	1 - 6	0.01 - 0.05	2 - 23	0.01 - 0.2

4.1. Flow Rates

Much has changed in the twenty years when the NIOSH 2549 Method was last revised. There is a far greater breadth of knowledge on thermal desorption techniques and significant engineering advances that can be illustrated from the above Table 1. For instance, the flow rates listed for the method range from 0.01 to 0.05 L/min. It has been found for sampling on TD tubes, as reflected in other methods such as EPA TO-17, that a flow rate of 0.05 to 0.2 L/min are most conducive to sorbent/sorbate interaction for the majority of VOCs and SVOCs encountered (Woolfenden & McClenny, 1999).

4.2. Low Flow Rate and Volatile Trace Level Sampling

In some cases lower flow rates may be required for time weighted averages or there may be a need to collect trace levels of volatile compounds. When this is the case, there is a chance that back diffusion may occur. Again, historically this would have been problematic. There is a solution in using tubes with anti-diffusive technology (Woolfenden & Cole, 1999). The SafeLok (Figure 6) is an anti-diffusive spiral path inserted into both ends of a sample tube. When carrier gas is applied with heating, compounds that were sampled onto the tube easily come off. In the interim, while sampling at low flow rates for very volatile samples, during storage, and while placing the tube in the instrument, there is no ingress or egress of compounds onto the tube. Of course, these cannot be used with diffusive sampling methods or direct desorption of materials because the SafeLok insert is not removable.

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Figure 6. Schematic of SafeLok tube packed with two sorbents and a standard thermal desorption tube with and without SafeLok insert. [6]

The volumes that should be sampled are very much contingent on the sorbent(s) being used and the breakthrough volume of the compound on that particular sorbent(s) (Woolfenden, 2010a). A standard 1.0 to 6.0 L is no longer the only data available. In fact, a number of the compounds seen in Table 1 can be seen in other methods as well, with varying volumes required. An example would be 1,1,1-trichloroethane. If one were to use a strictly a graphitized sorbent black, such as Carbograph 2 TD, there is no safe sampling volume at which the compound would be retained on sorbent. On the other hand Tenax TA, a porous polymer, lists a breakthrough volume at 2.2. L and a safe sampling volume of 1.1 L (Appendix C).

4.3. Measurement Range

Notably absent from Table 2, below, is a listed measurement range for thermal desorption. Due to the ability to run high splits or split-less methods on the engineering of the modern TD system, the range can be from part per trillion (ppt) to percent level concentrations. The split being integral to range for TD-GC/MS methods is further supported by ISO 16017-1:2003 and ISO 16017-1:2003. It defines the upper limit of the range as set not only by

[6] Source: Markes International Consumables Catalogue, 2013-14, p. 6.

instrument capacity for split, but also sorptive capacity and linear dynamic range of the gas chromatograph column and detector chosen. The lower limit of the useful range was defined in terms of detector signal/noise ratios and sorbent artefacts that may interfere with blank levels.

For reference, NIOSH (1998) describes the measurement range for solvent extraction defined as:

> Range of substance, in mass per sample, from the LOQ (or from 10 times the LOD, if LOQ is not known) to an upper limit characteristic of the analytical method, e.g., the limit of linearity or the mass at which precision of the method starts to become worse than $\check{S}_r = 0.1$.

The point of interest in the ranges is principally that the ranges tend to be higher, in keeping with the higher LODs of the solvent extraction methods. This supports the advantage of thermal desorption in terms of sensitivity of the technique.

Table 2. Comparison of NIOSH TD/GC-MS and CS2 /CCT/GC-FID method LODs and Measurement Ranges

Chemical	Method No. TD/GC-MS	Method estimated TD LOD (in ng)	Method No. CS2/CCT/GC-FID	Method estimated CS2 LOD (in ng)	CS2 Measurement Range
1,1,1 -Trichloroethane	2549	100 ng per tube or less	1003	1000 ng/sample	18 to 1450 ppm @ max sample volume 8L
1,1,2 -Trichloro- 1,2,2 -trifluoroethane	2549	100 ng per tube or less	1020	5000 ng/sample	0.015 to 14 mg/sample
Acetone	2549	100 ng per tube or less	1300	20,000 ng/sample	2.4 to 14.2 mg/sample
Benzene	2549	100 ng per tube or less	1501	500 ng/sample	0.004-0.35mg/sample
Cyclohexanone	2549	100 ng per tube or less	1300	20,000 ng/sample	3.8 to 18.0 mg/sample
Dichloromethane	2549	100 ng per tube or less	1005	400 ng/sample	1.4 to 2600 µg /sample
Ethyl acetate	2549	100 ng per tube or less	1457	500 ng/sample	1.5 to 1,000 µg /sample
Limonene	2549	100 ng per tube or less	1552	400 ng/sample	2 to 840 µg/sample
Methyl isobutyl ketone	2549	100 ng per tube or less	1300	20,000 ng/sample	0.06 to 10 mg /sample
n-Decane	2549	100 ng per tube or less	1500	60 ng/sample	2 - 584 ug/sample
n-Heptane	2549	100 ng per tube or less	1500	60 ng/sample	2 - 16300 ug/sample
n-Hexane	2549	100 ng per tube or less	1500	400 ng/sample	10 -14500 ug/sample
n-Octane	2549	100 ng per tube or less	1500	300 ng/sample	11 -18900 ug/sample
n-Pentane	2549	100 ng per tube or less	1500	600 ng/sample	19 - 1180 ug/sample
Pinene	2549	100 ng per tube or less	1552	400 ng/sample	2 to 840 µg/sample
Toluene	2549	100 ng per tube or less	1501	700 ng/sample	0.024-4.51 mg/sample
o-xylene	2549	100 ng per tube or less	1501	800 ng/sample	0.044-10.4 mg/sample
m-xylene	2549	100 ng per tube or less	1501	800 ng/sample	0.043-0.864 mg/sample
p-xylene	2549	100 ng per tube or less	1501	700 ng/sample	0.043-0.861 mg/sample

In Table 3, one can see how the analyte masses relate to atmospheric concentrations in this quick guide to analyte mass on thermal desorption tubes. Remember that mass on tube does not necessarily equate to mass on column, as there are two opportunities to split the desorption effluent. This facilitates the highest concentrations being spit to avoid overloading of the detector.

Table 2. Quick guide to analyte masses collected on a thermal desorption tube by pumped sampling of 10 L of air (at room temperature and pressure).[7]

Atmospheric concentration	Molar mass (g mol–1)	Molar mass (g mol–1)2	Molar mass (g mol–1)3	Molar mass (g mol–1)4	Molar mass (g mol–1)5
	50	75	100	150	200
1000 ppm	20 mg	30 mg	40 mg	60 mg	80 mg
10 ppm	200 µg	300 µg	400 µg	600 µg	800 µg
1 ppm	20 µg	30 µg	40 µg	60 µg	80 µg
10 ppb	200 ng	300 ng	400 ng	600 ng	800 ng
1 ppb	20 ng	30 ng	40 ng	60 ng	80 ng
100 ppt	2 ng	3 ng	4 ng	6 ng	8 ng

In order to determine the concentration from mass collected on TD tube in a more exact manner, the following equation may be used:

Equation 1. Mass collected on thermal desorption tube

$$\frac{Mass\ (g)}{Molar\ Mass\ (g\ mol-1)}\ x\ \frac{25\ L\ mol{-}1}{Volume\ pumped\ onto\ tube\ (L)} = concentration\ (as\ a\ fraction)$$

4.4. Sample Stability

Another item of note is the sample stability of collected sample in the referenced NIOSH methods. The solvent extraction methods allow for a 30 day time period for sample stability at 5°C. In the case of Method 2459, the sample stability is listed as compound dependent and tubes are to be stored at -10°C.

[7] Source: Courtesy of and use granted by Markes International, Ltd., Application Note 025, Calculating atmospheric concentrations from analyte masses retained on sorbent tubes.

In the case of thermal desorption tubes, it was found that benzene, toluene, and m-xylene on Tenax tubes had sample stability far exceeding that sample stability in the cited NIOSH solvent extraction methods. Stability studies revealed that with the use of brass compression caps with PTFE ferrules, there was no statistically relevant change in the compound stability over a period of 14 months (Vandendriessche & Griepink, 1989). The temperature ranges for holding tubes in storage were from 0 to -4°C, at ambient temperature, and at 40°C. It was noted that, even in the case of elevated temperatures, there were no systemic differences, and speculated that this would remain unchanged even over the course of several years (Vandendriessche & Griepink, 1989).

Multi-sorbent bed tubes can also be stored for long periods of time, akin to single bed tubes. In this case however, one would want to keep their tubes under refrigeration for periods of time exceeding 1 week (Harshman et al., 2016). This minimizes migration of low-volatility compounds onto the stronger sorbents, which can then become irreversibly adsorbed to the sorbent material.

In one of the most recent studies available, analysis of breath samples were performed using three temperatures: 37 °C, 21 °C, and 4 °C. While long term storage data for some of the compounds showed agreement, in many cases there were significant changes in abundance over the 31 d test period for 45 of the 74 compounds assessed. This translated to gain or loss of 1–2 standard deviations in abundance after the fourteen day mark. Previously studied compounds included on the examination of compound stability were generally in line with what was reported previously (Harshman et al., 2016). Eighteen of 74 had been assessed and compounds such as *n*-hexane, 4-methyl-2- pentanone and toluene were noted to have agreement for 4-week stability on Tenax TA [21]. Refrigeration of tubes containing isoprene, ethanol, limonene, toluene, and

N,N′-dimethylacetamide noted 2 week stability on Tenax GR (van der Schee et al., 2012), which was also in keeping with data generated in the this report (Harshman, et al., 2016).

This updated information certainly suggests that an evaluation of the sample stability be considered dependent on the compound itself and empirical results obtained to ensure the best possible data. Also this seems to indicate that while not always necessary, the storage of all tubes (single or multi-bed) in refrigeration helps to lessen incidence of positive or negative drift in standard deviation from the mean.

4.5. Humidity and Temperature Effects

It is a universally acknowledged fact that high humidity and temperatures may affect TD samples. One example of this would be in stack sampling, where a midget impinger is used prior to the sample tube in the sampling train to collect condensate that would otherwise affect the quantitative analysis of the VOCs. While stack gases are an extreme example of high percent relative humidity (% RH), generally for the majority of applications, the use of sorbent selection and dry purge techniques are sufficient to overcome this limitation.

High relative humidities are particularly difficult to control in the case of volatile C_2-C_5 aliphatic hydrocarbons, which generally require the use of hydrophilic carbonized molecular sieve sorbent media such as Carboxens. This in turn can lead to low collection efficiencies and loss of target analytes during the dry purge process (Ho et al., 2017). That being said, there is an argument for online monitoring methods that pull the sample directly onto the focusing trap for the very volatile compounds, which can use nafion dryers (for non-polar compounds), or a new technology, KORI-xr (for polar compounds), that allow for removal of moisture from sample without loss of target compounds. In this case thermal desorption is still an apropos solution, but the sample introduction method would not preferentially be tubes.

Conflicting results exist with regard to temperature effects on thermal desorption tube collection. In one of the more recent works, *The stability of Tenax TA thermal desorption tubes in simulated field conditions on the HAPSITE ER* (Harshman et al., 2015) extreme loading temperatures from 4 to 77°C did not affect the analytical reliability seen with Tenax TA tubes.

4.6. Comparison of Results Obtained with Solvent Extraction versus Thermal Desorption

In a study by Ramirez, Cuadras, Rovira, Borrull, and Marcé (2010), comparison of CS_2 extraction of coconut charcoal tubes and thermal desorption was described. In this study, 90 compounds were assessed using both methods. The compounds were those that would be found in typical industrial and urban air matrices (Ramírez et al., 2010).

The experimental set-up called for use of a two-bed thermal desorption tube, containing Carbograph 1 TD, a graphitized carbon black sorbent, and Tenax TA, a porous polymer. Both of these compounds are inherently hydrophobic (Guardia & Armenta, 2016). This helps with water management when sampling from humid matrices.

The overall conclusions reached showed the repetitivity, recovery, and detection and quantification limit of the thermal desorption methods were generally better than those of the solvent extraction methods (Ramirez, et al., 2010). Out of the 90 VOCs that were sampled, the solvent extraction method could only quantify 18 compounds, as compared to 50 for thermal desorption respectively. Of additional note was that thermal desorption methods required lesser sampling volumes, resulting in lesser sample times, and thus enabling one to see temporal variation. In the case of the solvent extraction samples, the requirement for larger sample volumes and sample times in turn could only show daily average compound data.

The results of another study by Kim, et al. (2016), comparison was made of use of solvent extraction with GC/MS to use of TD-GC/MS for quantification of phthalates in

polymers. In this study, it was found that the relative standard deviation (RSD) for solvent extraction was below 7.4% with recoveries of 78.3%–117.4%. TD-GC/MS compared favorably with average recoveries of 92–103% and low method detection limits (MDLs) at <30mg/kg with 9.0% RSD (Kim et al., 2016). The greater implication of this work was that these results suggest that the TD-GC/MS method could also be used for the international standard method for the quantification of phthalates in polymers.

The Kim, et al. (2016) study segues into what is perhaps one of the major points in the undertaking of this work; over the past 20 years the innovation in thermal desorption techniques continue to add more and more nationally and internationally recognized methods that TD complies with. It is not merely the 1996 NIOSH 2549 that represents the bulk of knowledge regarding the efficacy of this instrumentation and thermal desorption tube sampling techniques, but rather that work was the foundation upon which greater scientific gains continue to be applied for the analysis of a wide variety of volatile and semi-volatile compounds.

4.7. Compliance of Thermal Desorption in Additional Standard Methods

The NIOSH Method 2549 is listed as a screening method. This offers some insight wherein early limitations were ascribed to the method. The authors of the method, Grote and Ardith (2002) describe in a later work the utility of thermal desorption, while able to handle a broad spectrum of compound classes, as predominantly a first attempt in compound characterization. They list the limiting factor for use of thermal desorption as high exposures that make use impractical. The claim is that post identification quantification must be performed with other more conventional sorbent-solvent desorption methods. By 2002, although not well known and still in its infancy, the dawn of more advanced thermal desorption units with multiple split

options had already begun, which would lead to eventual removal of this barrier. Quantification is indeed now possible with high and low concentration exposures.

In 2017 there are far greater numbers of methods that use thermal desorption tubes, in active and diffusive sampling, than existed at the time of the NIOSH 2549 methods writing and inception. Not only does one see the adoption of these methods, it should be noted that the majority produce quantitative data. While use of thermal desorption tubes have become less niche and more popular in the common scientific lexicon, this objectively illustrates its capacity to be used as a quantitative method; not just for screening. The following Table 4 provides a list of some of the current methods utilizing TD tubes.

Table 3. Methods using thermal desorption tubes as sample introduction method[8]

Pumped Sampling Methods	Year published/ last revision	Title/Scope
NIOSH Method 2549	1996	Volatile Organic Compounds (Screening)
ISO 16017-1	2000	Indoor, ambient and workplace air -- Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography -- Part 1: Pumped sampling
ASTM D-6196	2015	Standard Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air
US EPA Method TO-17	1999	Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes
Chinese EPA Method HJ 644	2013	Volatile organic compounds - Ambient air Determination of volatile organic compounds Sorbent adsorption and thermal desorption / gas chromatography mass spectrometry HJ 644-2013
Chinese EPA Method HJ 734	2014	Volatile organic compounds - Stationary source emission: Determination of volatile organic compounds Sorbent adsorption and thermal desorption gas chromatography mass spectrometry method HJ 734-2014
EN 14662-1	2005	Ambient air quality. Standard method for measurement of benzene concentrations. Pumped sampling followed by thermal desorption and gas chromatography
CEN/TS 13649	2014	Stationary source emissions. Determination of the mass concentration of individual gaseous organic compounds. Sorptive sampling method followed by solvent extraction or thermal desorption
UK Environment Agency Meth	2014	Monitoring trace components in landfill gas: LFTGN 04
Diffusive Sampling Methods		
US EPA Method 325	2015	Method 325B—Volatile Organic Compounds from Fugitive and Area Sources
EN 14662-4	2005	Ambient Air Quality - Standard Method For Measurement Of Benzene Concentrations - Part 4: Diffusive Sampling Followed By Thermal Desorption And Gas Chromatography
ISO 16017-2	2003	Indoor, ambient and workplace air -- Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography -- Part 2: Diffusive sampling
ASTM 6196	2015	Standard Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air
US EPA Method TO-17	1999	Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes

[8] Courtesy of and use granted by Markes International, Ltd., Thermal Desorption Applications Guide: Environmental monitoring; A comprehensive guide to monitoring chemicals in the environment and the workplace

5. Conclusions and Suggestions for Future Work

The questions raised in this review have taken an in depth look at solvent extraction versus thermal desorption. The primary questions discussed were the appropriateness of thermal desorption being limited to a screening method, the importance of environmental and occupational safety and health concerns raised by solvent extraction methods, and if the historic precedent favoring solvent extraction remained accurate in the face of thermal desorption instrumentation advancements since the initial publishing of the NIOSH Volatile Organic Compound Screening Method 2549. It is clear from the data that thermal desorption should now be considered for quantitative analysis.

In reviewing updates to thermal desorption engineering, and thus capability, it is now a reliable quantitative method that can even be run at various split levels and split effluent can be recollected. As the technology has progressed, it has offered many different sample introduction options that have been written into methods for recommending and enforcement bodies. As changes in the regulatory climate continue and advancements in analytical capability in conjunction with toxicological and epidemiological data continue to shape OELs, it is imperative that methods be able to meet the requirements for lower and lower limits of quantitation and detection. It has been shown in evaluation of thermal desorption as compared to CS_2 solvent extraction that the sensitivity and range are much improved by thermal desorption methods.

The analytical advantages aside when comparing the CS2-GC/FID and TD-GC/MS, one also appreciates the environmental and occupational health ramifications of solvent use. Using less solvent in the lab or eliminating processes that necessitate its use are in keeping with green chemistry practices. There does seem to be an irony in that the very people charged with protecting worker health are exposed to unnecessary risk with use of CS_2. The hierarchy of

controls would dictate that the best protection for workers is the elimination of the risk. It serves the best interest of the public, workers, and the environment to eliminate or limit solvent use in general where possible; and in particular in the case of methods that could otherwise be accomplished using thermal desorption.

For future work, using the important foundational work of the NIOSH 2549 Screening Method, expansion of the data with to-date information sourced from other existing thermal desorption methods and empirical data should be undertaken. The limitations that consigned TD use to screening have been overcome with the march of technological advancement. In the twenty years since the method's inception, a great many other methods and studies have advanced the understanding of thermal desorption tube capabilities and limitations.

Thermal desorption offers reusable tubes, little to no solvent use is necessary, and one does not have to dispose of solvent or have the same ventilation concerns raised by solvent use. This assuages issues of environmental and health and safety ramifications that are raised by solvent use. The instrumentation has advanced in such a way as to offer quantitation and lower LODs than that of solvent extraction.

Thermal desorption is no longer the niche technology it once was. Armed with this information, a review of NIOSH Method 2549 with an eye toward generating methods for quantitation of compounds that are no longer reliant on higher risk solvent extraction methods seems advisable. While time and funding of such an undertaking may present its own set of challenges, when carbon disulfide-GC/FID versus thermal desorption-GC/MS methods are viewed through the lens of analytical proficiency and human and environmental health risk, it would seem more universal acceptance of a method that offers less risk and gains in sensitivity seems a winning proposition.

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Appendix A: NIOSH Method 2549

VOLATILE ORGANIC COMPOUNDS (SCREENING) 2549

FORMULA see Table 1 MW: see Table 1 CAS: see Table 1 RTECS: see Table 1

METHOD: 2549, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA:
NIOSH: varies with compound
ACGIH:

PROPERTIES: See Table 1

SYNONYMS: VOCs; See individual compounds in Table 1

SAMPLING

SAMPLER:	THERMAL DESORPTION TUBE (multi-bed sorbent tubes containing graphitized carbons and carbon molecular sieve sorbents [See Appendix])
FLOW RATE:	0.01 to 0.05 L/min
VOL-MIN:	1 L
-MAX:	6 L
SHIPMENT:	Ambient in storage containers
SAMPLE STABILITY:	Compound dependent (store @ -10 °C)
BLANKS:	1 to 3 per set

ACCURACY

RANGE STUDIED:	not applicable
BIAS:	not applicable
OVERALL PRECISION ($\hat{S}_{rT}$):	not applicable
ACCURACY:	not applicable

MEASUREMENT

TECHNIQUE:	THERMAL DESORPTION, GAS CHROMATOGRAPHY, MASS SPECTROMETRY
ANALYTE:	See Table 1
DESORPTION:	Thermal desorption
INJECTION VOLUME:	Defined by desorption split flows (See Appendix)
TEMPERATURE-DESORPTION:	300 °C for 10 min.
-DETECTOR (MS):	280 °C
-COLUMN:	35 °C for 4 min; 8 °C/min to 150 °C, 15 °C/min to 300 °C
CARRIER GAS:	Helium
COLUMN:	30 meter DB-1, 0.25-mm ID, 1.0-µm film, or equivalent
CALIBRATION:	Identification based on mass spectra interpretation and computerized library searches.
RANGE:	not applicable
ESTIMATED LOD:	100 ng per tube or less
PRECISION ($\hat{S}_r$):	not applicable

APPLICABILITY: This method has been used for the characterization of environments containing mixtures of volatile organic compounds (See Table 1). The sampling has been conducted using multi-bed thermal desorption tubes. The analysis procedure has been able to identify a wide range of organic compounds, based on operator expertise and library searching.

INTERFERENCES: Compounds which coelute on the chromatographic column may present an interference in the identification of each compound. By appropriate use of background subtraction, the mass spectrometrist may be able to obtain more representative spectra of each compound and provide a tentative identity (See Table 1).

OTHER METHODS: Other methods have been published for the determination of specific compounds in air by thermal desorption/gas chromatography [1-3]. One of the primary differences in these methods is the sorbents used in the thermal desorption tubes.

REAGENTS:

1. Air, dry
2. Helium, high purity
3. Organic compounds of interest for mass spectra verification (See Table 1).*
4. Solvents for preparing spiking solutions: carbon disulfide (low benzene chromatographic grade), methanol, etc.(99+% purity)

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Thermal sampling tube, ¼" s.s. tube, multi-bed sorbents capable of trapping organic compounds in the C_3-C_{16} range. Exact sampler configuration depends on thermal desorber system used. See Figure 1 for example.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible tubing.
3. Shipping containers for thermal desorber sampling tubes.
4. Instrumentation: thermal desorption system, focusing capability, desorption temperature appropriate to sorbents in tube (~300 °C), and interfaced directly to a GC-MS system.
5. Gas chromatograph with injector fitted with 1/4" column adapter, 1/4" Swagelok nuts and Teflon ferrules (or equivalent).
6. Syringes: 1-µL, 10-µL (liquid); 100-µL, 500-µL (gas tight)
7. Volumetric Flasks, 10-mL.
8. Gas bulb, 2 L

SPECIAL PRECAUTIONS: Some solvents are flammable and should be handled with caution in a fume hood. Precautions should be taken to avoid inhalation of the vapors from solvents as well. Skin contact should be avoided.

SAMPLING:

NOTE: Prior to field use, clean all thermal desorption tubes thoroughly by heating at or above the intended tube desorption temperature for 1-2 hours with carrier gas flowing at a rate of at least 50 mL/min. Always store tubes with long-term storage caps attached, or in containers that prevent contamination. Identify each tube uniquely with a permanent number on either the tube or tube container. Under no circumstances should tape or labels be applied directly to the thermal desorption tubes.

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the caps of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
   NOTE: With a multi-bed sorbent tube, it is extremely important to sample in the correct direction, from least to maximum strength sorbent.
3. For general screening, sample at 0.01 to 0.05 L/min for a maximum sample volume of 6 L. Replace caps immediately after sampling. Keep field blanks capped at all times. Tubes can act as diffusive samplers if left uncapped in a contaminated environment.
4. Collect a "humidity test" sample to determine if the thermal adsorption tubes have a high water background.
   NOTE: At higher sample volumes, additional analyte and water (from humidity) may be collected on the sampling tube. At sufficiently high levels of analyte or water in the sample, the mass spectrometer may malfunction during analysis resulting in loss of data for a given sample.
5. Collect a "control" sample. For indoor air samples this could be either an outside sample at the same location or an indoor sample taken in a non-complaint area.
6. Ship in sample storage containers at ambient temperature. Store at -10 °C.

SAMPLE PREPARATION:

7. Allow samples to equilibrate to room temperature prior to analysis. Remove each sampler from its storage container.

8. Analyze "humidity test" sampler first to determine if humidity was high during sampling (step 10).
9. If high humidity, dry purge the tubes with purified helium at 50 to 100 mL/min for a maximum of 3 L at ambient temperature prior to analysis. .
10. Place the sampler into the thermal desorber. Desorb in reverse direction to sampling flow.

CALIBRATION AND QUALITY CONTROL:

11. Tune the mass spectrometer according to manufacturer's directions to calibrate.
12. Make at least one blank run prior to analyzing any field samples to ensure that the TD-GC-MS system produces a clean chromatographic background. Also make a blank run after analysis of heavily concentrated samples to prevent any carryover in the system. If carryover is observed, make additional blank runs until the contamination is flushed from the thermal desorber system.
13. Maintain a log of thermal desorber tube use to record the number of times used and compounds found. If unexpected analytes are found in samples, the log can be checked to verify if the tube may have been exposed to these analytes during a previous sampling use.
14. Run spiked samples along with the screening samples to confirm the compounds of interest. To prepare spiked samples, use the procedure outlined in the Appendix .

MEASUREMENT:

15. See Appendix for conditions. MS scan range should cover the ions of interest, typically from 20 to 300 atomic mass units (amu). Mass spectra can either be identified by library searching or by manual interpretation (see Table 1). In all cases, library matches should also be checked for accurate identification and verified with standard spikes if necessary.

EVALUATION OF METHOD:

The method has been used for a number of field screening evaluations to detect volatile organic compounds. Estimate of the limit of detection for the method is based on the analysis of spiked samples for a number of different types of organic compounds. For the compounds studied, reliable mass spectra were collected at a level of 100 ng per compound or less. In situations where high levels of humidity may be present on the sample, some of the polar volatile compounds may not be efficiently collected on the internal trap of the thermal desorber. In these situations, purging of the samples with 3 L of helium at 100 mL/min removed the excess water and did not appreciably affect the recovery of the analytes on the sample.

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TABLE 1. COMMON VOLATILE ORGANIC COMPOUNDS WITH MASS SPECTRAL DATA

Compound /Synonyms	CAS# RTECS	Empirical Formula	MW[a]	BP[b] (°C)	VP[c] @ 25 °C mm Hg	kPa	Characteristic Ions, m/z
Aromatic Hydrocarbons							
Benzene /benzol	71-43-2 CY1400000	C_6H_6	78.11	80.1	95.2	12.7	78*
Xylene /dimethyl benzene	1330-20-7 ZE2100000	C_8H_{10}	106.7				91, 106*, 105
o-xylene				144.4	6.7	0.9	
m-xylene				139.1	8.4	1.1	
p-xylene				138.4	8.8	1.2	
Toluene /toluol	108-88-3 XS5250000	C_7H_8	92.14	110.6	28.4	3.8	91, 92*
Aliphatic Hydrocarbons							
n-Pentane	109-66-0 RZ9450000	C_5H_{12}	72.15	36.1	512.5	68.3	43, 72*, 57
n-Hexane /hexyl-hydride	110-54-3 MN9275000	C_6H_{14}	86.18	68.7	151.3	20.2	57, 43, 86*, 41
n-Heptane	142-82-5 MI7700000	C_7H_{16}	100.21	98.4	45.8	6.1	43, 71, 57, 100*,41
n-Octane	111-65-9 RG8400000	C_8H_{18}	114.23	125.7	14.0	1.9	43, 85, 114*, 57
n-Decane /decyl hydride	124-18-5 HD6500000	$C_{10}H_{22}$	142.29	174	1.4	0.2	43, 57, 71, 41, 142*
Ketones							
Acetone /2-propanone	67-64-1 AL3150000	C_3H_6O	58.08	56	266	35.5	43, 58*
2-Butanone /methyl ethyl ketone	78-93-3 EL6475000	C_4H_8O	72.11	79.6	100	13	43, 72*
Methyl isobutyl ketone /MIBK, hexone	108-10-1 SA9275000	$C_6H_{12}O$	100.16	117	15	2	43, 100*, 58
Cyclohexanone /cyclohexyl ketone	108-94-1 GW1050000	$C_6H_{10}O$	98.15	155	2	0.3	55, 42, 98*, 69
Alcohols							
Methanol /methyl alcohol	67-56-1 PC1400000	CH_3OH	32.04	64.5	115	15.3	31, 29, 32*
Ethanol /ethyl alcohol	64-17-5 KQ6300000	C_2H_5OH	46.07	78.5	42	5.6	31, 45, 46*
Isopropanol /1-methyl ethanol	67-63-0 NT8050000	C_3H_7OH	60.09	82.5	33	4.4	45, 59, 43
Butanol /butyl alcohol	71-36-3 EO1400000	C_4H_9OH	74.12	117	4.2	0.56	56, 31, 41, 43

Compound /Synonyms	CAS# RTECS	Empirical Formula	MW[a]	BP[b] (°C)	VP[c] @ 25 °C mm Hg	kPa	Characteristic Ions, m/z
Glycol Ethers							
Butyl cellosolve /2-butoxyethanol	111-76-2 KJ8575000	$C_6H_{14}O_2$	118.17	171	0.8	0.11	57, 41, 45, 75, 87
Diethylene glycol ethyl ether /Carbitol	111-90-0 KK8750000	$C_6H_{14}O_3$	134.17	202	0.08	0.01	45, 59, 72, 73, 75, 104
Phenolics							
Phenol /hydroxybenzene	108-95-2 SJ3325000	C_6H_5OH	94.11	182	47	0.35	94*, 65, 66, 39
Cresol	1319-77-3 GO5950000	C_7H_7OH	108.14				108*, 107, 77, 79
2-methylphenol	95-48-7			190.9	1.9	0.25	
3-methylphenol	108-39-4			202.2	1.0	0.15	
4-methylphenol	106-44-5			201.9	0.8	0.11	
Chlorinated Hydrocarbons							
Methylene chloride /dichloromethane	75-09-2 PA8050000	CH_2Cl_2	84.94	40	349	47	86*, 84, 49, 51
1,1,1-Trichloroethane /methyl chloroform	71-55-6 KJ2975000	CCl_3CH_3	133.42	75	100	13.5	97, 99, 117, 119
Perchloroethylene /hexachloroethane	127-18-4 KX3850000	CCl_3CCl_3	236.74	187 (subl)	0.2	<0.1	164*, 166, 168, 129, 131, 133, 94, 96
o-,p-Dichlorobenzenes		$C_6H_4Cl_2$	147.0				146*, 148, 111, 113, 75
/1,2-dichlorobenzene	95-50-1 CZ4500000			172-9	1.2	0.2	
/1,4-dichlorobenzene	106-46-7 CZ4550000			173.7	1.7	0.2	
1,1,2-Trichloro-1,2,2-trifluoroethane /Freon 113	76-13-1 KJ4000000	CCl_2FCClF_2	187.38	47.6	384	38	101, 103, 151, 153, 85, 87
Terpenes							
d-Limonene	5989-27-5 OS8100000	$C_{10}H_{16}$	136.23	176	1.2		68, 67, 93, 121, 136*
Turpentine (Pinenes)	8006-64-2	$C_{10}H_{16}$	136.23	156 to 170	4 @ 20°		93, 121, 136*, 91
α-pinene	80-56-8			156			
β-pinene	127-91-3			165			
Aldehydes							
Hexanal /caproaldehyde	66-25-1 MN7175000	$C_6H_{12}O$	100.16	131	10	1.3	44, 56, 72, 82, 41

Compound /Synonyms	CAS# RTECS	Empirical Formula	MW[a]	BP[b] (°C)	VP[c] @ 25 °C mm Hg	kPa	Characteristic Ions, m/z
Benzaldehyde /benzoic aldehyde	100-52-7 CU4375000	$C_7H_{12}O$	106.12	179	1.0	0.1	77, 105, 106*, 51
Nonanal /pelargonic aldehyde	124-19-6 RA5700000	$C_9H_{18}O$	142.24	93	23	3	43, 44, 57, 98, 114
Acetates							
Ethyl acetate /acetic ether	141-78-6 AH5425000	$C_4H_8O_2$	88.1	77	73	9.7	43, 88*, 61, 70, 73, 45
Butyl acetate /acetic acid butyl ester	123-86-4 AF7350000	$C_6H_{12}O_2$	116.16	126	10	1.3	43, 56, 73, 61
Amyl acetate /banana oil	628-63-7 AJ1925000	$C_7H_{14}O_2$	130.18	149	4	0.5	43, 70, 55, 61
Other							
Octamethylcyclotetra-siloxane	556-67-2 GZ4397000	$C_8H_{24}O_4Si_4$	296.62	175			281, 282, 283

[a] Molecular Weight
[b] Boiling Point
[c] Vapor Pressure
* Indicates molecular ion

APPENDIX

Multi-bed sorbent tubes: Other sorbent combinations and instrumentation/conditions shown to be equivalent may be substituted for those listed below. In particular, if the compounds of interest are known, specific sorbents and conditions can be chosen that work best for that particular compound(s). The tubes that have been used in NIOSH studies with the Perkin Elmer ATD system are ¼" stainless steel tubes, and are shown in the diagram below:

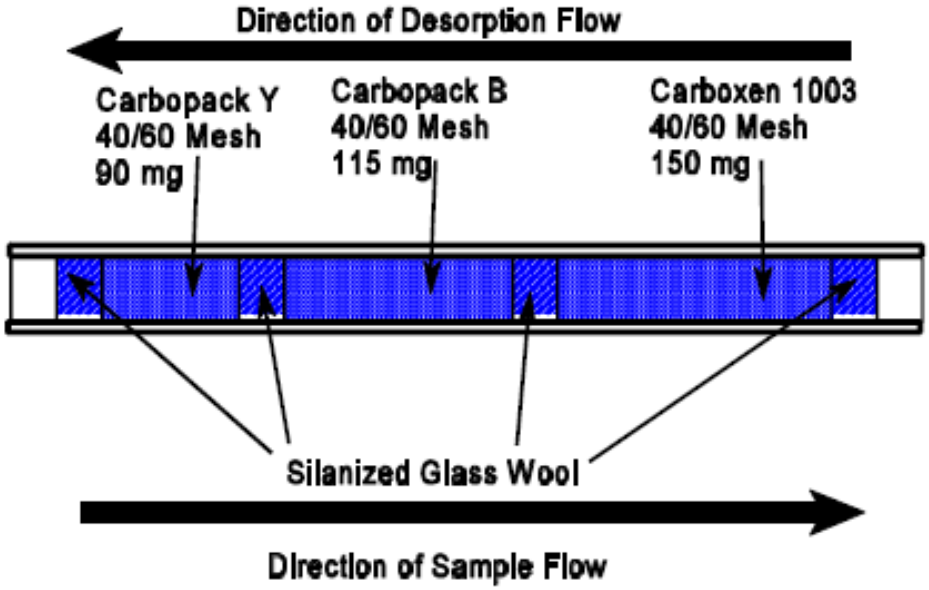

Figure 1

Carbopack™ and Carboxen™ adsorbents are available from Supelco, Inc.

Preparation of spiked samples Spiked tubes can be prepared from either liquid or gas bulb standards.

Liquid standards: Prepare stock solutions by adding known amounts of analytes to 10-mL volumetric flasks containing high purity solvent (carbon disulfide, methanol, toluene). Solvents are chosen based on solubility for the analytes of interest and ability to be separated from the analytes when chromatographed. Highly volatile compounds should be dissolved in a less volatile solvent. For most compounds, carbon disulfide is a good general purpose solvent, although this will interfere with early eluting compounds.

Gas bulb standards: Inject known amounts of organic analytes of interest into a gas bulb of known volume filled with clean air [4]. Prior to closing the bulb, place a magnetic stirrer and several glass beads are placed in the bulb to assist in agitation after introduction of the analytes. After injection of all of the analytes of interest into the bulb, warm the bulb to 50 °C and place it on a magnetic stirring plate and stir for several minutes to ensure complete vaporization of the analytes. After the bulb has been stirred and cooled to room temperature, remove aliquots from the bulb with a gas syringe and inject into a sample tube as described below.

Tube spiking: Fit a GC injector with a ¼" column adapter. Maintain the injector at 120 °C to assist in vaporization of the injected sample. Attach cleaned thermal desorption tubes to injector with ¼" Swagelok nuts and Teflon ferrules, and adjust helium flow though the injector to 50 mL/min. Attach the sampling tube so that flow direction is the same as for sampling. Take an aliquot of standard solution (gas standards 100 to 500 µL; liquid standards, 0.1 to 2 µL) and inject into the GC injector. Allow to equilibrate for 10 minutes. Remove tube and analyze by thermal desorption using the same conditions as for field samples.

Instrumentation: Actual media, instrumentation, and conditions used for general screening of unknown environments are as follows: Perkin-Elmer ATD 400 (automated thermal desorption system) interfaced directly to a Hewlett-Packard 5980 gas chromatograph/HP5970 mass selective detector and data system.

ATD conditions:

Tube desorption temperature: 300°C
Tube desorption time: 10 min.
Valve/transfer line temperatures: 150°C
Focusing trap: Carbopack B/Carboxen 1000, 60/80 mesh, held at 27°C during tube desorption
Focusing trap desorption temperature: 300°C
Desorption flow: 50-60 mL/min.
Inlet split: off
Outlet split: 20 mL/min.
Helium: 10 PSI

GC conditions:

DB-1 fused silica capillary column, 30 meter, 1-µm film thickness, 0.25-mm I.D.
Temperature program: Initial 35°C for 4 minutes, ramp to 100°C at 8°/min., then ramp to 300°C at 15°/min, hold 1-5 minutes.
Run time: 27 min.

MSD conditions:

Transfer line: 280°C
Scan 20-300 amus, EI mode
EMV: set at tuning value
Solvent delay: 0 min. for field samples; if a solvent-spiked tube is analyzed, a solvent delay may be necessary to prevent MS shutdown caused by excessive pressure.

Appendix B: Markes International Ltd. Application Note 038, Occupational exposure limit levels for VOCs Compatible with TD-GC

MARKES international

Technical Support

Released: October 2009

Application Note 038

Occupational exposure limit levels for VOCs compatible with TD–GC

Summary

This Application Note tabulates those chemicals with 'standard' occupational exposure limits at or below 10 ppm that are compatible with analysis by TD–GC(–MS). It also provides information on sorbents, sampling methods and safe sampling volumes (SSVs).

Introduction

Growing awareness of the importance of workplace health & safety, and improved knowledge of the potential health impact of long-term exposure to chemicals, have caused general lowering of workplace limit levels for inhalation exposure to chemical vapours in recent years. For some particularly hazardous chemicals, limit levels have been reduced below the limits of detection for traditional solvent extraction methods. (see Application Note 046).

Limit levels are often sub-divided into two categories:

1. 'Maximum' – Typically applied to substances which may cause the most serious health effects such as cancer or asthma. Also used for compounds for which there is no known 'safe' level.
2. 'Standard' – Set at a level below which there are no known risks to human health.

In addition to the general trend to lower regulated limits for inhalation exposure, improved understanding of the variability of actual workplace measurement data has also driven down the concentrations of vapours in most workplaces. For example, it is not uncommon for actual personal exposure measurements to vary by nearly two orders of magnitude for a given population of workers supposedly doing the same task. This is primarily due to differences in behaviour from individual to individual. Given this wide distribution, the only certain way of ensuring that no-one is exposed to vapour concentrations above the limit level is to keep the mean concentration at, or below, one-tenth of the official limit level.

In the case of 'Maximum' exposure limits (see above), best practice requires concentrations to be kept as low as possible, and actual exposures at 1 or 2% of the limit value would be normal in workplaces exercising optimum control.

Thermal desorption offers the sensitivity required for monitoring these compounds in workplace air at levels of 0.1 ppm and below. For the most toxic chemicals, with the lowest limit levels, TD is the only feasible analytical option.

Moreover, GC-compatible vapour-phase organics with higher limit levels can also be monitored efficiently by TD methods, because of the single- or double-splitting capability of modern TD technology.

Notes

†	Maximum limit (ppm).
*	No quantitative field validation available (may be semi-quantitative only). Recommendations are based on best advice and experience with similar compounds.
obs	Obsolete value.
SSV	Safe sampling volume.
U	Uptake rates in ng ppm^{-1} min^{-1} over 8 hours unless stated otherwise.

References

1. ISO Methods: (a) ISO 16017-1; (b) ISO 16017-2.
2. Markes International: (a) database; (b) Application Note 020; (c) Application Note 032; (d) Application Note 035; (e) Application Note 039.
3. US EPA Method TO-17.
4. UK Health & Safety Laboratory: (a) Method MDHS 53; (b) Method MDHS 63; (c) Method MDHS 80; (d) Method MDHS 96; (e) calculated values.

Trademarks

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Aromatics

Compound	CAS No.	Limit (ppm)			Sampling method	Sorbent	Notes
		UK	EU	Sweden			
Aniline	62-53-3	1	–	1	Pumped	Tenax TA [1a]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 220 L [1a]
Benzene	71-43-2	1	1	0.5	Pumped, Diffusive (tube)	Chromosorb 106 [1a,1b], Carbograph 1TD [1b]	$SSV_{Chromosorb\ 106\ (300\ mg)}$ = 28 L [1a], $U_{Carbograph\ 1TD}$ = 2.02 (14 days) [1b], $U_{Chromosorb\ 106}$ = 1.72 [1b]
Benzene-1,2-diol*	120-80-9	5	–	–	Pumped	Tenax TA (inert tube) [2a]	
Benzene-1,3-diol	108-46-3	10	10	10	Pumped	Tenax TA [2a]	
Cresol (all isomers)	1319-77-3	–	5	1	Pumped	Tenax TA [2b]	SSV > 3000 L (all isomers) [2b]
Dinitrobenzene	25154-54-5	0.15	–	–	Pumped	Tenax TA [2a]	
Diphenyl ether	101-84-8	1	–	–	Pumped	Tenax TA [2a]	
Divinylbenzene	1321-74-0	10_{obs}	–	–	Pumped	Tenax TA [2a]	
4-Ethylmorpholine	100-74-3	5	–	–	Pumped	Tenax TA [2a]	
N-Methylaniline*	100-61-8	0.5	–	–	Pumped	Tenax TA [2a]	
o-Methylaniline	95-53-4	0.2	–	–	Pumped	Tenax TA [2a]	
Naphthalene	91-20-3	–	10	10	Pumped	Tenax TA [3]	
Nitrobenzene	98-95-3	0.2	0.2	1	Pumped	Tenax TA [1a]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 14,000 L [1a]
Nitrotoluene (all isomers)	–	5_{obs}		1	Pumped	Tenax TA [2a]	
Phenol	108-95-2	2	2	1	Pumped	Tenax TA [1a]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 240 L [1a]
Pyridine	110-86-1	5	5	1	Pumped	Tenax TA [3], PoraPak N [1a]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 8 L [3], $SSV_{PoraPak\ N\ (500\ mg)}$ = 200 L [1a]

Amines

Compound	CAS No.	Limit (ppm)			Sampling method	Sorbent	Notes
		UK	EU	Sweden			
Cyclohexylamine*	108-91-8	10	10	5	Pumped	Tenax TA (inert tube) [2a]	
Diethylamine*	109-89-7	10	5	10	Pumped	Chromosorb 106 or PoraPak N (inert tube) [2a]	
Diisopropylamine	108-18-9	5	–	5	Pumped	Chromosorb 106 or PoraPak N [2a]	
Dimethylamine*	124-40-3	2	2	2	Pumped	UniCarb (inert tube) [2a]	
N,N-Dimethyl-ethylamine*	598-56-1	10	–	–	Pumped	Chromosorb 106 (inert tube) [2a]	
Ethylamine*	75-04-7	2	5	–	Pumped	Chromosorb 106 or UniCarb (inert tube) [2a]	
Methylamine	74-89-5	10_{obs}	–	10	Pumped	UniCarb [2a]	
Piperazine*	110-85-0	0.1_{obs} mg/m³	0.1	–	Pumped	Tenax TA (inert tube) [2a]	
Piperidine*	110-89-4	1	–	–	Pumped	Tenax TA [2a]	
Triethylamine	121-44-8	2	2	–	Pumped	Chromosorb 106 (inert tube) [2a]	
Trimethylamine	75-50-3	10_{obs}	–	–	Pumped	UniCarb (inert tube) [2a]	

Esters and amides

Compound	CAS No.	Limit (ppm)			Sampling method	Sorbent	Notes
		UK	EU	Sweden			
n-Butyl acrylate	141-32-2	1	–	10	Diffusive (tube)	Tenax TA [1b]	$U_{Tenax\ TA}$ = 2.6 [1b]
Diethyl phthalate	84-66-2	5 mg/m³	–	–	Pumped	Quartz wool–Tenax TA [2d]	
Diisobutyl phthalate	84-69-5	5 mg/m³	–	–	Pumped	Quartz wool–Tenax TA [2d]	
Diisodecyl phthalate	26761-40-0	5 mg/m³	–	–	Pumped	Quartz wool–Tenax TA [2d]	
Diisononyl phthalate	28553-12-0	5 mg/m³	–	–	Pumped	Quartz wool–Tenax TA [2d]	
Diisooctyl phthalate	27554-26-3	5 mg/m³	–	–	Pumped	Quartz wool–Tenax TA [2d]	
N,*N*-Dimethyl acetamide	127-19-5	10	10	10	Pumped	Tenax TA [2a]	
2-Ethoxyethyl acetate	111-15-9	10	–	–	Pumped, Diffusive (tube)	Tenax TA [1a,1b], Chromosorb 106 [1a,1b]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 15 L [1a], $SSV_{Chromosorb\ 106\ (300\ mg)}$ = 4000 L [1a], $U_{Tenax\ TA}$ = 2.1 [1b], $U_{Chromosorb\ 106}$ = 2.3 [1b]
Ethyl acrylate	140-88-5	5	–	–	Pumped	Tenax [1a]	$SSV_{Tenax\ (200\ mg)}$ = 24 L [1a]
2-Hydroxypropyl acrylate*	999-61-1	0.5	–	1	Pumped	Tenax TA [2a]	
Methoxyethyl acetate	110-49-6	5	–	–	Pumped, Diffusive (tube)	Chromosorb 106 [1a], PoraPak Q [1b]	$SSV_{Chromosorb\ 106\ (300\ mg)}$ = 860 L [1a], $U_{PoraPak\ Q}$ = 2.8 [1b]
Methyl acrylate	96-33-3	10_{obs}	–	10	Pumped	Chromosorb 106 [3], Tenax TA [1a]	$SSV_{Chromosorb\ 106\ (200\ mg)}$ = 6.5 L [3]
Vinyl acetate	108-05-4	10_{obs}	–	5	Pumped, Diffusive (tube)	Chromosorb 106 [3,4e]	$U_{Chromosorb\ 106\ (300\ mg)}$ = 1.93 [3]

Sulfur compounds

Compound	CAS No.	Limit (ppm)			Sampling method	Sorbent	Notes
		UK	EU	Sweden			
Benzenethiol	108-98-5	0.5_{obs}	–	–	Pumped	Tenax TA (inert tube) [2a]	
Carbon disulfide	75-15-0	10	5_{obs} †	5	Diffusive (tube)	UniCarb [1b]	$U_{UniCarb}$ = 2.6 [1b]
Diethyl sulfate	64-67-5	0.05	–	–	Pumped	Tenax TA [4d]	$SSV_{Tenax\ TA\ (200\ mg)}$ > 96 L [4d]
Dimethyl sulfate	77-78-1	0.05	–	–	Pumped	Tenax TA [4d]	$SSV_{Tenax\ TA\ (200\ mg)}$ > 96 L [4d]
Ethanethiol	75-08-1	0.5	–	–	Pumped	Chromosorb 106 (glass tube) [3]	
Hydrogen sulfide	7783-06-4	5	–	10	On-line, Canister	'H_2S' trap [2c]	
Methanethiol	74-93-1	0.5	–	1	Pumped	UniCarb (inert tube) [3]	

Halogenated compounds

Compound	CAS No.	Limit (ppm)			Sampling method	Sorbent	Notes
		UK	EU	Sweden			
Benzyl chloride	100-44-7	0.5	–	1	Pumped, Diffusive (tube)	Tenax TA [3,4e]	$U_{Tenax\ TA}$ = 2.72 [3,4e]
Bis(chloromethyl) ether	542-88-1	0.001	–	Banned	Pumped	Tenax TA (glass tube) [2a]	
Bromoform [Tribromomethane]	75-25-2	0.5_{obs}	–	–	Pumped	Tenax TA [2b]	$SSV_{Tenax\ TA\ (200\ mg)}$ ~ 100 L [2b]
Bromomethane	74-83-9	5	–	–	Diffusive (tube)	Chromosorb 106 [4c]	$U_{Chromosorb\ 106\ (300\ mg)}$ = 2.45 [4c]
2-Chloroacetophenone	532-27-4	0.05	–	–	Pumped	Tenax TA [2a]	
Chlorobenzene	108-90-07	1 †	10	5	Pumped	Tenax TA [1a]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 26 L [1a]
2-Chlorobutadiene*	126-99-8	10_{obs}	–	–	Pumped	Chromosorb 106 [2a]	
Chloroform [Trichloromethane]	67-66-3	2	2	–	Diffusive (tube)	Tenax GR [1b], Chromosorb 102 [1b], Chromosorb 106 [1b]	$U_{Tenax\ GR}$ = 2.18 [1b], $U_{Chromosorb\ 102}$ = 2.35 [1b], $U_{Chromosorb\ 106}$ = 2.47 [1b]
1,2-Dibromoethane	106-93-4	0.5	–	–	Pumped	'Air Toxics' [3]	SSV > 5 L (at <65% RH) [3]
1,2-Dichloroethane	107-06-2	5	–	1	Pumped, Diffusive (tube)	Chromosorb 106 [1a,4e], Chromosorb 102 [1b], Tenax GR [4e]	$SSV_{Chromosorb\ 106\ (300\ mg)}$ = 17 L [1a], $U_{Chromosorb\ 106}$ = 2.03 [4e], $U_{Chromosorb\ 102}$ = 1.9 [1b], $U_{Tenax\ GR}$ = 1.72 [4e]
1,1-Dichloroethene	75-35-4	10	–	–	Pumped, Diffusive (tube)	Carboxen 1000 [3], UniCarb [1b]	SSV >75 L (at <65% RH) [3]
Dichlorofluoromethane	75-43-4	10	–	–	Pumped	UniCarb [2a]	
Halothane [2-Bromo-2-chloro-1,1,1-trifluoroethane]	151-67-7	10	–	5	Diffusive (tube)	Tenax TA [1a]	$U_{Tenax\ TA}$ = 2.59 [1a]
Hexachloroethane	67-72-1	5	–	–	Pumped	Tenax TA [2a]	
Iodoform [Triiodomethane]	75-47-8	0.6	–	–	Pumped	Tenax TA [2a]	
Iodomethane	74-88-4	2	–	–	Pumped	UniCarb [2a]	
1,1,2,2-Tetrabromoethane	79-27-6	0.5	–	1	Pumped	Tenax TA [2a]	
Tetrabromomethane [Carbon tetrabromide]	558-13-4	0.1_{obs}	–	–	Pumped	Tenax TA [2a]	
Tetrachloromethane [Carbon tetrachloride]	56-23-5	2	–	–	Pumped, Diffusive (tube)	Tenax TA [1a], Tenax GR [1b], Chromosorb 106 [1a], Chromosorb 102 [1b]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 6.2 L [1a], $SSV_{Chromosorb\ 106\ (300\ mg)}$ = 22 L [1a], $U_{Tenax\ GR}$ = 3.72 [1b], $U_{Chromosorb\ 102}$ = 2.87 [1b]
1,2,4-Trichlorobenzene	120-82-1	1	2_{obs}	–	Pumped	'Air Toxics' [3]	SSV > 5 L (at <65% RH) [3]
Trichloronitromethane	76-06-2	0.1	–	–	Pumped	Tenax TA [2a]	
Vinyl chloride	75-01-4	3	–	1	Diffusive (tube)	UniCarb [1b]	$U_{UniCarb}$ = 2.0 [1b]

Ketones

Compound	CAS No.	Limit (ppm)			Sampling method	Sorbent	Notes
		UK	EU	Sweden			
Cyclohexanone	108-94-1	10	10	10	Pumped	Tenax TA [1a]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 170 L [1a]
Hexan-2-one [Methyl butyl ketone]	591-78-6	5	–	1	Pumped	Tenax TA [2a]	
5-Methyl-heptan-3-one	541-85-5	10	10	–	Pumped	Tenax [2a]	

Epoxides

Compound	CAS No.	Limit (ppm)			Sampling method	Sorbent	Notes
		UK	EU	Sweden			
Epichlorohydrin [1-Chloro-2,3-epoxypropane]	106-89-8	0.5	–	–	Diffusive (tube)	Chromosorb 106 [1b]	$U_{Chromosorb\ 106}$ = 2.45 [1b]
Ethylene oxide	75-21-8	5	–	1	Pumped, Diffusive (tube)	Carboxen 569 [1a], UniCarb [1b]	$SSV_{Carboxen\ 569}$ = 70 L [1a], $U_{UniCarb}$ = 1.6 [1b]
Phenyl 2,3-epoxypropyl ether	122-60-1	1_{obs}	–	–	Pumped	Tenax TA [2a]	
Propylene oxide	75-56-9	5	–	2	Pumped, Diffusive (tube)	Chromosorb 106 [1a,4c]	$SSV_{Chromosorb\ 106\ (300\ mg)}$ = 1 L [1a], $U_{Chromosorb\ 106}$ = 1.24 [4c]

Other compounds

Compound	CAS No.	Limit (ppm)			Sampling method	Sorbent	Notes
		UK	EU	Sweden			
Acetic acid	64-19-7	10	10	–	Pumped	PoraPak N [1a]	$SSV_{PoraPak\ N\ (500\ mg)}$ = 50 L [1a]
Acrylonitrile	107-13-1	2	–	–	Pumped, Diffusive (tube)	PoraPak N [1a,1b]	$SSV_{PoraPak\ N\ (500\ mg)}$ = 8 L [1a], $U_{PoraPak\ N}$ = 1.35 [1b]
Allyl alcohol	107-18-6	2	2	–	Pumped	Chromosorb 106 [2a]	
Butadiene	106-99-0	10	–	0.5	Pumped, Diffusive (tube)	Carbopack X [1b,4a], Mol. Sieve 13X [4b]	$SSV_{CarboPack\ X\ (500\ mg)}$ > 25 L [4a], $U_{Mol.\ Sieve\ 13X}$ = 1.3 [4b], $U_{CarboPack\ X}$ = 1.64 [1b]
Chlorpyrifos [O,O-Diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate]	2921-88-2	0.2 mg/m³	–	–	Pumped	Tenax TA (inert tube) [2a]	
Dichlorvos [2,2-Dichlorovinyl dimethyl phosphate]	62-73-7	0.1_{obs}	–	–	Pumped	Quartz wool and Tenax TA (glass tube) [2a]	
Dicyclopentadiene	77-73-6	5	–	–	Pumped	Tenax TA [2a]	
Dimethylformamide	68-12-2	10	–	–	Pumped	Tenax TA [3]	
2-Ethoxyethanol	110-80-5	10	2	–	Pumped, Diffusive (tube)	Chromosorb 106 [1a], Tenax TA [1b]	$SSV_{Chromosorb\ 106\ (300\ mg)}$ = 75 L [1a], $U_{Tenax\ TA}$ = 1.8 [1b]
Ethylene dinitrate*	628-96-6	0.2_{obs}	–	–	Pumped	Tenax TA (inert tube) [2a]	
Furfural	98-01-1	2	–	2	Pumped, Diffusive (tube)	Tenax TA [1a,1b]	$SSV_{Tenax\ TA\ (200\ mg)}$ = 300 L [1a], $U_{Tenax\ TA}$ = 2.5 [1b]
Furfuryl alcohol	98-00-0	5_{obs}	–	5	Diffusive	Tenax TA [4e]	$U_{Tenax\ TA}$ = 2.5 [4e]
Indene	95-13-6	10	–	–	Pumped	Tenax TA [3]	
Methacrylonitrile	126-98-7	1	–	–	Pumped	Tenax TA [2a]	
2-Methoxyethanol	106-86-4	5	–	–	Pumped, Diffusive (tube)	Chromosorb 106 [1a,1b], PoraPak Q [1b]	$SSV_{Chromosorb\ 106\ (300\ mg)}$ = 300 L [1a], $U_{Chromosorb\ 106}$ = 2.1 [1b], $U_{PoraPak\ Q}$ = 1.5 [1b]
Mevinphos [2-Methoxycarbonyl-1-methylvinyl dimethyl phosphate]*	7786-34-7	0.01_{obs}	–	–	Pumped	Quartz wool and Tenax TA (glass tube) [2a]	
Propanoic acid*	79-09-4	10	10	–	Pumped	Tenax TA [2a]	

Appendix C: Markes International Ltd. Application note 020, Confirming sorbent tube retention volumes and checking for analyte breakthrough

MARKES international

Technical Support

TDTS 20

Confirming sorbent tube retention volumes and checking for analyte breakthrough

It is recommended that this Application Note is read in conjunction with Application Note TDTS 5 (Advice on sorbent selection, tube conditioning, tube storage and air sampling).

Introduction

Information on how to determine sorbent tube retention volumes, breakthrough volumes and safe sampling volumes is presented in Application Note TDTS 5 and in various international standard methods for thermal desorption, *e.g.* EN ISO 16017-1, Annexes A and B. However, as sorbent tubes age it is possible for retention volumes to fall, risking breakthrough of the most volatile target compounds. It is also possible for breakthrough volumes to fall under extreme environmental conditions (*e.g.* high humidity and high temperature), though the impact of such effects varies significantly for different sorbents.

This Application Note describes a simple procedure for checking analyte breakthrough prior to or during field monitoring, using pairs of tubes linked together in series. This guidance also complies with recommendations in standard thermal desorption methods for air monitoring.

Field validation of quantitative retention during sampling

As a routine check of pumped tube retention during field air monitoring studies, two identical, conditioned sorbent tubes should be linked together in series using an inert stainless steel union with combined PTFE ferrules (part number C-UN010). The sampling end of the back-up tube should be connected to the outlet end of the front (sampling) tube. The sampling pump is attached to the exhaust end of the back-up tube. At least one such tube pair should be deployed in all routine monitoring exercises and, in large scale studies, it is recommended that at least one in ten monitoring locations are sampled using such tube pairs.

After monitoring, the back-up tubes should be analysed in the same analytical sequence as all the sampling tubes and study blanks.

- If the mass of one or more target analytes on the back-up tube is >5% of the mass on the front sampling tube, *breakthrough* of that compound or compounds can be said to have occurred. The amount can quantified by adding the mass of analyte measured on the back-up tube to that determined on the front sampling tube.
- If the mass of one or more target analytes on the back-up tube is >10% of the mass on the front sampling tube, breakthrough of that compound or compounds is significant, and data for any such compounds should not be viewed as quantitative.

Extended checks of breakthrough and other tube performance indicators

After a batch of tubes has been used extensively (*e.g.* 20 field monitoring exercises or thermal cycles) a representative number of tubes from that batch should be more stringently checked for breakthrough. In this case it is recommended that at least six tube pairs are prepared as above and used to sample a standard or real atmosphere under conditions which are as close as possible to the worst-case real-life scenario, *i.e.* highest natural humidity, highest ambient temperature and highest expected VOC concentrations.

The sampling points of all the tube pairs should placed close together to ensure that, as far as possible, they are all sampling the same atmosphere. The selected sampling location should be well ventilated. Three different pump flow rates between 10 and 200 mL/min should be used for sampling, with duplicates at each level. All the tubes should be analysed in one sequence, and the results evaluated to ensure that compound masses increase relative to the volume of air sampled and are reproducible at each volume. Selective loss of one or more analytes at higher volumes indicates breakthrough. Detection of >5% of one or more analytes on the back-up tubes can be used to confirm breakthrough.

If one or more analyte is observed to increase at a higher rate than the sample volume, this can be an indication of artefact formation or sorbent/analyte breakdown. Such effects can be caused, for example, by the air containing above-ambient concentrations of reactive gases such as ozone, or by sorbent degradation. In the latter case, the tubes would need repacking.

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Appendix – Breakthrough volumes

Notes on the tables

- Markes has not undertaken any validation work on the following data. It is always recommended that safe sampling volumes are checked using one of the procedures outlined above
- Breakthrough volumes have been extrapolated to relate to a standard ¼" stainless steel TD tube, packed with the typical mass of sorbent
- SSV = Safe sampling volume
- U = Unretained.

1. On 200 mg Carbotrap C–Carbograph 2TD at 20 °C

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alkanes			
Methane	–164	U	–
Ethane	–89	U	–
Propane	–42	U	–
Butane	–0.5	U	–
Pentane	36	U	–
Hexane	69	0.3	0.15
Heptane	98	1.4	0.7
Octane	125	5.6	2.8
Nonane	151	20	10
Decane	174	100	50
Undecane	196	500	250
Dodecane	216	2600	1300
Tridecane	235	7400	3700
Tetradecane	254	22000	11000
Pentadecane	271	46000	23000
Hexadecane	287	100000	50000
Heptadecane	302	300000	150000
Octadecane	316	800000	400000
Alcohols			
Methanol	65	U	–
Ethanol	78	U	–
Propan-1-ol	97	U	–
Butan-1-ol	118	U	–
Pentan-1-ol	138	0.42	0.21
Hexan-1-ol	158	1.42	0.71
Heptan-1-ol	176	6.6	3.3
Octan-1-ol	195	16	8
Nonan-1-ol	213	40	20
Decan-1-ol	231	90	45
Undecan-1-ol	243	240	120
Dodecan-1-ol	259	800	400
Tridecan-1-ol	–	2000	1000
Tetradecan-1-ol	289	3200	1600
Pentadecan-1-ol	–	7200	3600
Halogenated compounds			
Monohalogenated compounds			
Chloromethane	–24	U	–
Chloroethene (Vinyl chloride)	–13	U	–
2-Chloroethyl vinyl ether	109	0.1	0.05
Chlorobenzene	132	1	0.5
Dihalogenated compounds			
1,1-Dichloroethane	57	U	–
1,2-Dichloroethane	83	U	–
1,1-Dichloroethene	32	U	–
1,2-Dichloroethene	49	U	–
1,2-Dichloropropane	95	U	–
1,3-Dichloropropene	104–112	U	–
1,2-Dichlorobenzene	181	6	3
1,3-Dichlorobenzene	173	6	3
1,4-Dichlorobenzene	174	6	3
Trihalogenated compounds			
Bromodichloromethane	90	U	–
Dibromochloromethane	119	U	–
Chlorodifluoromethane	–41	U	–
Trichloromethane	61	U	–
Tribromomethane	149	0.1	0.5
1,1,1-Trichloroethane	74	U	–
1,1,2-Trichloroethane	110	U	–
Trichloroethene	87	U	–
Tetrahalogenated compounds			
Dichlorodifluoromethane	–30	U	–
Trichlorofluoromethane	24	U	–
Tetrachloromethane	76	U	–
1,1,2,2-Tetrachloroethane	146	0.2	0.1
Tetrachloroethene	121	0.4	0.02

2. On 200 mg Tenax TA at 20 °C

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alkanes			
Methane	–164	U	–
Ethane	–89	U	–
Propane	–42	U (0.03)	–
Butane	–0.5	0.2	0.1
Pentane	36	1	0.5
Hexane	69	6.4	3.2
Heptane	98	34	17
Octane	125	160	80
Nonane	151	1400	700
Decane	174	4200	2100
Undecane	196	25000	12500
Dodecane	216	126000	63000

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alkanes (continued)			
Tridecane	235	25000	12500
Tetradecane	254	60000	30000
Pentadecane	271	114000	57000
Hexadecane	287	210000	105000
Heptadecane	302	340000	170000
Octadecane	316	560000	280000
Nonadecane	330	800000	400000
Eicosane	343	1.32×10^6	660000
n-C_{21}	357	2.0×10^6	1.0×10^6
n-C_{22}	369	3.2×10^6	1.6×10^6
n-C_{23}	380	5.0×10^6	2.5×10^6
n-C_{24}	391	8.2×10^6	4.1×10^6
n-C_{25}	402	1.25×10^8	6.25×10^6
n-C_{26}	412	2.5×10^7	1.25×10^6
n-C_{27}	442	5.0×10^7	2.5×10^6
n-C_{28}	432	1.04×10^8	5.2×10^6
n-C_{29}	441	2.2×10^8	1.1×10^6
n-C_{30}	450	5.0×10^8	2.5×10^6
Aromatics			
Benzene	80	12.5	6
Toluene	111	76	38
Xylene	138–144	610	305
Ethylbenzene	137	360	180
n-Propylbenzene	159	1700	850
Isopropylbenzene	152	960	480
n-Butylbenzene	183	3600	1800
n-Hexylbenzene	226	87200	43600
Ethyltoluene	162	2000	1000
Styrene	145	600	300
Methylstyrene	167	2400	1200
Nitrobenzene	211	28000	14000
p-Cymene	177	2600	1300
Butylated hydroxy toluene (BHT)	265	2700	1350
Trimethylbenzene	165–176	3600	1800
o-Cresol	191	6600	3300
p-Cresol	202	6200	3100
o-Ethyltoluene	164	2000	1000
m-Ethyltoluene	161	2000	1000
p-Ethyltoluene	162	2000	1000
Naphthalene	218	20000	10000
Biphenyl	256	63200	31600
Phenanthrene	340	112400	56200

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Terpenes and alkaloids			
Limonene	176	2400	1200
Nicotine	247	20000	10000
Geraniol	229	126000	63000
Cotinine	–	280000	140000
Alkenes			
But-1-ene	–6	0.1	0.05
Pent-1-ene	30	0.9	0.45
Pent-2-ene	37	1.2	0.6
Hex-1-ene	63	4.6	2.3
Hex-2-ene	68	6.4	3.2
Hex-3-ene	66	5.6	2.8
Hept-1-ene	94	24	12
Oct-1-ene	121	112	56
Oct-2-ene	123	164	82
Oct-3-ene	121	130	65
Non-1-ene	–	640	320
Dec-1-ene	170	1260	630
Undec-1-ene	–	2820	1410
Dodec-1-ene	214	5600	2800
Tridec-1-ene	–	8400	4200
Tetradec-1-ene	–	12600	6300
Pentadec-1-ene	–	20000	10000
Hexadec-1-ene	–	31600	15800
Heptadec-1-ene	–	50200	25100
Octadec-1-ene	–	80000	40000
Nonadec-1-ene	–	200000	100000
Eicos-1-ene	–	500000	250000
Esters			
Methyl acetate	57	1.6	0.8
Ethyl acetate	71	54	27
Propyl acetate	102	36	18
Isopropyl acetate	90	12	6
n-Butyl acetate	126	170	85
Isobutyl acetate	115	265	132.5
tert-Butyl acetate	98	176	88
Pentyl acetate	149	940	470
Hexyl acetate	172	9000	4500
Methyl acrylate	81	13	6.5
Ethyl acrylate	100	48	24
Methyl methacrylate	100	55	27.5

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Glycol ethers			
Methoxyethanol	125	6	3
Ethoxyethanol	136	10	5
Butoxyethanol	170	70	35
2-(2-Butoxyethoxy)-ethanol	–	50200	25100
Methoxypropanol	118	27	13.5
Methoxyethyl acetate	145	16	8
Ethoxyethyl acetate	156	30	15
Butoxyethyl acetate	92	300	150
Aldehydes			
Acetaldehyde	20	0.1	0.05
Propanal	48	1	0.5
2-Methylpropanal	63	3.4	1.7
Butanal	75	6	3
3-Methylbutanal	91	13	6.5
Pentanal	103	22	11
Hexanal	131	100	50
Heptanal	153	700	350
Octanal	169	2500	1250
Nonanal	191	12600	6300
2-Methylcyclohexane carboxaldehyde	–	500	250
3-Methylcyclohexane carboxaldehyde	–	600	300
4-Methylcyclohexane carboxaldehyde	–	800	400
Furfural	162	600	300
Ketones			
Acetone	56	1.2	0.6
Butan-2-one (Methyl ethyl ketone)	80	6.4	3.2
Pentan-2-one	102	36	18
Pentan-3-one	102	40	20
4-Methylpentan-2-one (Methyl isobutyl ketone)	116	52	26
Hexan-2-one	128	200	100
Heptan-2-one	151	1000	500
Heptan-3-one	147	800	400
Heptan-4-one	144	700	350
Octan-2-one	173	4000	2000
Octan-3-one	167	1160	580
Nonan-2-one	195	10000	5000
Nonan-4-one	187	6400	3200
Cyclohexanone	155	340	170
3,5,5-Trimethylcyclohex-2-en-1-one	214	11200	5600
Benzaldehyde	179	220	110

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alcohols			
Methanol	65	U	–
Ethanol	78	0.4	0.2
Propan-1-ol	97	2.2	1.1
Propan-2-ol	82	1	0.5
2-Methylpropan-2-ol	83	10	5
Butan-1-ol	118	10	5
Butan-2-ol	108	5.6	2.8
2-Methylbutan-1-ol	129	16	8
3-Methylbutan-1-ol	130	32	16
2-Methylbutan-2-ol	101	0.2	0.1
Dimethylaminoethanol	133	36	18
Pentan-1-ol	138	76	38
Pentan-2-ol	119	34	17
Pentan-3-ol	115	9	4.5
Hexan-1-ol	158	360	180
Heptan-1-ol	176	2000	1000
Octan-1-ol	195	2800	1400
Nonan-1-ol	213	17800	8900
Decan-1-ol	231	56200	28100
Undecan-1-ol	243	141600	70800
Dodecan-1-ol	259	280000	140000
Tridecan-1-ol	–	400000	200000
Tetradecan-1-ol	289	640000	320000
Pentadecan-1-ol	–	1.12×10^6	560000
Hexadecan-1-ol	–	1.80×10^6	900000
Heptadecan-1-ol	–	3.56×10^6	1.78×10^6
Octadecan-1-ol	–	7×10^6	3.5×10^6
Nonadecan-1-ol	–	2×10^7	1×10^7
Eicosan-1-ol	–	5.62×10^7	2.81×10^6
Docosan-1-ol	–	4×10^8	2×10^8
Phenol	182	480	240
o-Cresol	191	6600	3300
p-Cresol	201	6200	3100
Glycols			
Ethylene glycol	197	7	3.5
Propane-1,2-diol	186	20	10
Butane-1,3-diol	203	157	78.5
(2-Hydroxyethoxy)-ethan-2-ol (Diethylene glycol)	245	1260	630

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Halogenated compounds			
Monohalogenated compounds			
Chloromethane	–24	U	–
Chloroethane	12	0.8	0.4
Chloroethene (Vinyl chloride)	–13	0.1	0.05
2-Chloroethyl vinyl ether	109	40	20
Chlorobenzene	131	52	26
Dihalogenated compounds			
Dichloromethane	40	0.9	0.45
1,1-Dichloroethane	57	2.2	1.1
1,2-Dichloroethane	84	10.8	5.4
1,1-Dichloroethene	32	0.8	0.4
1,2-Dichloroethene	49	1.8	0.9
1,2-Dichloropropane	95	16	8
1,3-Dichloropropene	104–112	30	15
1,2-Dichlorobenzene	181	660	330
1,3-Dichlorobenzene	173	540	270
1,4-Dichlorobenzene	174	58	290
Trihalogenated compounds			
Bromodichloromethane	90	18	9
Dibromochloromethane	119	63	31.5
Chlorodifluoromethane	–41	U	–
Trichloromethane (Chloroform)	61	3.8	1.9
Tribromomethane (Bromoform)	149	200	100
1,1,1-Trichloroethane	74	2.2	1.1
1,1,2-Trichloroethane	114	68	34
Trichloroethene	87	11	5.5
Tetrahalogenated compounds			
Dichlorodifluoromethane	–30	U	–
Trichlorofluoromethane	24	0.4	0.2
Tetrachloromethane	76	12.4	6.2
Tetrachloromethane	76	4.2	2.1
1,1,1,2-Tetrachloroethane	130	156	78
1,1,2,2-Tetrachloroethane	146	340	170
Tetrachloroethene	121	96	48
Acids			
Acetic acid	118	1.1	0.55
Propanoic acid	141	6.4	3.2
Butanoic acid	164	28	14
Pentanoic acid	186	140	70
Hexanoic acid	205	620	310
Acid anhydrides			
Maleic anhydride	202	176	88

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Amines			
Methylamine	–6	0.1	0.05
Ethylamine	17	0.9	0.45
n-Propylamine	48	3.2	1.6
n-Butylamine	77	13	6.5
sec-Butylamine	83	4.6	2.3
Isobutylamine	68	5	2.5
tert-Butylamine	44	U	–
n-Pentylamine	104	52	26
Isopentylamine	95	26	13
n-Hexylamine	129	200	100
Cyclohexylamine	133	180	90
n-Heptylamine	154	1000	500
n-Octylamine	178	3600	1800
n-Nonylamine	202	9000	4500
n-Decylamine	216	28200	14100
Pyridine	116	16	8
Aniline	183	440	220
Benzylamine	184	1000	500

3. On 200 mg Tenax GR at 20 °C

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alkanes			
Methane	–164	U	–
Ethane	–89	U	–
Propane	–42	U	–
Butane	–0.5	U (0.08)	–
Pentane	36	0.34	0.17
Hexane	69	1.3	0.65
Heptane	98	6	3
Octane	125	18	9
Nonane	151	50	25
Decane	174	240	120
Dodecane	216	820	410
Tetradecane	254	2400	1200
Hexadecane	287	9400	4700
Octadecane	316	40000	20000
Eicosane	343	170000	85000
Aldehydes			
Propanal	48	0.6	0.3
2-Methylpropanal	63	1.2	0.6
Butanal	75	1.9	0.95
3-Methylbutanal	91	4.4	2.2
Pentanal	103	5	2.5
Hexanal	131	14	7
Heptanal	153	56	28
Octanal	169	120	60
Nonanal	191	160	160

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Ketones			
Acetone	56	0.7	0.35
Butan-2-one (Methyl ethyl ketone)	80	2.4	1.2
Pentan-2-one	102	4.8	2.4
Pentan-3-one	102	5	2.5
Hexan-2-one	128	14	7
2-Methylcyclohexanone	–	24	12
3-Methylcyclohexanone	–	12	6
4-Methylcyclohexanone	–	13	6.5
Heptan-2-one	151	40	20
Heptan-3-one	147	39	19.5
Heptan-4-one	144	32	16
Octan-2-one	173	100	50
Octan-3-one	167	42	21
Nonan-2-one	195	300	150
Nonan-5-one	186	280	140
Alcohols			
Methanol	65	U	–
Ethanol	78	U (0.16)	–
Propan-1-ol	97	0.6	0.16
propan-2-ol	82	0.32	0.3
Butan-1-ol	118	2	0.55
Butan-2-ol	98	1.1	1
Pentan-1-ol	138	4.6	1.6
Pentan-2-ol	119	3.2	2.3
Hexan-1-ol	158	20	10
Heptan-1-ol	180	46	23
Octan-1-ol	195	100	50
Nonan-1-ol	213	170	85
Decan-1-ol	231	400	200
Undecan-1-ol	243	600	300
Dodecan-1-ol	259	1200	600
Tridecan-1-ol	–	2000	1000
Tetradecan-1-ol	289	3600	1800
Pentadecan-1-ol	–	4400	2200

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Halogenated compounds			
Monohalogenated compounds			
Chloromethane	–24	U	–
Chloroethane	12	0.1	0.05
Chloroethene (Vinyl chloride)	–13	U	–
2-Chloroethyl vinyl ether	109	6	3
Chlorobenzene	132	20	10
Dihalogenated compounds			
Dichloromethane	40	0.5	0.25
1,1-Dichloroethane	57	0.8	0.4
1,2-Dichloroethane	83	2.4	1.2
1,1-Dichloroethene	32	0.5	0.25
1,2-Dichloroethene	49	0.6	0.3
1,2-Dichloropropane	95	2.2	1.1
1,3-Dichloropropene	104–112	4	2
1,2-Dichlorobenzene	181	160	80
1,3-Dichlorobenzene	173	120	60
1,4-Dichlorobenzene	174	140	70
Trihalogenated compounds			
Bromodichloromethane	90	2	1
Dibromochloromethane	119	10	5
Chlorodifluoromethane	–41	U	–
Trichloromethane (Chloroform)	61	1.2	0.6
Tribromomethane (Bromoform)	149	40	20
1,1,1-Trichloroethane	74	1.8	0.9
1,1,2-Trichloroethane	110	6	3
Trichloroethene	87	3.4	1.7
Tetrahalogenated compounds			
Dichlorodifluoromethane	–30	U	–
Trichlorofluoromethane	–	0.1	0.05
Tetrachloromethane	76	2	1
1,1,2,2-Tetrachloroethane	146	38	19
Tetrachloroethene	121	7.6	3.8
Amines			
n-Butylamine	77	2.4	1.2
sec-Butylamine	83	1	0.5
Isobutylamine	68	1.3	0.65
tert-Butylamine	44	U	–
n-Pentylamine	104	14	7
Isopentylamine	95	4	2
n-Hexylamine	129	40	20
Cyclohexylamine	133	5	2.5
n-Heptylamine	154	70	35
n-Octylamine	178	170	85
n-Decylamine	216	400	200
Benzylamine	184	70	35

4. On 200 mg Carbotrap/Carbograph 1TD/Carbopack B at 20°C

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alkanes			
Methane	–164	U	—
Ethane	–89	U	—
Propane	–42	U	—
Butane	–0.5	U	—
Pentane	36	1.2	0.6
Hexane	69	16	8
Heptane	98	90	45
Octane	125	1500	750
Nonane	151	14000	7000
Decane	174	200000	100000
Undecane	96	600000	300000
Dodecane	216	1.6×10^6	800000
Alcohols			
Methanol	65	U	—
Ethanol	78	U	—
Propan-1-ol	97	0.64	0.32
Butan-1-ol	118	6	3
Pentan-1-ol	138	20	10
Hexan-1-ol	158	60	30
Heptan-1-ol	176	180	90
Octan-1-ol	180	600	300
Nonan-1-ol	213	3000	1500
Decan-1-ol	231	6000	3000
Halogenated compounds			
Monohalogenated compounds			
Chloromethane	–24	U	—
Chloroethene (Vinyl chloride)	–13	U	—
2-Chloroethyl vinyl ether	109	2.6	1.3
Chlorobenzene	132	20	10
Dihalogenated compounds			
Dichloromethane	40	0.04	0.02
1,1-Dichloroethane	57	0.2	0.1
1,2-Dichloroethane	83	0.3	0.15
1,1-Dichloroethene	32	0.1	0.05
1,2-Dichloroethene	49	0.2	0.1
1,2-Dichloropropane	95	1.2	0.6
1,3-Dichloropropene	104–112	1.3	0.65
1,2-Dichlorobenzene	181	102	51
1,3-Dichlorobenzene	173	102	51
1,4-Dichlorobenzene	174	102	51
Halogenated compounds (continued)			
Trihalogenated compounds			
Dibromochloromethane	119	1.5	0.75
Trichloromethane (Chloroform)	61	0.2	0.1
Tribromomethane (Bromoform)	149	3.8	1.9
1,1,1-Trichloroethane	74	0.6	0.3
1,1,2-Trichloroethane	110	1.6	0.8
Trichloroethene	87	1.6	0.8
Tetrahalogenated compounds			
Dichlorodifluoromethane	–30	U	—

5. On 300 mg Carbopack X

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Carbon disulfide[a]	46	6.5	3
Buta-1,3-diene	–4	>25	>17
Benzene	80	10800	5400

[a] At 30°C, 80% relative humidity.

6. On 300 mg Chromosorb 106

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alkanes			
Pentane	35	11.2	56
Hexane	69	60	30
Heptane	98	325	162
Octane	125	2076	1038
Nonane	151	14000	7000
Decane	174	74000	37000
Aromatics			
Benzene	80	53	26
Toluene	111	165	82
Xylene	138–144	1554	777
Ethylbenzene	137	730	365
Trimethylbenzene	165–176	5650	2825
Esters			
Methyl acetate	58	5.2	2.6
Ethyl acetate	71	39	19.5
Propyl acetate	102	297	148.5
Isopropyl acetate	90	147	73.5
n-Butyl acetate	126	1460	730
Isobutyl acetate	115	880	440
tert-Butyl acetate	98	327	163.5

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Glycol ethers			
Methoxyethanol	125	9.6	4.8
Ethoxyethanol	136	150	75
Methoxyethyl acetate	145	1720	860
Ethoxyethyl acetate	156	8100	4050
Ketones			
Acetone	56	2.9	1.45
Butan-2-one (Methyl ethyl ketone)	80	21	10.5
4-Methylpentan-2-one (Methyl isobutyl ketone)	118	490	245
Alcohols			
Ethanol	78	2.4	1.2
Propan-1-ol	97	17	8.5
Propan-2-ol	82	9	4.5
Butan-1-ol	118	96	48
Butan-2-ol	108	60	30
Halogenated compounds			
Tetrachloromethane	76	44	22
1,2-Dichloroethane	84	34	17
1,1,1-Trichloroethane	74	17	8.5

7. On 500 mg PoraPak N

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alkanes			
Pentane	35	8.2	4.1
Hexane	69	32	16
Heptane	98	90	45
Aromatics			
Benzene	80	52	26
Pyridine	116	390	195
Ketones			
Butan-2-one (Methyl ethyl ketone)	80	95	47.5
Alcohols			
Ethanol	78	7.5	3.75
Propan-1-ol	97	40	20
Butan-1-ol	118	10	5
Butan-2-ol	108	5.6	2.8
Octan-1-ol	180	2800	1400
Phenol	182	480	240
Acids			
Acetic acid	116	97	48.5
Nitriles			
Acetonitrile	82	7	3.5
Acrylonitrile	82	7	3.5
Propionitrile	97	23	11.5

8. On 300 mg UniCarb

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Butane	–0.5	1640	820
Pentane	35	63000	31500
Hexane	69	3.9×10^6	1.95×10^6
Benzene	80	1×10^6	500000
Dichloromethane	40	395	197
1,1,1-Trichloroethane	74	17600	8800
Methanol	65	264	132
Ethanol	78	6900	3450
Carbon disulfide[a]	46	26	13

[a] At 30°C, 80% relative humidity.

9. On 600 mg Carbosieve SIII at 20°C

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Alkanes			
Methane	–164	U (0.05)	–
Ethane	–89	0.7	–
Propane	–42	5.1	2.55
Butane	–0.5	37.8	18.9
Pentane	36	360	180
Hexane	69	3000	1500
Heptane	98	6000	3000

10. On 500 mg Carboxen 569 at 20°C

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Aromatics			
Benzene	80	42.5	21.25
Toluene	111	1350	675
Ethylbenzene	137	1250	625
Isopropylbenzene	152	3750	1875
Trimethylbenzene	165–176	3750	1875
Xylene	138–144	5500	2750
Benzaldehyde	179	6000	3000
p-Cymene	177	10000	5000
Propylbenzene	159	11000	5500
Terpenes			
Limonene	176	8000	4000
Terpinene	182	10000	5000

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Aldehydes			
Propanal	48	1.2	0.6
Butanal	75	2.6	1.3
2-Methylpropanal	63	4.25	2.125
Pentanal	103	35	17.5
Hexanal	131	600	300
Heptanal	153	10500	5250
Octanal	169	30000	15000
Nonanal	191	90000	45000
Ketones			
Acetone	56	3.5	1.75
Butan-2-one (Methyl ethyl ketone)	80	2	1
Pentan-2-one	102	10.5	5.25
Pentan-3-one	102	20	10
Hexan-2-one	128	400	200
2-Methylcyclohexanone	–	65000	32500
3-Methylcyclohexanone	–	400	200
4-Methylcyclohexanone	–	400	200
Heptan-2-one	151	60000	30000
Heptan-3-one	147	60000	30000
Heptan-4-one	144	60000	30000
Octan-3-one	167	35000	17500
Halogenated compounds			
Tribromomethane (Bromoform)	149	1000	500
1,1,2,2-Tetrachloroethane	146	2000	1000
Amines			
n-Butylamine	77	5.5	2.75
sec-Butylamine	83	5.2	2.6
Isobutylamine	68	4.1	2.05
tert-Butylamine	44	1.6	0.8
n-Pentylamine	104	95	47.5
Isopentylamine	95	10.5	5.25
n-Hexylamine	129	3×10^6	1.5×10^6
Benzylamine	184	60000	30000
Other			
Carbon disulfide[a]	46	72	36

[a] At 30°C, 80% relative humidity.

11. On 350 mg Carbograph 5TD at 20°C

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Buta-1,3-diene	–4	~10	~7

12. On 600 mg Molecular sieve 13X at 20°C

Compound	b.p. (°C)	Retention volume (L)	SSV (L)
Buta-1,3-diene	–4	>100	>70

13. Breakthrough volumes for water

It is important to use at least twice the volumes below when purging water from the sorbent bed, to ensure complete elution. It is also important that the water is kept in the gas phase.

Sorbent	Temp. (°C)	Breakthrough volume	
		Manufacturers' data (mL/g)[a]	Extrapolated to typical mass of sorbent in ¼" stainless steel tube (mL)
Carbotrap C	20	25	5
Tenax TA	20	65	13
	40	–	7[a]
	60	–	3.6[a]
Tenax GR	20	47	9.4
Carbotrap	20	39	7.8
Carboxen 569	20	60	12
Carbosieve SIII	20	320	64

[a] For 200 mg Tenax TA.

Trademarks

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