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Rapid Separation and Identification of Carbonyl Compounds by HPLC

Application

Environmental

Authors

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Abstract

A fast HPLC method for the analysis of DNPH derivatized carbonyls found in air samples is demonstrated. A 1.8-µm StableBond C18 separated a standard of the major 13 DNPH derivatized carbonyls. An air sample was analyzed in under 10 minutes and found to contain several carbonyls.

Introduction

Carbonyl compounds are important constituents in urban and global atmospheres. In urban atmospheres, these compounds frequently initiate photochemical smog and sustain reactions leading to ozone formation. Outdoor sources include motor vehicle exhaust and other forms of incomplete hydrocarbon combustion. Indoor sources, such as aldehydes found in insulation, tobacco smoke, furniture, and particle board, also contribute to the overall environmental concerns. Measurement of low-level atmospheric carbonyl compounds requires techniques that are sensitive and free of interferences. Unfortunately, many known carbonyl compounds in air samples (for example, formaldehyde and acetone) have no chromophores and are not detected by the UV detector. Thus, for low-molecular-weight aldehydes and ketones in air and water, HPLC methods have been developed for the in-situ derivatization of carbonyls using 2,4-dinitrophenyl-hydrazine (DNPH) (Figure 1).

Official Methods for Carbonyl Compounds

There are several official regulatory agency methods for DNPH-derivatized carbonyls based on the sample matrix (see Table 1).

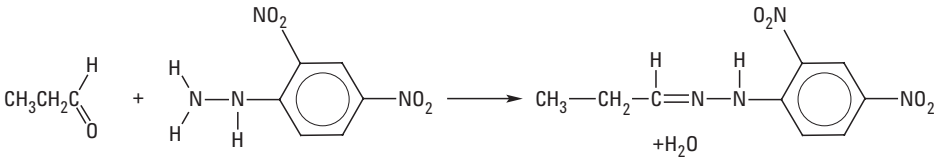

Figure 1. Chemical reaction for derivatizing of carbonyls from air or water samples.

Table 1. Methods for Analysis of DNPH-Derivatized Carbonyls

Method Number	Matrix
EPA TO-11	Ambient air
EPA 8315A	Liquid, solid, and gas samples
ASTM D5197	Ambient air
NIOSH 2016 and 2532	Ambient indoor air
EPA 554	Drinking water

EPA = U.S. Environmental Protection Agency
ASTM = American Society for Testing Materials
NIOSH = National Institute for Occupational Safety and Health

These methods are all variations of the general approach discussed in the experimental section. In some cases, for toxic air samples, an ozone scrubber must be installed prior to the DNPH cartridge since ozone interferes with the carbonyl-DNPH reaction.

Experimental

The carbonyl-containing air sample is passed through a silica gel cartridge that has been coated with DNPH or impinged into an acidified DNPH solution. For water samples, the reaction occurs directly by the addition of DNPH to the water, buffered at pH 3. Carbonyl compounds are rapidly derivatized to hydrazones under these conditions. These colored hydrazones are then eluted from the trapping cartridge using acetonitrile; or for water samples, extracted from solution with methylene chloride. These extracts are then concentrated, reconstituted in a suitable solvent, and injected into a reversed-phase column for separation and quantitation.

Once the derivatized hydrazones are collected and extracted (or eluted), reversed-phase HPLC is the preferred method to analyze these compounds [1-5]. Since the hydrophobicities of the hydrazones vary widely, gradient conditions are required to elute them in a reasonable time.

Results and Discussion

Figure 2 depicts the separation of the major DNPH-derivatized carbonyl standards that are on the list of important environmental toxins. This is a commercially available standard solution (3-µg/mL) purchased from Sigma (St. Louis, MO). The Stable-Bond C18 1.8 µm 4.6 mm × 150 mm column (pn 829975-902) showed excellent resolution,

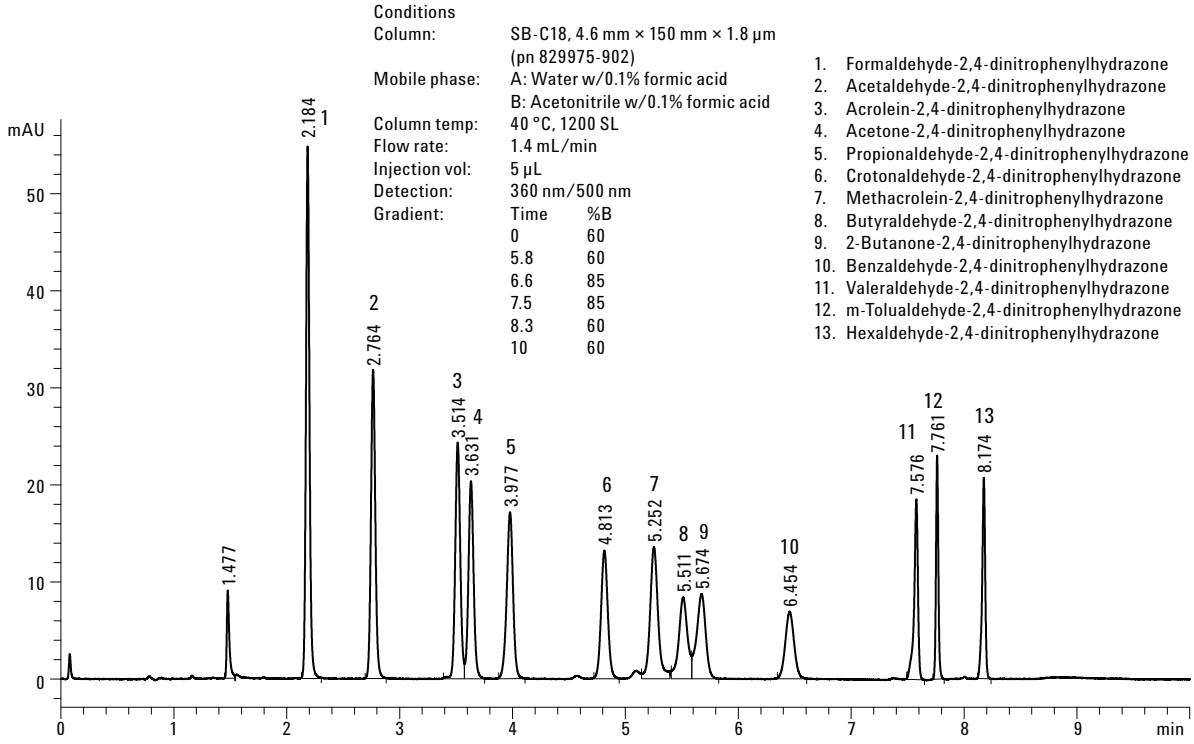

Figure 2. Commercial DNPH standard and analysis conditions.

including partial separation of peaks 8 and 9 of the standard. The separation of 2-butanone-2,4-DNPH and butyraldehyde-2,4-DNPH is noteworthy since this pair is unresolved on a number of reversed-phase columns. The high surface coverage of the C18 phase is partially responsible for the good selectivity. The initial portion of the chromatogram is isocratic, allowing easy transfer of the method to any instrument as well as potential scaling to smaller diameter columns used with mass spectroscopic detection. Higher flow-rate analyses are easily accomplished using the Agilent 1200 System; however, the maximum pressure measured throughout these gradients was approximately 370 bar.

The 60% acetonitrile initial mobile phase composition eluted these nonpolar compounds in a reasonable time. A higher aqueous mobile phase composition results in a loss of resolution of peaks 3 and 4 (acrolein-DNPH and benzaldehyde-DNPH). A higher organic composition compromises the resolution of other peaks, most readily seen in the 7-8-9 group (crotonaldehyde-DNPH, formaldehyde-DNPH, and hexaldehyde-DNPH). A wavelength of 360 nm was used. This wavelength avoids detecting extraneous peaks that usually have stronger absorbance at lower UV wavelengths. Finally, formic acid was added at 0.1 % concentration to both the water and acetonitrile. This will improve the ionization of the analytes when using MS detection, add greater stability to the column, and prevent secondary interactions, while not complicating the mobile phase preparation.

Analysis of Carbonyl Compounds in Ambient Air Samples

Outdoor air was collected on DNPH-coated traps and run through the extraction procedure. This extract was kindly provided by Vermont's Department of Environmental Conservation's (DEC) Environmental Laboratory, Waterbury, VT, USA. The extracts were directly injected into the Agilent StableBond SB-C18 column. A blank extract was also run. The blank was prepared using a collection cartridge with a DNPH loading; however, this cartridge was not carried through the entire sampling process.

Figure 3 shows the HPLC results of an actual air-sample collected near Burlington, Vermont. In this sample, small amounts of formaldehyde, acetaldehyde, and acetone were found. Some unknown peaks were observed that were also present in the blank. One compound eluted about 5.5 minutes and was attributed to unreacted DNPH; the others were unidentified.

Conclusions

Using DNPH collection and HPLC analysis, small amounts of carbonyl-containing compounds in air can be separated and measured in a short time. The Agilent StableBond SB-C18 column gave excellent selectivity and provided a fast separation of the EPA list of carbonyl compounds in about 8 minutes.

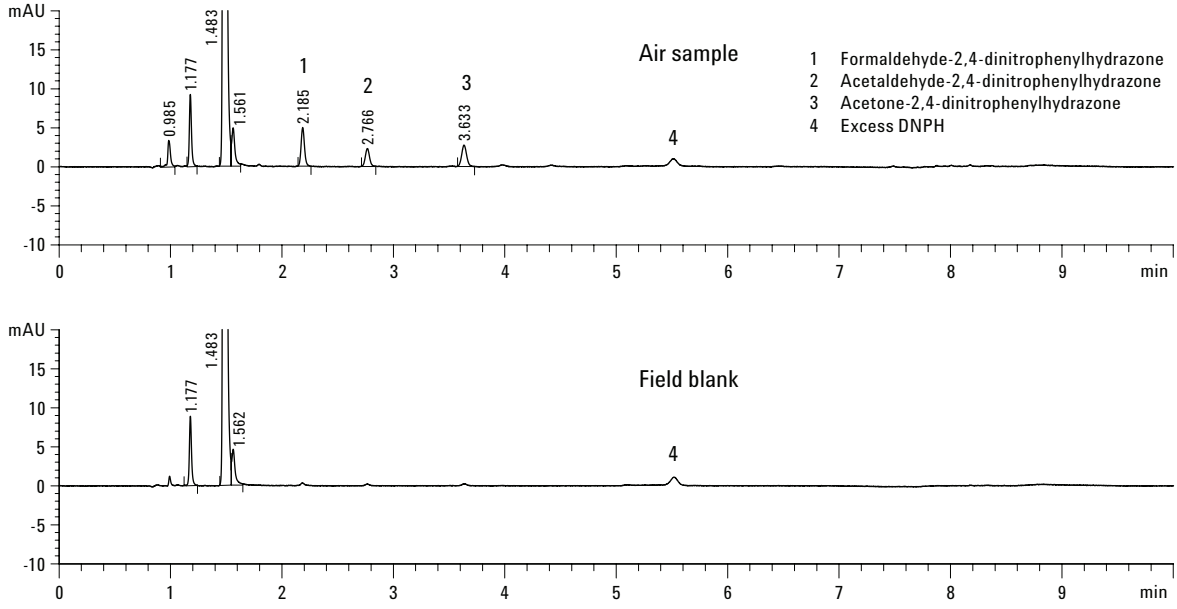

Figure 3. Burlington site top (sample) bottom (field blank) SB-C18 4.6 mm × 150 mm × 1.8 µm.

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Printed in the USA
April 30, 2008
5989-7483EN

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High-Throughput Semiquantitative Screening of Ambient Air Samples by ORS-ICP-MS and Integrated Sample Introduction System (ISIS)

Application

Environmental

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Abstract

A new method has been developed to analyze large numbers of air samples for trace metal content. To aid sample throughput, an Agilent Integrated Sample Introduction System (ISIS) was used with an Agilent 7500c Octopole Reaction System-ICP-MS operating in semiquantitative analysis mode. Using this methodology, 2,500 samples were analyzed for dissolved and extractable elemental composition in approximately 2 weeks. Instrument stability and reliability was demonstrated by good recoveries for the NIST 1643e water CRM. Data handling made use of macros to download and export sample results in a format easily imported by statistical analysis software.

Introduction

ICP-MS is unique it its ability to rapidly determine the approximate elemental composition of unknown samples using a process called “semiquantitative analysis” or “semiquant.” In semiquant, the mass spectrometer is rapidly scanned over the entire mass range, thereby detecting the response for every possible element or isotope. From these responses, semiquant can estimate the relative concentration of each element based on a table of known relative responses for all isotopes. If the concentration of a single or a few components is known, for example, an added internal standard(s), then the concentrations of the remaining elements can be determined.

Traditionally, a limitation of semiquant has been the possibility of uncorrected polyatomic interferences leading to false positive results. While the advent of collision reaction cell (CRC) technology has significantly reduced this problem in quantitative ICP-MS, in most cases, it has not benefited semiquant in the same way. This is because semiquant must be performed with all elements acquired under identical conditions so that response factors can be interpolated across the mass range. Reactive CRC processes create new interferences and therefore cannot be used for all elements simultaneously. However, helium (He) collision mode does not create any new interferences and can be used to reduce virtually all polyatomic interferences using a process called kinetic energy discrimination. Semiquant analysis using He mode only is much less prone to interferences than traditional semiquant and can be used even in complex, unknown matrices. For these reasons, it is particularly useful in surveys where nothing is known about the possible composition of the samples, and therefore calibration for every possible element would be expensive and time consuming.

Since absolute quantitative accuracy and precision are not expected, semiquant can rely on fewer replicates and shorter integration times than quantitative analysis. In this work, the entire mass range is scanned in about 40 seconds. However, in order to take full advantage of the rapid acquisition, equally rapid sample handling is required. By using the Agilent Integrated Sample Introduction System (ISIS) in a segmented flow configuration, sample uptake and rinseout were reduced to about 20 seconds each. The result was a complete, fully automated semiquant survey of unknown samples

in 1 minute per sample.

Midwest Research Institute (MRI)

MRI is an independent, not-for-profit research organization headquartered in Kansas City, Missouri, with laboratory facilities in Palm Bay, Florida, and Rockville, Maryland. MRI also manages the National Renewable Energy Laboratory in Golden, Colorado. The Institute performs research in energy, engineering, life sciences, national security, and defense.

Brevard Teaching and Research Laboratory (BTRL) was one of the earliest laboratories in Florida to acquire ICP-MS and has been using the technique for trace element analysis since 1991. The company was purchased by MRI in 1996 and recently acquired an Agilent 7500c to support research in bioanalytical and forensic applications.

Project Description

MRI was recently contracted to analyze 2,500 air samples collected using a SpinCon Advanced Air Sampler (Sceptor Industries, Kansas City, MO) for elemental composition. The SpinCon is a wet-concentrator air sampler designed to collect particulate matter and other airborne molecular material directly into a collection solution. The composition of the solution can be optimized to maximize recovery of specific analytes. The volume available for elemental analysis was approximately 5 mL; no information about sample composition was provided. After preliminary discussions with the client, it was determined that semiquantitative analysis would be sufficient, provided a measure of data quality could be defined and sample turnaround requirements could be satisfied. Finally, a turnaround time of 1 month was required to meet project scheduling demands.

Experimental

Materials and Methods

An Agilent 7500c ICP-MS with Octopole Reaction System (ORS) and ISIS was configured with an in-house design for rapid sample throughput (see Table 1 for operating parameters). A customized ISIS program was developed using Agilent's multi-pump module (MPM) builder software[1] to control the ISIS valve and pumps for this application. The system was operated in a so-called "stream selection" mode to maximize sample throughput.

Calibration and check solutions were prepared from National Institute of Standards and Technology (NIST) traceable material. The instrument was calibrated before each use with a 29-component multi-element standard prepared from stock solutions obtained from SPEX Certiprep, Inc. (Metuchen, NJ).

NIST standard reference material 1643e, Trace Elements in Water, was diluted 10-fold with 1% nitric

Table 1. Instrumental Parameters for Agilent 7500c ORS ICP-MS

Parameter	Value
RF power	1500 W
Plasma gas flow	15.0 L/min
Auxiliary gas flow	1.0 L/min
Makeup gas flow	0.30 L/min
Helium (ORS) gas flow	2.0 mL/min
Sampling depth	6.0 mm
Spray chamber temperature	7 °C
Number of isotopes acquired	196
Integration time per isotope	100 ms

Sample Preparation

Air samples were collected using the SpinCon air sampler at a rate of 450 L/min directly into a 10-mL volume of a proprietary collection solution. A 5-mL aliquot was shipped to MRI (FL) and stored at 4 °C until processed.

Samples were prepared for dissolved and extractable element analysis in a final matrix of 1% nitric acid by volume. For dissolved element analyses, the sample was mixed thoroughly and a 200-µL aliquot removed then centrifuged at 1,000 rpm for 10 minutes. A 100-µL aliquot of the supernatant was removed and diluted to 1,000 µL with 1% nitric acid directly into an autosampler tube. For extractable element analysis, a 200-µL aliquot of sample was mixed with the processing reagents and shaken at room temperature for 10 minutes to simulate field processing. The sample was then diluted to a final volume of 2,000 µL with 1% nitric acid, centrifuged at 1,000 rpm for 10 minutes, and a 1,000-µL aliquot transferred to an autosampler tube. With this procedure, each sample produced two fractions for analysis, resulting in a total of 5,000 individual analyses.

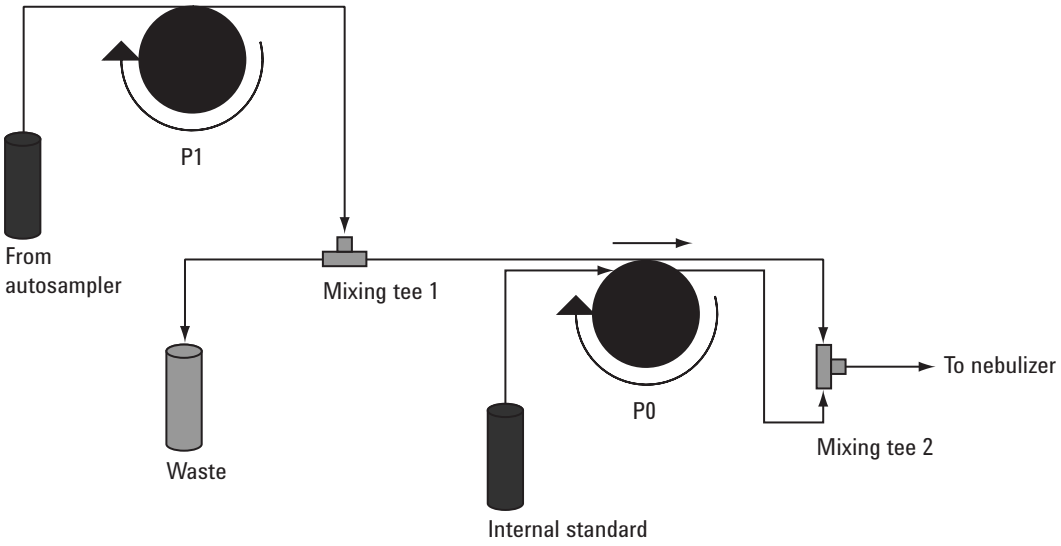
[1] Available from Agilent by special request. The MPM builder allows the user to develop sophisticated, custom ISIS applications and integrate them into routine, automated ICP-MS analysis.

ISIS Programming

In the standard high-throughput ISIS application (Figure 1), the ISIS peristaltic pump (P1) is used to rapidly deliver the sample or rinse solution to the nebulizer peristaltic pump (P0), which operates at a fixed speed. The advantages of this constant flow approach are that the plasma is never disturbed by changes in the sample loading rate and stabilization delays are minimized, since less time is wasted waiting for the pump tubing to stretch and relax, as occurs when the pump speed is changed. A drawback is that at constant flow, approximately 35 seconds are required to move the sample from mixing tee 1 to the nebulizer and allow for signal stabilization. An additional 10 seconds are required to transfer the sample from the autosampler tube to mixing tee 1. With this configuration a stable signal profile is obtained approximately 45 seconds after the autosampler probe enters a sample.

Another consideration when using the standard ISIS configuration is the time penalty incurred to flush the sample still in the pump tubing when the analysis is complete, which is in addition to the normal rinse period. The rinse time required for this application was evaluated with a 1,000-µg/L cobalt standard. Using a cyclonic spray chamber with an internal volume of 50 mL, the rinse time to reduce the signal by three orders of magnitude (< 1 µg/L) was approximately 40 seconds.

Given the constraints of the project, higher throughput was needed. Using standard high-throughput conditions with 40-second read time, the total time required for a single sample is approximately 120 seconds (rinse in/stabilize, 40 seconds; data acquisition, 40 seconds; and rinse out, 40 seconds). Using the CETAC ASX-510 autosampler, a fully loaded tray of 270 samples (three racks with 90 samples each) with calibration and QC checks every 20 samples requires approximately 10 hours, which is longer than the standard 8-hour shift.



P1 - feeds sample or rinse to mixing tee 1
P0 - feeds sample and internal standard to mixing tee 2 and drains spray chamber

Figure 1. Configuration for standard high-throughput application.

Based on previous designs of segmented and continuous flow techniques used at MRI in the past, a customized application (Figure 2) was developed which significantly reduced the time required to rinse the sample in and out of the ICP-MS system. This approach, termed stream-selection, reduces the overall cycle time by eliminating the delay associated with the nebulizer pump, with one major difference from the standard high-throughput approach: a switching valve is required. Like the standard high-throughput application, liquid handling may be performed using one ISIS pump in combination with the on-board nebulizer pump. The preferred configuration does away with the standard nebulizer pump entirely and uses two ISIS pumps for liquid handling.

In this configuration, the sample and rinse streams are independent and the ISIS valve selects which stream goes to the nebulizer. In addition, the flow rate of the sample stream is not coupled to the nebulizer and can be adjusted without disturbing the plasma. With this design, one ISIS pump (Figure 2, P1) is used to feed rinse solution to the nebulizer and add the internal standard. The other ISIS pump (Figure 2, P2) is used to manage the sample. During the load step, the sample is transferred at the maximum uptake rate to the valve. The pump is then slowed to the analysis speed and after a short delay (3 to 5 seconds) to allow the tubing to relax, the sample flow is switched online to the internal standard mixing tee and nebulizer. This arrangement maintains the advantages of constant-flow nebulization, with two additional benefits: the transfer time of the sample to the spray chamber is minimal since there is no pump between the valve and the nebulizer, and rinsing of the spray chamber can begin immediately upon completion of data acquisition by switching the valve back to the load position.

Using this system, a stable signal can be attained in approximately 20 seconds after the autosampler probe enters a sample, and rinse out from 1,000 µg/L to < 1 µg/L can still be accomplished within ~20 seconds of the completion of data acquisition. With a 40-second read time, the total time required for a single sample is reduced from approximately 120 seconds to approximately 70 seconds (rinse in/stabilize, 20 seconds; data acquisition, 40 seconds; and rinse out, 10 seconds). Note that the programmed rinse time is only 10 seconds. Since rinsing of the spray chamber continues to occur during the 20-second load step for the following sample, the effective rinse time is actually 30 seconds. In certain circumstances (for example, samples of similar matrix composition with moderate analyte levels), the programmed rinse time could be eliminated altogether, reducing the cycle time even further. Using the CETAC ASX-510 autosampler, a fully loaded tray of 270 samples (three racks with 90 samples each) with calibration and QC checks every 20 samples requires approximately 6 hours, an improvement of approximately 40%. More significantly, the analysis can be completed in a single shift, with time available for a second run to be prepared and set up for after-hours analysis. A typical work day using this configuration is shown in Table 2, and a total of 540 samples can be processed daily.

Table 2. Typical Work Schedule with the Stream Selection Application

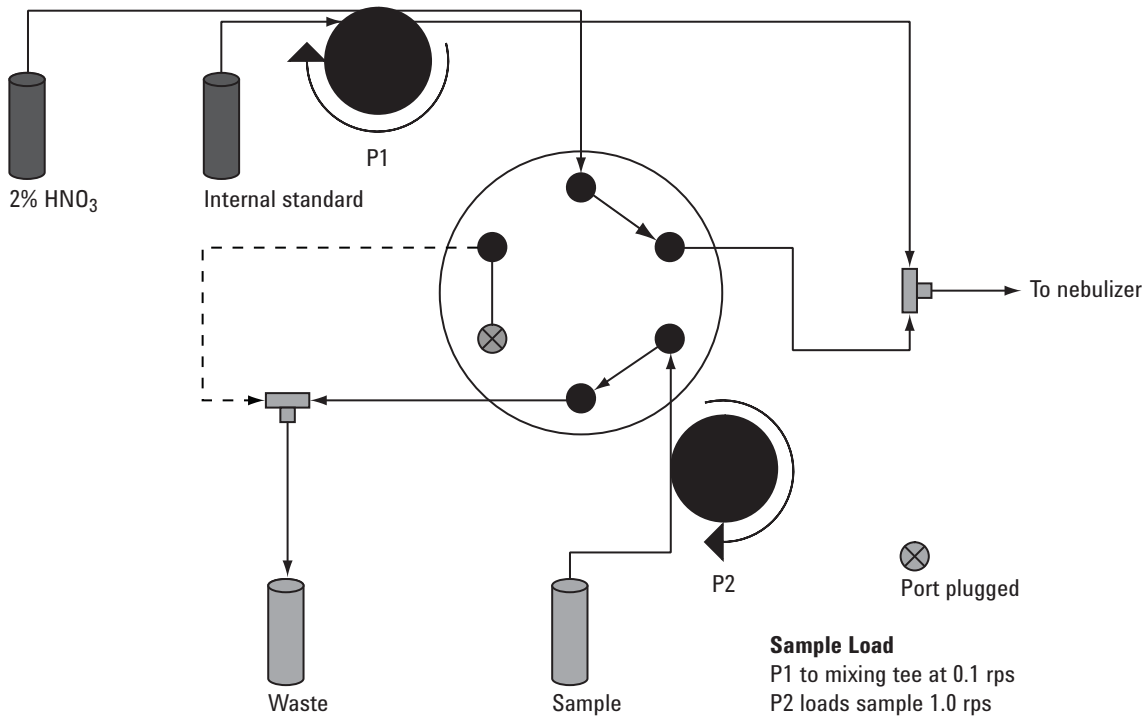
Time	Activity
8:00 - 8:30 a.m.	Instrument maintenance - check cones, pump tubing, and torch. Replace if necessary
8:30 - 9:15 a.m.	Plasma ignition and warm-up, load samples, setup software,download results from previous run
9:15 - 9:30 a.m.	Tuning and performance check
9:30 a.m.	Start run #1 (270 samples)
10 a.m. - 2:30 p.m.	Sample preparation for second run
3:30 p.m.	First run complete
3:30 - 4:00 p.m.	Instrument maintenance - check cones, pump tubing, and torch
4:00 - 4:30 p.m.	Plasma ignition and warm-up, load samples, set up software
4:30 - 4:45 p.m.	Tuning and performance check
4:45 p.m.	Start run #2 (270 samples)
10:45 p.m.	Run complete, instrument to standby

Results and Discussion

SRM Results

NIST 1643e was read 72 times over the course of the study. A control chart for six elements, selected to cover the full range of concentrations and shown with target recovery limits of ± 30%, is presented in Figure 3. Actual recoveries and %RSDs are presented in Table 3. Note that measured concentrations were actually 10 times lower than the certificate value and these results are corrected for dilution.

2A - Sample Load



2B - Sample Inject

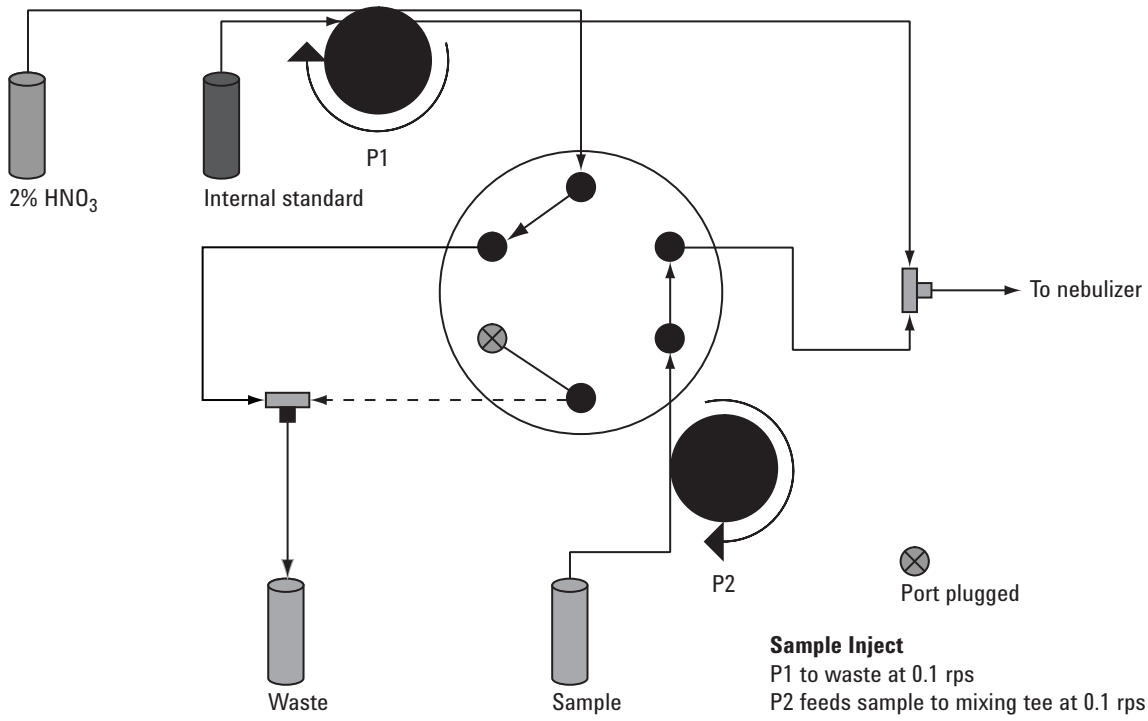


Figure 2. Configuration for stream selection application.

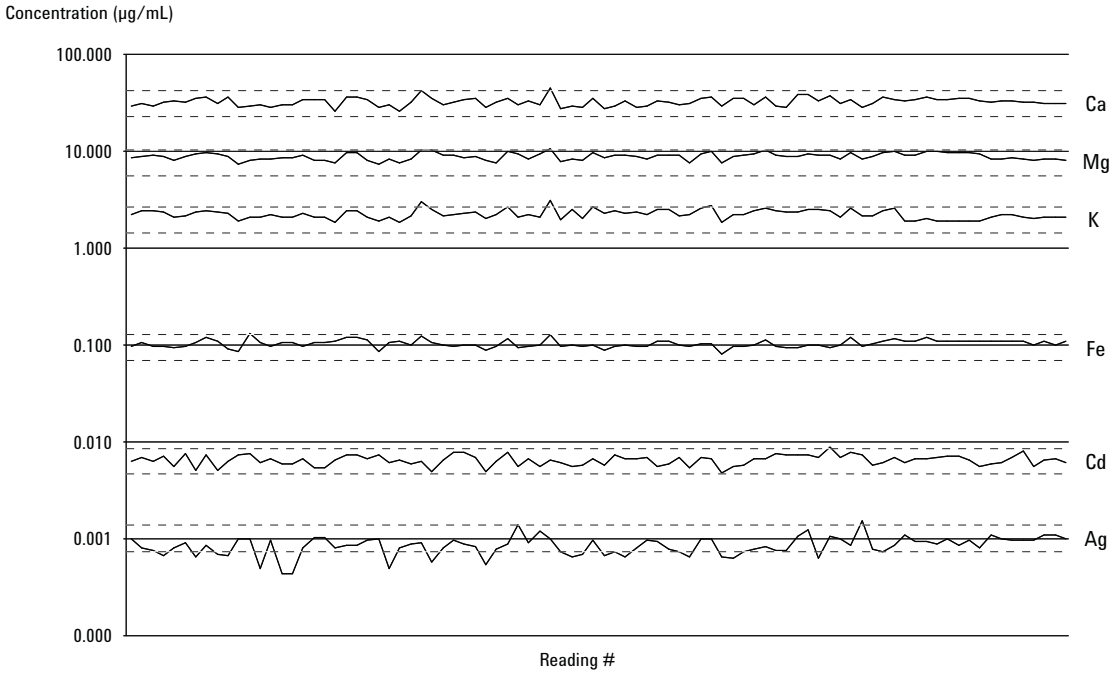


Figure 3. Long-term stability of six representative elements in NIST 1643e (diluted 10x) covering the range of concentrations.

Table 3. Recovery of Certified Concentrations in NIST 1643e, n = 72

Element	Expected (mg/L)	Actual (mg/L)	%RSD (n = 72)	Recovery (%)
Be	0.014	0.014	19	98.5
Na	20.74	22.09	11	107
Mg	8.037	8.867	8.5	110
Al	0.142	0.148	25	105
K	2.034	2.246	11	110
Ca	32.30	32.54	10	100
V	0.038	0.039	8.9	103
Cr	0.020	0.021	11	106
Mn	0.039	0.041	8.4	105
Fe	0.098	0.104	9.0	106
Co	0.027	0.027	7.7	101
Ni	0.062	0.063	10	101
Cu	0.023	0.022	15	94.1
Zn	0.079	0.079	12	101
As	0.060	0.064	12	106
Rb	0.014	0.013	16	92.2
Sr	0.323	0.312	6.4	96.6
Mo	0.121	0.118	7.7	97.4
Ag	0.001	0.001	22	81.4
Cd	0.007	0.007	12	99.3
Sb	0.058	0.056	10	96.3
Ba	0.544	0.516	15	94.9
Tl	0.007	0.007	25	94.5
Pb	0.020	0.018	19	88.6

Sample Results

Samples were analyzed without incident for the duration of the project. Using this approach, 2,500 samples were analyzed for dissolved and soluble element composition (a total of 5,000 analyses) in approximately10 days. Analytical results were exported to a dedicated database using post-run macros for statistical analysis.

As expected, the elemental distribution in most samples was dominated by the mineral elements, with Na, K, Ca, and Mg accounting for > 98% of the total elemental composition. Elements typically associated with urban airborne particulates, such as aluminum, iron, and zinc, were found in moderate (> 0.5 mg/L) to high (> 1 mg/L) concentrations in all samples. This was expected since sampling took place primarily in urban areas.

In all cases, measured concentrations were higher in the extractable analysis compared to the dissolved analysis. This was expected since particulate matter in the sample was expected to release loosely bound elemental components to the extracting solvent. Several samples were found to contain levels of toxic metals at least 10 times higher than the average value, but no conclusions can be made since site-specific information was not provided.

Conclusions

It has been demonstrated that with careful selection of the collection fluid, samples collected by the SpinCon advanced air sampler are directly compatible with trace element analysis. By using semiquant analysis in He-only mode, with custom ISIS programming to maximize throughput, it was possible to analyze 2,500 samples for dissolved and extractable elemental composition in approximately 2 weeks, meeting the project turnaround time requirements. This ISIS program could also be used to improve throughput in quantitative applications with similar results. The performance of the Agilent 7500c system was stable and reliable for the duration of the project as demonstrated by good recoveries for the NIST 1643e water CRM. The use of macros to download and export sample results significantly reduced the time spent preparing analysis reports and produced data in a format easily imported by our statistical analysis software.

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Printed in the USA
January 30, 2007
5989-6123EN

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Screening for 171 Volatile Organic Air Pollutants Using GC/MS with Deconvolution Reporting Software and a New Indoor Air Toxics Library

Application

Environmental

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Abstract

A retention-time-locked mass spectral database was created specifically for indoor air analysis by thermal desorption/gas chromatography/mass spectroscopy (TD/GC/MS). This Indoor Air Toxics Database contains locked retention times and mass spectra for 171 volatile and semivolatile organic compounds that are targets in various indoor air methods. In combination with Agilent's Deconvolution Reporting Software (DRS), it is possible to identify any of these compounds in just 2 to 3 minutes after a TD/GC/MS analysis. A key feature of DRS is the ability to deconvolute overlapping mass spectra so that unresolved GC peaks can be identified reliably. Agilent's DRS generates a report that combines results from three data analysis programs – the Agilent ChemStation, the Automated Mass Spectral Deconvolution and Identification System, and the National Institute of Standards and Technology MS Search Program. Air samples from an office building and a carpet warehouse were collected on Tenax TA-packed TD tubes and were analyzed by TD/GC/MS. Using the Indoor Air Toxics Database, DRS was able to identify more than 80 compounds in the office air and 102 in the carpet store air. Data analysis was automated and required about 3 minutes per sample to complete.

Introduction

At sea-level and 15 °C, air is 99.9997147% nitrogen, oxygen, argon, carbon dioxide, neon, methane, helium, krypton, hydrogen, and xenon [1]. The remaining constituents are mostly organic chemicals that can number into the thousands. Some of these are either irritating or toxic to people who are exposed to them. Indoor air usually contains more volatile and semivolatile organic compounds (VOCs and SVOCs) than outdoor air. For example, the USEPA's "Total Exposure Assessment Methodology studies found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas" [2].

Sources for VOCs in homes and offices include building materials such as plywood, particle board, and paints; furnishings such as carpets, furniture, and office machines; stored fuels, solvents, aerosol sprays, cleaning products and household chemicals; heating and cooling systems; manufacturing processes; and even dry-cleaned clothing. Since most people in industrialized countries spend 80% to 90% of their time in a home, school, office building, or a vehicle, indoor air pollution is a major concern.

This application discusses a new method for the analysis of 171 naturally occurring and anthropogenic VOCs and SVOCs that are found in air. The focus is primarily on toxic compounds found in indoor air that may contribute to sick-building syndrome or cause untoward health affects.

This new method makes it possible to screen GC/MS chromatograms for all 171 toxic VOCs in 2 to 3 minutes after data acquisition. The method

uses Agilent's Deconvolution Reporting Software (DRS) [3–9] together with a mass spectral database that contains the locked retention times (RTs) for each of the 171 analytes.

While the method can accommodate any means for VOC sample introduction, it was designed for use with the Markes International UNITY™ Thermal Desorber. Air samples are conveniently collected on TD tubes that may be packed with one or more sorbents. In UNITY, these tubes are heated under a reverse flow of carrier gas to sweep the trapped volatiles into a sorbent-packed cold trap. The concentrated sample is then transferred to the GC column by heating the cold trap rapidly under a reverse flow of helium.

Experimental

Table 1 lists the instrumentation, software, and analytical parameters used by Agilent for air analysis with DRS and the new Indoor Air Toxics Library.

Table 1. Instrumentation and Conditions of Analysis

Thermal desorption system	**Markes UNITY with a Markes UltrA™ autosampler**
Prepurge time	1.0 min
Primary desorb	280 °C for 5.0 min
Trap low temp	–10 °C
Trap desorb	300 °C for 3.0 min
Trap	General purpose hydrophobic
Flow path temp	140 °C
Nominal carrier gas pressure	30.9 psi
Desorb flow	20 mL/min
Split ratio	Varies from 50:1 to splitless depending upon the sample
Sample tube	3.5-inch × 0.25-inch deactivated stainless steel packed with Tenax TA
Sample pump	**SKC Pocket Pump 210-1002 (SKC, Inc. Eighty Four, PA USA)**
Software for pump control	SKC DataTrac software for Pocket Pump Ver. 2.07
Pump flow rate	200 mL/min
Gas chromatograph	**Agilent 6890N**
Column	Agilent 60 m × 0.25 mm × 1.4 µm DB-VRX (p/n 122-1564)
Carrier gas	Helium in the constant pressure mode
Retention time locking	Toluene locked to 12.468 min or Toluene-d8 locked to 12.366 min (nominal column head pressure = 30.91 psi)
Oven temperature program	45 °C (3 min), 10 °C/min to 190 °C (0 min), 20 °C /min to 250 °C (8 min)
Mass selective detector	**Agilent 5975 inert**
Tune file	Atune.u
Mode	Scan
Scan range	33 to 300 u
Source, quad, transfer line temperatures	230, 150, and 260 °C, respectively
Solvent delay	0.00 min
Multiplier voltage	Autotune voltage
Software	
GC/MSD ChemStation	Agilent p/n G1701DA (Ver. D02.00 sp1 or higher)
DRS	Agilent p/n G1716AA (Ver. A.03.00) DRS
Library searching software	NIST MS Search (Ver. 2.0d or greater) (comes with NIST '05 mass spectral library — Agilent p/n G1033A)
Deconvolution software	Automated Mass Spectral Deconvolution and Identification Software (AMDIS_32 Version 2.62; comes with NIST'05 mass spectral library — Agilent p/n G1033A)
MS libraries	NIST'05 Mass Spectral Library (Agilent p/n G1033A) and Agilent Indoor Air Toxics Libraries in Agilent and NIST formats (p/n G1673AA)
DRS setpoints	
Minimum match factor	60
RI window	10 (seconds)
Component width	12
Adjacent peak subtraction	one
Resolution	High
Sensitivity	High
Shape requirements	High
Use uncertain peaks?	Yes and no. Samples were analyzed under both conditions

Sample Collection

Indoor air samples were collected on Tenax® TA-packed TD tubes by active sampling using the SKC pocket pump. Six- or twelve-liter air samples were collected by pumping at 200 mL/min for either 30 minutes or 1 hour. Tenax TA is classified as a weak sorbent and is not very effective at trapping compounds that are less volatile than n-heptane. As seen in Figure 1, many of the more volatile compounds were identified by this procedure even though they were not trapped quantitatively.

Results and Discussion

Figure 1 shows a GC/MS chromatogram for a sample of air collected inside of an office building. While there are only about a dozen major peaks in the chromatogram, there are numerous minor ones. It is usually easy to identify the larger peaks with conventional GC/MS analysis, especially when they are well separated chromatographically. However, the toxicity of airborne chemicals varies over many orders of magnitude, and some of the smaller peaks may be far more significant than the larger ones. As seen in the inset, many peaks are poorly resolved while others may be completely obscured by much larger overlapping analytes. It is a tedious process to identify all of the important analytes in such chromatograms. DRS is designed to simplify this process while producing far more accurate peak identifications.

DRS

Agilent's DRS combines the results from three complimentary GC/MS data analysis packages. First, the GC/MS ChemStation software performs a normal quantitative analysis for all calibrated compounds using a target ion and up to three qualifiers. An amount is reported for all calibrated compounds that are detected.

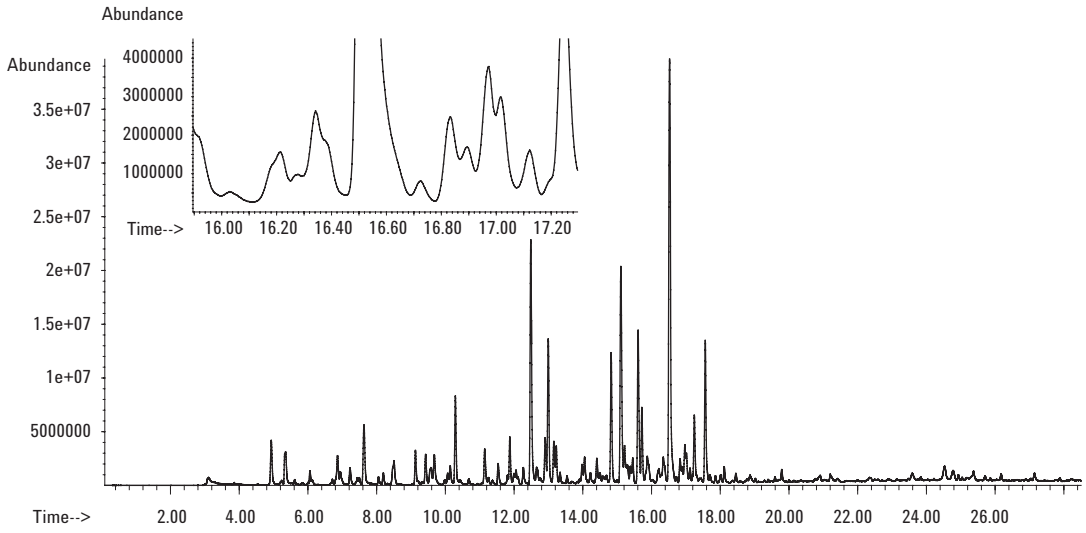

Figure 1. TD/GC/MS chromatogram of an air sample collected in an office building. The inset shows that many peaks are poorly resolved and could be difficult to identify with normal GC/MS data analysis.

Then, DRS sends the data file to a spectral deconvolution package developed by the National Institute for Standards and Technology (NIST). This software, called Automated Mass Spectral Deconvolution and Identification System (AMDIS), deconvolutes the spectra of overlapping chromatographic peaks [10]. While a thorough discussion of deconvolution is beyond the scope of this paper, the basic principles are illustrated in Figure 2.

The chromatographic peak shown in black looks Gaussian, but it is actually the result of at least three compounds that were only partially resolved. The spectrum at the apex of this peak is composed of ions from all three compounds, some of which are common to two or three of the overlapping analytes. AMDIS deconvolutes the chromatogram and pulls out "cleaned spectra" from the overlapping peaks. In most cases, AMDIS is very successful at isolating a compound's spectrum from column bleed, other analytes, and co-extracted interferences, even when interference abundances are far greater than the target analyte.

Using the deconvoluted full spectrum, AMDIS searches each peak against Agilent's RTL Indoor Air Toxics Library and reports a hit if the match quality exceeds a user-settable threshold. As a further requirement for compound identification, the user can require the analyte's RT to fall within a specified time window. Because retention time locking (RTL) is used to reproduce the database RTs with high precision, this window can be quite small – typically 10 to 20 seconds.

As a confirmation step, the deconvoluted spectra of all AMDIS hits are searched against the 163,000-compound NIST mass spectral library; for this step, there is no RT requirement. More details about DRS can be found in earlier publications [3–9].

Figure 3 shows the report generated by DRS for the office air sample shown in Figure 1. Each identified compound is reported with its RT, CAS #, and compound name. If the sample contains an internal standard and if the compound has been calibrated, an amount is reported in the fourth column. The amounts are calculated by the ChemStation software when it identifies a compound. As shown in Figure 3, values of "0" are reported when the ChemStation finds the compound but there is no internal standard and/or calibration table. For this example, a minimum match factor of 60 was required by AMDIS but only one match value was less than 70 and only six more were less than 80. Column 6 reports the difference (in seconds) between each analyte's RT in the current chromatogram and the Indoor Air Toxics RTL Database. For this analysis, AMDIS was configured so that peaks had to elute within 10 seconds of their database RT to be identified as a hit. It is straightforward to match the database RTs using RTL, so most of the differences were well under the 10-second requirement.

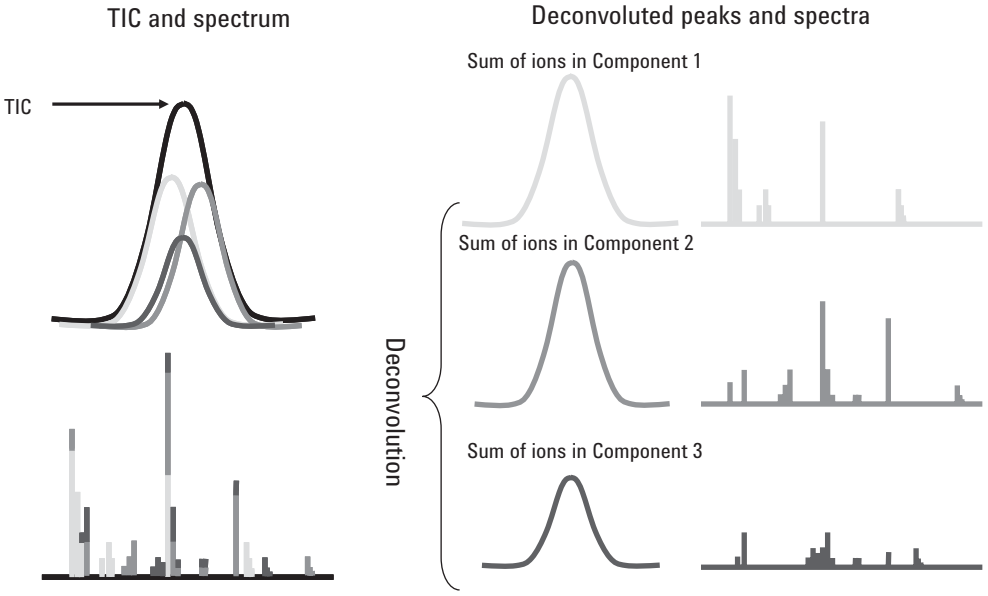

Figure 2. An illustration showing how AMDIS deconvolution software can extract "clean" spectra from unresolved chromatographic peaks. The deconvoluted spectra can be searched against normal mass spectral libraries with a high probability of finding a good match.

MSD Deconvolution Report
Sample Name: Sample 1
Data File: C:\Documents and Settings\lfs-wyliep\My Documents\My GC_MS Data\Thermal Desorption Data August 05\Aug 11_05\Little Falls Office Air 12 L near Sheila.D
Date/Time: 02:36 PM Thursday, Jun 15 2006

The NIST library was searched for the components that were found in the AMDIS target library.

			Agilent	AMDIS		NIST	
R.T.	Cas #	Compound Name	ChemStation Amount (ng)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
3.8545	75070	Acetaldehyde	0	100	3.6	97	1
4.3465	74839	Bromomethane		87	3.1	97	1
5.1977	75694	Trichlorofluoromethane	0	82	4.6	63	1
5.2307	67630	2-Propanol		95	4.8	92	1
5.3256	67641	Acetone		94	4.4	89	1
5.8065	109875	Dimethoxymethane		80	4.5	86	1
5.8447	75650	tert-Butanol		97	3.8	90	1
5.9033	107131	Acrylonitrile		72	4.8	96	1
6.0007	75092	Dichloromethane	0	100	3.8	93	1
6.2969	75150	Carbon disulphide		99	3.9	95	1
6.4849	71238	1-Propanol		97	5.3	88	1
6.8607	107835	2-Methylpentane		99	2.4	95	1
6.9439	1634044	Methyl tert-butylether	0	92	2.2	93	1
7.227	96140	3-Methylpentane	0	100	3.2	94	1
7.6239	110543	n-Hexane		97	3.0	87	1
7.6543	78933	2-Butanone (MEK)		95	4.0	92	1
8.056	141786	Ethyl acetate	0	98	3.0	95	1
8.0896	67663	Chloroform		96	3.0	93	1
8.472	96377	Methylcyclopentane	0	92	2.8	87	1
8.5039	109999	Tetrahydrofuran (THF)	0	100	2.9	96	1
8.9263	107062	1,2-Dichloroethane		96	2.5	91	1
9.0558	71556	1,1,1-Trichlorethane	0	97	1.8	91	1
9.1309	71363	1-Butanol	0	100	2.9	90	1
9.3141	108214	Isopropyl acetate		99	2.1	95	1
9.3658	563804	3-Methyl-2-butanone		82	2.4	91	1
9.4254	110827	Cyclohexane		73	1.8	66	5
9.4332	591764	2-Methylhexane		93	2.3	83	1
9.5361	56235	Tetrachloromethane	0	98	1.9	96	1
9.5869	71432	Benzene	0	98	2.1	94	1
9.6552	107982	1-Methoxy-2-propanol		76	2.8	87	1
9.6749	589344	3-Methylhexane	0	100	1.0	94	1
10.1401	540841	2,2,4-Trimethylpentane	0	97	1.2	94	1
10.2925	142825	n-Heptane		96	1.4	93	1
10.4336	79016	Trichloroethene	0	98	1.4	94	1
10.5149	75274	Bromodichloromethane		80	2.2	81	5
10.6556	123911	1,4-Dioxane		81	2.3	89	3
10.677	109604	Propyl acetate	0	97	1.9	94	1
10.6903	80626	Methyl methacrylate	0	97	1.0	87	1
11.1379	108872	Methylcyclohexane	0	99	0.9	94	1
11.5350	108101	4-Methyl-2-pentanone (MIBK)	0	99	1.3	92	1
11.8726	71410	1-Pentanol	0	100	1.2	94	1
12.2704	589811	3-Methylheptane		97	0.6	94	1
12.4818	108883	Toluene		99	0.8	94	1

Figure 3. DRS report for a sample of air collected inside of an office building. A TD/GC/MS chromatogram of this sample is shown in Figure 1. In about 3 minutes, nearly 90 compounds were identified in this sample using DRS and Agilent's Indoor Air Toxics Database.

12.6892	111660	1-Octene		89	0.6	80	1
12.7378	68122	N,N-Dimethylformamide		71	7.3	93	1
12.9064	111659	n-Octane		100	0.9	95	1
12.9954	66251	n-Hexanal		99	1.3	90	1
13.2226	123864	n-Butyl acetate	0	98	-0.1	95	1
13.5330	127184	Tetrachloroethene	0	94	-0.1	92	1
14.4034	111273	1-Hexanol		94	-0.2	83	3
14.5296	108907	Chlorobenzene		86	0.1	92	1
14.6878	2216333	3-Methyloctane	0	98	-0.7	93	1
14.8209	100414	Ethylbenzene	0	99	-0.0	96	1
14.9607	108930	Cyclohexanol		61	-7.2		
14.9607	53771883	Cyclopentane, 1-methyl-3-(1-methylethyl)-				74	1
15.1076	108383	m-Xylene	0	100	0.3	95	1
15.109	106423	p-Xylene	0	100	-0.9	96	1
15.297	111842	n-Nonane	0	80	-0.1	83	1
15.6080	100425	Styrene	0	100	-0.2	96	1
15.6329	108941	Cyclohexanone	0	93	0.1	84	1
15.7194	95476	o-Xylene	0	99	-0.1	95	1
16.2615	98828	Isopropylbenzene (cumene)	0	99	-1.2	86	4
16.5140	80568	alpha-Pinene		99	-1.1	93	1
16.8949	108952	Phenol		83	0.2	86	2
16.9587	103651	n-Propylbenzene		82	-0.0	81	1
16.9629	79925	Camphene	0	98	-1.2	85	1
17.1163	620144	m-Ethyltoluene	0	99	-1.3	96	2
17.3947	108678	1,3,5-Trimethylbenzene		93	-0.7	87	4
17.5571	98839	alpha-Methylstyrene (2-propenyl benzene)		73	-0.9	69	5
17.5620	127913	beta-Pinene	0	99	-1.1	94	1
17.6099	611143	o-Ethyltoluene		76	-1.0	75	4
17.7008	124130	n-Octanal		95	1.2	89	1
17.9831	95636	1,2,4-Trimethylbenzene	0	97	-1.4	93	3
18.018	104767	2-Ethyl-1-hexanol	0	96	-1.0	94	1
18.1096	13466789	delta-3-Carene	0	98	-1.4	94	1
18.3657	541731	1,3-Dichlorobenzene	0	98	6.6	94	1
18.3666	106467	p-Dichlorobenzene	0	99	-0.9	91	3
18.4226	99876	p-Isopropyltoluene (p-Cymene)		89	1.0	91	1
18.4556	5989275	Limonene	0	98	-1.5	93	1
18.6311	526738	1,2,3-Trimethylbenzene		82	-1.2	79	2
19.1411	95136	Indene		81	-1.1	94	4
19.3949	98862	Acetophenone	0	99	-1.2	94	1
19.5943	124196	n-Nonanal	0	97	1.0	95	1
21.202	112312	n-Decanal	0	100	0.4	94	1
21.7534	91203	Naphthalene		94	-2.3	89	1
21.8340	87683	Hexachlorobutadiene		82	-1.2	56	3
23.8346	629594	n-Tetradecane	0	96	-3.6	90	1
25.3658	629629	n-Pentadecane	0	80	-4.3	92	1
26.1682	128370	2,6-di-t-Butyl-4-methylphenol (BHT)		98	-4.7	88	2
27.1476	544763	n-Hexadecane		99	-5.4	91	1

Figure 3. Continued

As a further check on a peak's identity, the deconvoluted spectrum of each hit is searched against the NIST'05 mass spectral library, which contains more than 163,000 compounds. If the compound identified by AMDIS (using the Indoor Air Toxics Library) is among the top 100 NIST'05 library hits, its match factor and hit number are reported in columns 7 and 8, respectively. For the office air sample, the first NIST library match corresponded with the AMDIS results most of the time; in all cases the best hit was among the top 5.

Isomers and compounds with similar structures can have virtually identical mass spectra. So it is not expected that the first NIST library hit will always be the best match for the deconvoluted spectrum. When searching the Indoor Air Toxics Library, DRS takes advantage of RT filtering, which helps to eliminate isomers and other compounds with similar structures and mass spectra. There is no RT requirement for the NIST'05 library search, so structural isomers might have equal or even slightly better NIST library matches than the true compound. If the NIST hit number in column 8 is large (perhaps greater than 5 or 10), it is wise to look at the AMDIS match value and RT difference. If the match value is low or the RT difference is high, manual peak evaluation is recommended. For most samples, no manual re-evaluation of the results is needed. An exception is discussed below.

Analysis of Air from a Carpet Store

Figure 4 shows a chromatogram obtained for an air sample that was collected inside a carpet warehouse. The warehouse had rolls of new carpet stacked floor to ceiling along each wall. A 12-L air sample was collected on a Tenax tube over a 1-hour period from random places inside the warehouse. Analysis was performed using the Markes UNITY Thermal Desorber in the splitless mode.

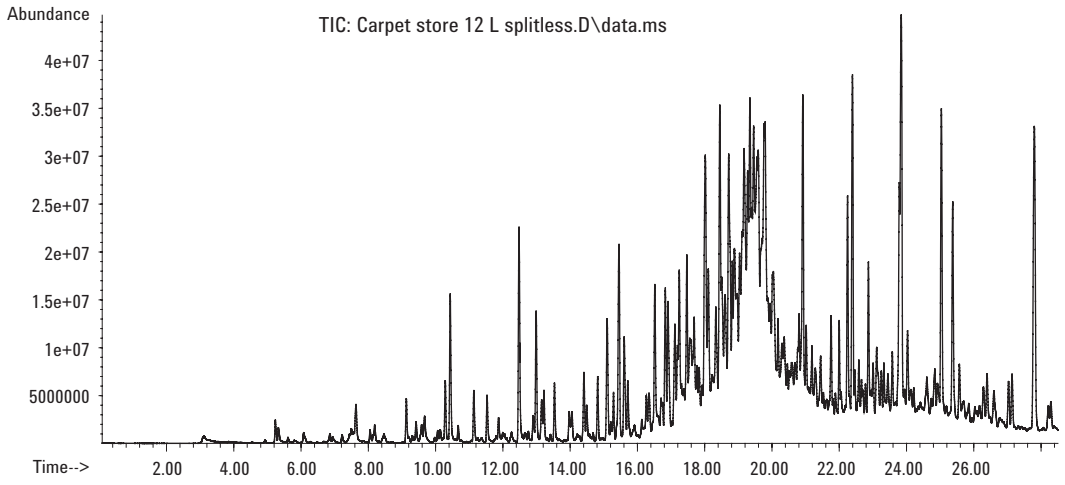

Figure 4. TD/GC/MS chromatogram of a 12-L air sample collected in a carpet store using a Tenax TA TD tube. Figure 5 shows the DRS report for this sample.

MSD Deconvolution Report
Sample Name: Sample 1
Data File: C:\Documents and Settings\lfs-wyliep\My Documents\My GC_MS Data\Thermal Desorption Data August 05\Aug 12_05\Carpet store 12 L splitless.D
Date/Time: 01:32 PM Friday, Jun 16 2006

The NIST library was searched for the components that were found in the AMDIS target library.

			Agilent	AMDIS		NIST	
R.T.	Cas #	Compound Name	ChemStation Amount (ng)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
3.8527	75070	Acetaldehyde	0	94	3.5	97	1
4.3398	74839	Bromomethane		74	2.7	92	1
5.1975	75694	Trichlorofluoromethane		75	4.6	82	2
5.2367	67630	2-Propanol	0	100	5.1	96	1
5.3270	67641	Acetone		97	4.5	91	1
5.4380	110009	Furan		64	3.1	96	15
5.7943	109875	Dimethoxymethane		100	3.7	94	1
5.8426	75650	tert-Butanol	0	99	3.6	92	1
5.8901	107131	Acrylonitrile		71	4.0	93	1
5.9976	75092	Dichloromethane		89	3.6	82	1
6.2886	75150	Carbon disulphide		99	3.4	95	1
6.4757	71238	1-Propanol	0	99	4.7	92	1
6.8530	107835	2-Methylpentane	0	100	1.9	95	1
6.9453	1634044	Methyl tert-butylether		92	2.3	96	1
7.2185	96140	3-Methylpentane	0	100	2.5	96	1
7.2754	108054	Vinyl acetate		87	3.3	93	2
7.4955	123728	n-Butanal		65	2.3	65	7
7.6153	110543	n-Hexane		89	2.5	79	2
7.6392	78933	2-Butanone (MEK)		87	3.1	90	1
8.0532	141786	Ethyl acetate	0	100	2.7	96	1
8.090	67663	Chloroform	0	96	3.0	92	1
8.1464	96333	Methyl acrylate	0	98	3.1	96	1
8.468	96377	Methylcyclopentane	0	90	3.0	84	1
8.5105	109999	Tetrahydrofuran (THF)		85	3.3	91	1
8.9170	107062	1,2-Dichloroethane		82	1.9	91	1
9.052	71556	1,1,1-Trichlorethane	0	93	1.6	74	1
9.1277	71363	1-Butanol	0	100	2.7	90	1
9.3090	108214	Isopropyl acetate		99	1.8	95	1
9.3634	563804	3-Methyl-2-butanone		68	2.2	62	78
9.4194	591764	2-Methylhexane		93	1.5	84	1
9.4233	110827	Cyclohexane		89	1.7	75	1
9.5320	56235	Tetrachloromethane	0	99	1.7	96	1
9.5854	71432	Benzene	0	100	2.0	95	1
9.6547	107982	1-Methoxy-2-propanol	0	81	2.7	88	1
9.6705	589344	3-Methylhexane	0	100	0.8	94	1
10.1347	540841	2,2,4-Trimethylpentane		81	0.9	94	1
10.2907	142825	n-Heptane		85	1.3	86	1
10.384	78875	1,2-Dichloropropane	0				
10.4263	79016	Trichloroethene	0	100	0.9	95	1
10.6464	123911	1,4-Dioxane		93	1.7	94	1
10.6681	109604	Propyl acetate	0	98	1.0	97	1
10.6875	80626	Methyl methacrylate		84	0.8	84	1
11.140	108872	Methylcyclohexane	0	98	1.0	94	1
11.5293	108101	4-Methyl-2-pentanone (MIBK)	0	100	1.0	92	1
11.7420	624920	Dimethyldisulphide		70	1.5	88	1
11.8714	71410	1-Pentanol	0	98	1.2	92	1
11.8873	107926	Butyric acid		67	5.3	88	2
12.2602	589811	3-Methylheptane		89	0.0	91	1
12.4812	108883	Toluene		99	0.8	94	1
12.6712	111660	1-Octene		84	-0.5	82	7
12.9043	111659	n-Octane		92	0.7		

Figure 5. DRS report for a sample of air collected inside a carpet store. A TD/GC/MS chromatogram of this sample is shown in Figure 4. In about 3 minutes, more than 100 compounds were identified in this sample using DRS and Agilent's Indoor Air Toxics Database.

12.9043	691372	1-Pentene, 4-methyl-				80	1
12.9861	66251	n-Hexanal		99	0.8	91	1
13.2195	123864	n-Butyl acetate	0	99	-0.3	96	1
13.5377	127184	Tetrachloroethene	0	99	0.2	97	1
14.4028	111273	1-Hexanol		84	-0.2	81	6
14.5265	108907	Chlorobenzene		94	-0.1	89	1
14.6812	2216333	3-Methyloctane		96	-1.1	81	1
14.8181	100414	Ethylbenzene	0	98	-0.2	95	1
15.0870	108930	Cyclohexanol		68	0.4	76	2
15.0958	108383	m-Xylene	0	100	-0.4	95	3
15.103	106423	p-Xylene	0				
15.2896	111842	n-Nonane		100	-0.6	95	1
15.4525	111762	2-Butoxyethanol		98	0.6	89	1
15.6036	100425	Styrene	0	100	-0.4	95	1
15.6243	108941	Cyclohexanone	0	97	-0.4	94	1
15.7114	95476	o-Xylene	0	99	-0.6	96	1
16.2610	98828	Isopropylbenzene (cumene)	0	98	-1.3	88	4
16.5167	80568	alpha-Pinene	0	99	-0.9	95	1
16.7452	871830	2-Methylnonane	0	84	-1.1	80	1
16.9015	108952	Phenol	0	98	0.6	92	2
16.9413	103651	n-Propylbenzene		94	-1.1	89	1
17.0899	95498	2-Chlorotoluene	0	94	0.5	82	1
17.1177	620144	m-Ethyltoluene		93	-1.2	91	3
17.3867	108678	1,3,5-Trimethylbenzene	0	98	-1.2	94	1
17.4708	124185	n-Decane	0	96	-1.3	88	1
17.4711	872059	1-Decene		72	8.5	69	78
17.5598	127913	beta-Pinene	0	86	-1.2	79	2
17.6038	611143	o-Ethyltoluene	0	97	-1.4	93	1
17.6819	124130	n-Octanal		83	0.1	77	2
17.9868	95636	1,2,4-Trimethylbenzene	0	97	-1.2	92	2
18.0191	104767	2-Ethyl-1-hexanol		95	-0.9	90	1
18.0434	622979	p-Methylstyrene		72	-1.1	88	11
18.0456	611154	o-Methystyrene		83	3.5	78	14
18.1146	13466789	delta-3-Carene	0	90	-1.1	90	1
18.1525	135988	sec-Butylbenzene		79	0.6	89	5
18.2952	99876	p-Isopropyltoluene (p-Cymene)		93	-6.6	89	6
18.3438	106467	p-Dichlorobenzene		65	-2.2		
18.3438	55030176	Carbonic acid, ethyl 3-(1-methylethoxy)phenyl ester				67	1
18.3616	541731	1,3-Dichlorobenzene		96	6.4	95	1
18.4515	5989275	Limonene		80	-1.7	78	1
18.6270	526738	1,2,3-Trimethylbenzene		98	-1.4	94	2
18.7574	111875	1-Octanol		76	-1.7	72	18
18.8820	95501	1,2-Dichlorobenzene		76	0.8	94	2
19.0131	104518	n-Butylbenzene		77	-1.4	72	13
19.1341	95136	Indene	0	81	-1.5	91	3
19.3458	1120214	n-Undecane		81	-1.5	81	1
19.3937	98862	Acetophenone		97	-1.3	92	1
19.5892	124196	n-Nonanal		84	0.7	63	1
20.8036	112345	2-(2-Butoxyethoxy)ethanol		82	-2.2	82	2
20.9162	112403	n-Dodecane	0	98	-2.6	87	6
21.1871	112312	n-Decanal		86	-0.5	64	1
21.760	91203	Naphthalene	0	99	-1.8	96	1
21.818	87683	Hexachlorobutadiene	0				
22.3957	629505	n-Tridecane	0	93	-2.0	61	42
23.8389	629594	n-Tetradecane		95	-3.3	91	1
25.3715	629629	n-Pentadecane	0	97	-4.0	92	1
25.4035	475207	Longifolene		86	-3.6	83	8
26.1677	128370	2,6-di-t-Butyl-4-methylphenol (BHT)		92	-4.8	81	6
27.1364	544763	n-Hexadecane	0	98	-6.1	91	1

Figure 5. Continued

Reviewing the Results

Agilent's DRS software identified 108 compounds in the carpet store air sample. For most compounds, the AMDIS match quality was high (>80) and the RT difference was small (<5 seconds). Furthermore, most compounds had an excellent match to the NIST'05 spectral library and were the top hit or at least among the top five. These compounds have been identified with very high confidence.

As mentioned earlier, it is a good idea to review compounds that have a large deviation from the database RT, have a borderline match to the Indoor Air Toxics Library, or are not among the top 5 to 10 hits in the NIST library search. Table 2 lists 11 compounds (of the 108 reported) where further evaluation was helpful.

Three compounds (1,2-dichloropropane, p-xylene, and hexachlorobutadiene) were found by the ChemStation but not by AMDIS (Table 1). Experience has shown that AMDIS rarely, if ever, fails to corroborate the presence of a compound identified by the ChemStation when it is actually present. Therefore, these compounds could be eliminated easily as false positives. While p-xylene might be present, it is impossible to distinguish it from m-xylene, which was also reported. These isomers are normally reported together.

AMDIS occasionally finds ions that may or may not belong to the spectrum for a peak it has found. So, AMDIS can be configured to search the NIST'05 library with or without these "uncertain" peaks included. The inclusion or exclusion of uncertain peaks can sometimes mean the difference between a good NIST'05 library match and a poor one. Therefore, it is a good idea to run DRS in both configurations if any of the NIST library confirmations are ambiguous. The new version of DRS software (G1716 Ver. A.03.00) allows the user to choose this setting in the Compound Identification Configuration screen shown in Figure 6, which can be reached from the DRS drop-down menu item.

Table 2 shows some examples where the inclusion of uncertain peaks makes a difference in the NIST'05 library search. For example, dimethyldisulfide was not found among the top 100 hits when uncertain peaks were included (columns 6 and 7 in Table 2). However, when those spectral peaks were excluded, dimethyldisulfide was the best spectral match (columns 8 and 9 in Table 2).

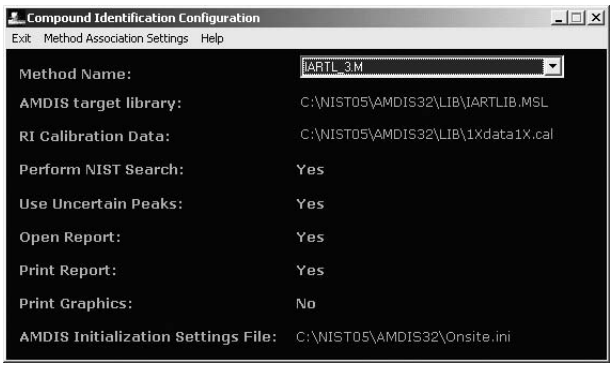

Figure 6. Compound Identification Configuration window in the DRS software. Users can edit these setpoints under Method Association Settings. One of the choices is whether or not to use uncertain peaks when searching the NIST'05 mass spectral library.

Table 2. Compounds with Ambiguous Identifications Using DRS Software with Initial AMDIS Setpoints That Included Uncertain Peaks. The data file was re-analyzed with uncertain peaks excluded. The last column shows the final assessment after analyzing the data with and without the uncertain peaks included for the NIST library search.

RT (min)	Name	Found by ChemStation	AMDIS match	RT dif (s)	NIST match using uncertain peaks	Hit number using uncertain peaks	NIST match not using uncertain peaks	Hit number not using uncertain peaks	Presence confirmed
10.384	1,2-Dichloropropane	Yes	None	None	None	None	None	None	No
11.742	Dimethyldisulfide	No	70	1.5	None	None	88	1	Yes
11.887	Butyric acid	No	67	5.3	62	6	88	2	Yes
15.103	p-Xylene	Yes	None	None	None	None	None	None	#
16.745	2-Methylnonane	Yes	84	-1.1	70	80	80	1	Yes
17.471	1-Decene	No	72	8.5	74	34	69	78	No
18.115	delta-3Carene	Yes	90	-1.1	85	8	90	1	Yes
18.757	1-Octanol	No	76	-1.7	72	75	72	18	No
19.013	n-Butylbenzene	No	77	-1.4	73	9	72	13	No
21.818	Hexachlorobutadiene	Yes	None	None	None	None	None	None	No
22.396	n-Tridecane	Yes	93	-2.0	84	9	61	42	Yes

m-Xylene was identified at 15.096 min. p-Xylene may be present but spectral and RT similarity makes it impossible to differentiate between it and m-xylene.

The only really ambiguous hits were those that had a relatively low AMDIS target library match and poor NIST'05 library matches with and without uncertain peaks included. For this sample, manual review was only needed for 1-decene, 1-octanol, n-butyl benzene, and n-tridecane. Of the four, only n-tridecane could be confirmed.

Of the 108 target VOCs reported, six were eliminated using these data review procedures. The AMDIS settings (Figure 6) for this analysis were chosen to be quite sensitive to small peaks obscured by high background. The minimum match factor was set to 60 (Figure 7A), while the resolution, sensitivity, and shape requirements were all set to 'high' (Figure 7B). These settings can identify more peaks, but as seen in Table 2, can sometimes report a few false positives. However, false positives are usually easy to spot by looking at the DRS report. They typically have a lower AMDIS target library match value with a larger than usual RT deviation and have a lower NIST'05 library match and hit number. Because DRS runs in 2 or 3 minutes, it is easy to change any of the AMDIS settings and re-analyze the data file.

DRS was able to identify numerous halogenated compounds, nonhalogenated solvents, aromatics, and monomers in the carpet store air. Many of these compounds undoubtedly evolved from the carpet and would be at their highest concentrations when the carpet is new. However, carpet also adsorbs VOCs and may evolve them at a later time.

Quantitative Analysis

It is impossible to quantify a compound that is not first identified by the method. DRS helps by making reliable identifications. As usual, quantitative analysis requires that the target compounds be calibrated using standards. As seen in Figures 3 and 5, AMDIS often finds analytes that were missed by the ChemStation. These compounds can be quantified (if calibrated) using the QEdit feature of the Agilent ChemStation.

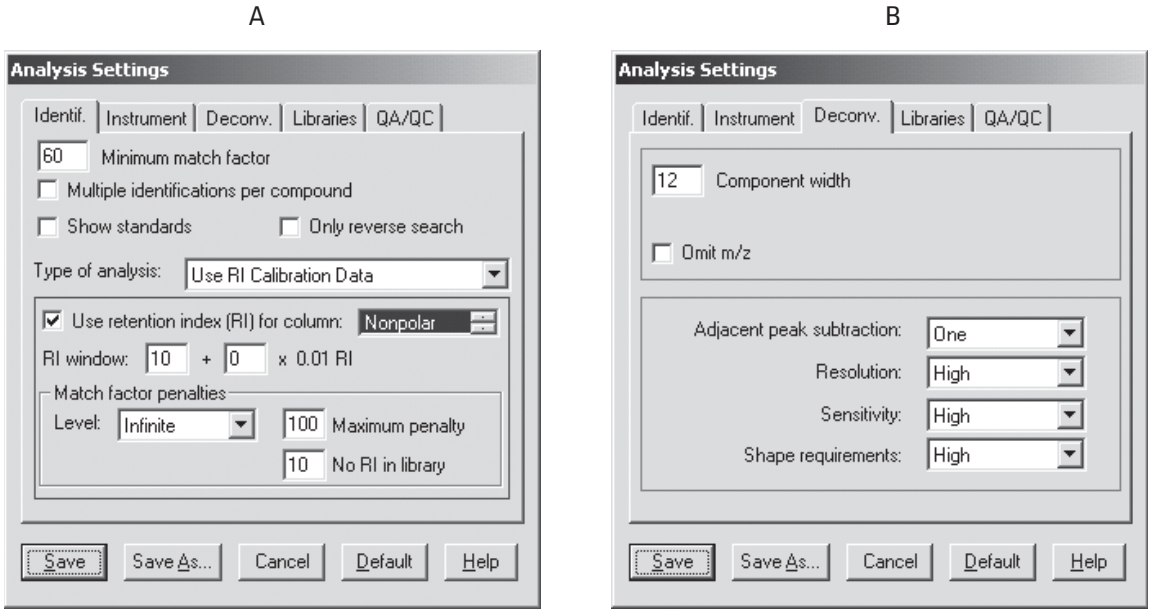

Figure 7. Two windows from the AMDIS software showing the deconvolution setpoints used for these analyses. These windows are accessed within the AMDIS software under the "Analyze/Settings" drop-down menu item.

Under **View**, choose **QEdit Quant Result**, which opens this software tool (Figure 8). Compounds marked with an 'X' in the Quick Edit list were found by the ChemStation. Cyclohexane was found by DRS but failed to meet the ChemStation's ion ratio requirements. By double-clicking on cyclohexane in the Quick Edit window, QEdit extracts cyclohexane's target and qualifier ions and highlights its expected RT with a dashed line. The user can integrate the peak using the mouse (hold down the right button and draw in the baseline) and save it to the integration report.

Rather than calibrate for all compounds, some methods allow certain target concentrations to be estimated. Such compounds are given toluene's response factor and are reported as "toluene equivalents."

Conclusions

Most indoor air contains a wide variety of volatile and semivolatile organic compounds, many of which may be irritating or even toxic to inhabitants. Most of these compounds are emitted from building materials, carpet and furnishings, cleaning products, stored solvents, and other materials. It is convenient to collect indoor air samples on TD tubes for analysis by TD/GC/MS. However, such samples can produce extremely complex chromatograms with dozens or even hundreds of unresolved peaks.

Agilent's Deconvolution Reporting Software and new Indoor Air Toxics Database can identify up to 171 target compounds in about 3 minutes following routine TD/GC/MS analysis. The method deconvolutes the spectra of overlapping peaks, creating

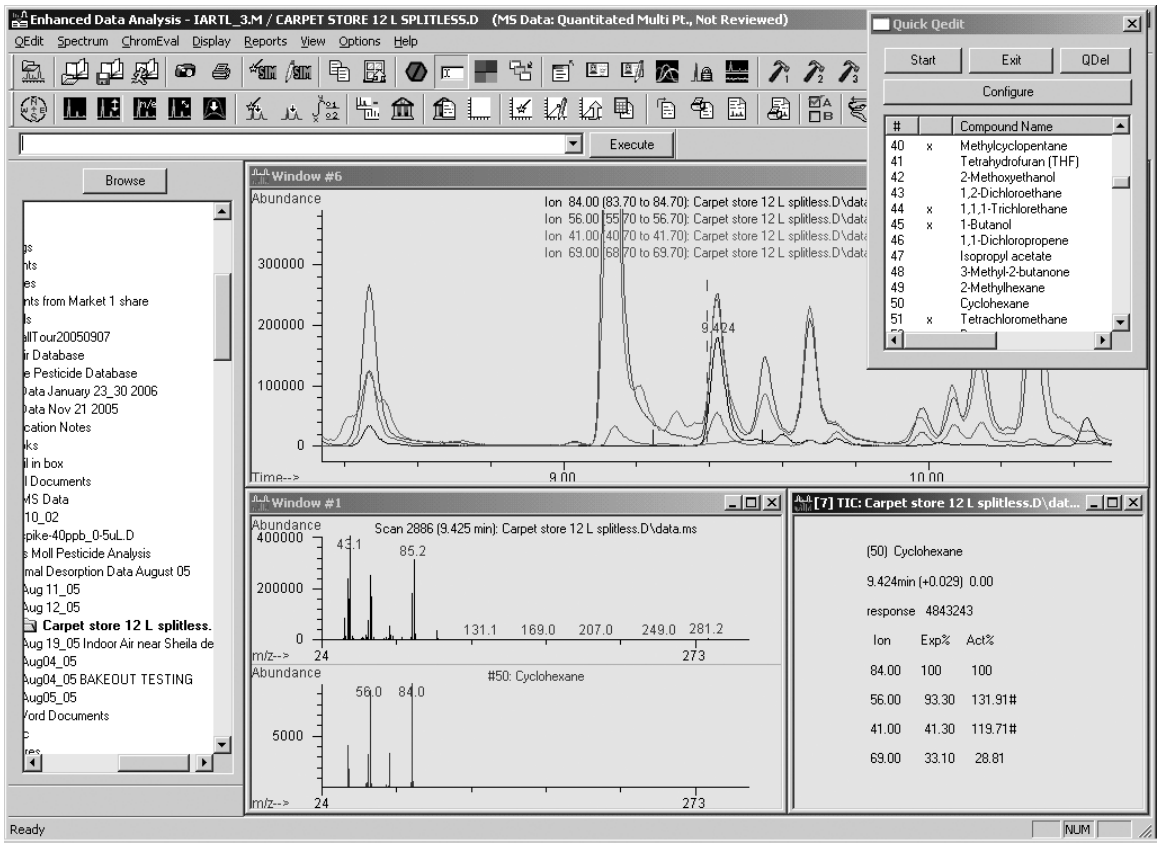

Figure 8. In this QEdit window, the user can verify integrations and integrate peaks that were initially missed by the ChemStation but identified by AMDIS as part of the DRS software.

"cleaned" spectra that can be searched against the Indoor Air Toxics Database and the NIST'05 Mass Spectral Library. This automated process is faster and more accurate than traditional GC/MS methods.

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Appendix 1

Appendix 1 lists all of the compounds in the RTL Indoor Air Toxics Database

1,1,1,2-Tetrachloroethane
1,1,1-Trichlorethane
1,1,2,2-Tetrachloroethane
1,1,2-Trichloroethane
1,1-Dichloroethane
1,1-Dichloroethene
1,1-Dichloropropene
1,1-Dimethoxyethane
1,2,3-Trichlorobenzene
1,2,3-Trichloropropane
1,2,3-Trimethylbenzene
1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
1,2-Dichlorobenzene
1,2-Dichloroethane
1,2-Dichloroethene (cis)
1,2-Dichloroethene (trans)
1,2-Dichloropropane
1,3,5-Trimethylbenzene
1,3-Butadiene
1,3-Dichlorobenzene
1,3-Dichloropropane
1,3-Diisopropylbenzene
1,4-Dioxane
1-Butanol
1-Decene
1-Hexanol
1-Methoxy-2-propanol
1-Octanol
1-Octene
1-Pentanol
1-Propanol
2-(2-Butoxyethoxy)ethanol
2,2,4-Trimethylpentane
2,2-Dichloropropane
2,6-di-t-Butyl-4-methylphenol (BHT)
2-Butanone (MEK)
2-Butoxyethanol
2-Butoxyethyl acetate
2-Chlorotoluene
2-Ethoxyethanol
2-Ethoxyethyl acetate
2-Ethyl-1-hexanol
2-Ethylhexyl acetate
2-Methoxyethanol
2-Methoxyethyl acetate
2-Methyl-2-propanethiol
2-Methylhexane
2-Methylnonane
2-Methylpentane
2-Propanol
3-Methyl-2-butanone
3-Methylheptane
3-Methylhexane
3-Methyloctane
3-Methylpentane
4-Chlorotoluene
4-Methyl-2-pentanone (MIBK)
Acetaldehyde
Acetic acid
Acetone
Acetophenone
Acrylonitrile
alpha-Cedrene
alpha-Methylstyrene (2-propenyl benzene)
alpha-Pinene
Aniline
Benzene
beta-Pinene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
Butyl acetate
Butyric acid
Camphene
Caprolactam
Carbon disulphide
Chlorobenzene
Chloroethane
cis-1,3-Dichloropropene
Cyclohexane
Cyclohexanol
Cyclohexanone
delta-3-Carene
Dibromochloromethane
Dibromomethane
Dichlorodifluoromethane
Dichloromethane
Diethyl disulfide
Dimethoxymethane
Dimethyl sulphide
Dimethyldisulphide
Dimethylphthalate
Epichlorohydrin
Ethanethiol
Ethyl acetate
Ethyl acrylate
Ethyl tert-butyl disulfide
Ethylbenzene
Ethynylbenzene (Phenylacetylene)
Furan
Hexachlorobutadiene
Indene
Isopropyl acetate
Isopropylbenzene (cumene)
Limonene
Longifolene
Methanethiol
Methyl acrylate
Methyl ethyl disulfide
Methyl methacrylate
Methyl tert-butyl disulfide
Methylchloride
Methylcyclohexane
Methylcyclopentane

Methyl-t-butylether
m-Ethyltoluene
m-Xylene
N,N-Dimethylformamide
Naphthalene
n-Butanal
n-Butyl acrylate
n-Butylbenzene
n-Decanal
n-Decane
n-Dodecane
n-Heptane
n-Hexadecane
n-Hexanal
n-Hexane
n-Nonanal
n-Nonane
n-Octanal
n-Octane
n-Pentadecane
n-Propylbenzene
n-Tetradecane
n-Tridecane
n-Undecane
o-Ethyltoluene
o-Methystyrene
o-Xylene
p-Dichlorobenzene
Phenol
p-Isopropyltoluene (p-Cymene)
p-Methylstyrene
Propyl acetate
Propylene glycol
Propylene oxide
p-Xylene
Pyridine
sec-Butylbenzene
Styrene
tert-Butanol
tert-Butylbenzene
Tetrachloroethene
Tetrachloromethane
Tetrahydrofuran (THF)
Tetrahydrothiophene
Toluene
Toluene-d8
trans-1,3-Dichloropropene
Trichloroethene
Trichlorofluoromethane
Trichloromethane
Vinyl acetate
Vinylchloride (chloroethene)

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Printed in the USA
August 3, 2006
5989-5435EN

Agilent Technologies

Round-the-Clock, Online and Cryogen-Free Monitoring of Hydrocarbons in Ambient Air Using Thermal Desorption-Gas Chromatography

An application of the UNITY™-Air Server thermal desorber system

Technical Overview

Background

The presence of volatile hydrocarbons in urban atmospheres is believed to contribute to the formation of ground level ozone, one of the main constituents of urban smog. The compounds of interest range in volatility from ethyne (acetylene) to trimethylbenzene and are generally referred to as 'ozone precursors'.

Vehicle emissions are thought to be the main source of these compounds. Recent European and US regulations[1, 2] require round-the-clock monitoring of target species in all major urban centers to establish and monitor the link between periods of high traffic density and high pollution levels. Key compounds include: benzene, toluene, xylene, and 1,3-butadiene. Continuous real-time monitoring provides an insight into emission episodes from local industry and can be used to monitor the effect of weather conditions such as wind direction, precipitation, and temperature inversion.

Introduction

The UNITY™-Air Server is a new, cost-effective thermal desorber for round-the-clock speciated measurement of multiple trace-level volatile organic compounds (VOCs) in air or pure gases. It combines automated, controlled-flow sampling with cryogen-free concentration technology. The system can be coupled to an Agilent gas chromatograph (GC) or a gas chromatograph/mass spectrometer (GC/MS), and is designed for unattended operation in remote field locations.

In summary, sample air is pulled through an optionally incorporated permeable membrane dryer directly onto an electrically-cooled, sorbent-packed focusing trap at a controlled flow rate. No liquid cryogen is required. The membrane dryer selectively eliminates water and other low molecular weight polar components, reducing the risk of interference from unknown species. It facilitates the use of flame ionization detection (FID) rather than MS detection.

To avoid contamination, sampling flows are controlled by an electronic mass flow controller and pump located downstream of the focusing trap. All sampling parameters are selected by the user and monitored by UNITY-Air Server software as an integral part of the analytical method. After sample collection, the flow path is purged with carrier gas to prevent carryover and to eliminate oxygen from the focusing trap. The trap then heats rapidly, at rates approaching 100 °C/s, to inject retained analytes into the capillary column as a highly concentrated band of vapor. This transfer may be performed splitless for maximum sensitivity. Once the trap has desorbed, it recools, re-equilibrates to the trapping temperature, and begins collection of the next sample while analysis of the previous sample is ongoing.

[1]Council Directive 96/62/EC: On ambient air quality assessment and management, and its "daughter" directive - 2000/69/EC relating to limit values for benzene and carbon monoxide in ambient air.

[2]1990 US Clean Air Act Amendment

The UNITY-Air Server also offers automatic interchange between three sample channels (typically sample, reference, and blank) for remote system calibration/validation as per user requirements. Six or eight channel options are also available.

This application note describes validation of the system for online monitoring of the 27 ozone precursors specified by European regulators, plus 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and isoprene. Table 1 in the Appendix shows the full list of 30 compounds.

Operation of the system for compliance with the 56-component US EPA ozone precursor list is also demonstrated. Table 2 in the Appendix shows the list of 56 compounds. Key factors taken into account when developing this method included the need for a system that could operate round-the-clock unattended, hence the requirement for cryogen-free operation. The system should allow hourly sample collection with as much of the hour as possible dedicated to sampling. Finally, detection limits should be below 0.5 ppb - ideally 0.1 ppb.

Defining the Ideal Cold Trap

Initial tests were carried out using the 30-component ppb-level certified gas standard described above (National Physical Laboratory, Teddington, UK). Individual concentrations are listed in Table 1 in the Appendix. Two types of ozone precursor focusing traps were tested:

Trap 1 - Three-bed trap: porous polymer sorbent (5 mm), graphitized carbon black (8 mm), and carbon molecular sieve (~45 mm).

Trap 2 - Four-bed trap: porous polymer sorbent (5 mm), graphitized carbon black (8 mm), carbon molecular sieve 1 (15 mm), and carbon molecular sieve 2 (30 mm).

Trap 1 is the stronger of the two, retaining the highly volatile compounds to a greater extent than trap 2. However, the strength of the sorbents in trap 1 caused slight broadening of early eluting peaks under the splitless conditions used for optimum sensitivity (sub ppb). Figure 1 shows a chromatogram of a splitless injection using the four-bed trap specifically designed for this application.

Breakthrough Tests

All the C2 hydrocarbons are highly volatile species. Ethyne (acetylene) has a boiling point of –89 °C and is the most difficult to trap. To retain it quantitatively without liquid cryogen requires careful selection of the cold trap sorbent(s) and focusing temperature.

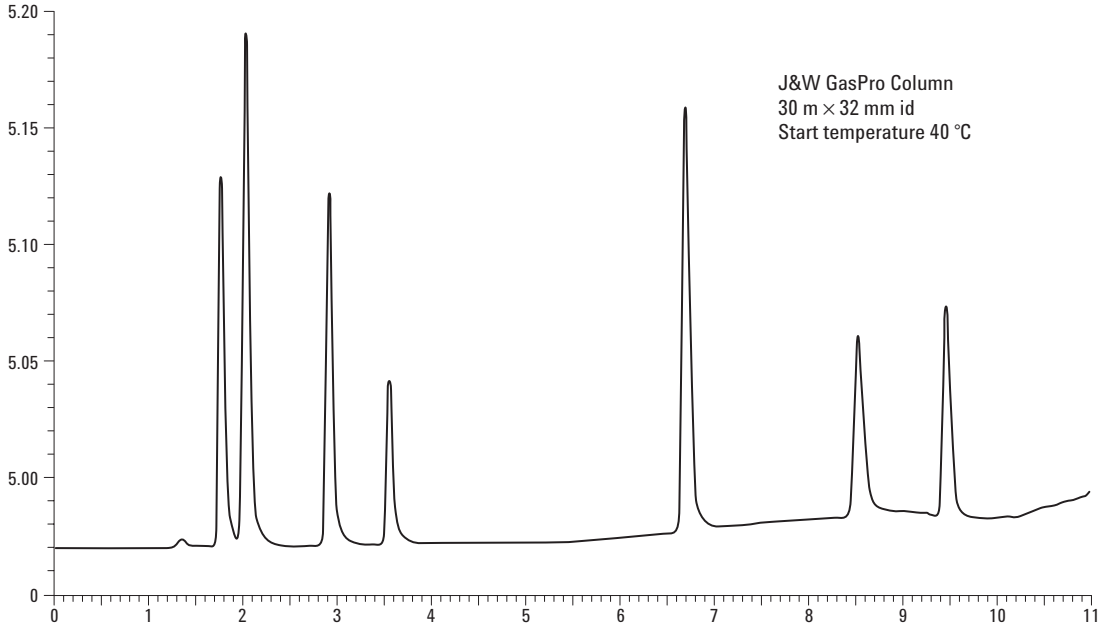

Figure 1. Chromatogram showing a splitless injection of 150 mL of calibration standard.

Breakthrough volume experiments were performed on the selected cold trap using the ppb-level certified gas standard generated by the National Physical Laboratory, Teddington, UK. Steadily increasing volumes of the gas standard were introduced and a graph of detector response versus sampled volume traced. Breakthrough occurs when the data deviates from a linear relationship, that is, when the species of interest are no longer quantitatively retained. Data from the low volumes of standard introduced were also used to estimate detection limits.

Analytical conditions used for determining the breakthrough volumes:

Column:	J&W GasPro, 30 m × 0.32 mm
GC Program:	40 °C (hold 5 min) Ramp 1: 5 °C/min to 90 °C Ramp 2: 20 °C/min to 260 °C Hold (10 min)
Prepurge time:	2 min
Sampling rate:	10 mL/min
Sampling time:	Various
Purge time:	1 min
Cold trap:	Ozone precursor trap
Cold trap low:	–15 °C
Cold trap high:	300 °C
Cold trap hold:	5 min
Transfer line:	100 °C

Figure 2 shows peak area versus sampled volume of calibration gas for acetylene and propane. Propane is a less volatile component that has a breakthrough volume of many liters on the cold trap used in these experiments.

Figure 2 shows that there is good reproducibility and negligible breakthrough for acetylene, even up at 600 mL of sampled gas. Field sampling volumes of 450 mL (45 min sampling at 10 mL/min) may therefore be used.

Detection/Quantitation Limits

Signal-to-noise ratios for the 150 mL volume of standard using the GC-FID are in the order of 300:1 for the light hydrocarbons at ~6 ppb. For compounds from n-butane upwards, which are at ~2 ppb concentration level, signal-to-noise ratio is 150:1. Assuming a minimum detection signal-to-noise ratio of 3:1 and a minimum quantifiable signal of double that, approximate detection/quantitation limits for 450 mL air samples were
calculated as follows:

Hydrocarbons	Detection ppb	Quantification ppb
C2 to C3	0.05	0.1
C4+	0.03	0.06

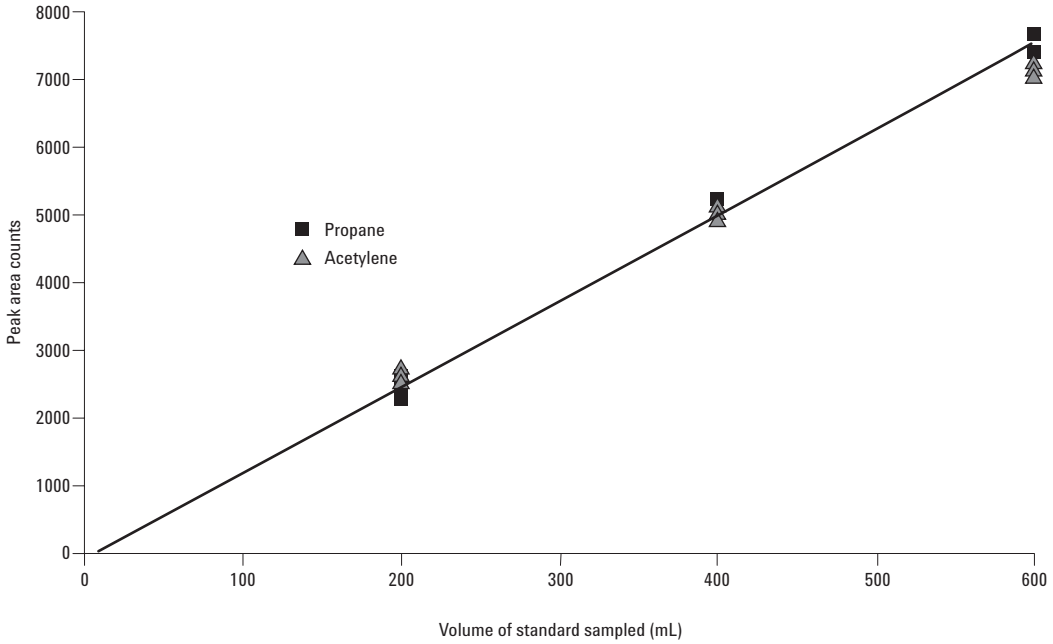

Figure 2. Peak area vs. volume sampled for acetylene and propane.

Reproducibility of Peak Area and Retention Time

Figure 3 shows four repeat analyses of the ozone precursor calibration standard on a J&W 30 m × 0.32 mm GasPro column. Although some coelution of C5 hydrocarbons was observed, excellent retention time (<1% RSD) and peak area (<2% RSD) precision were found across the analyte range for sequence of 12 analyses.

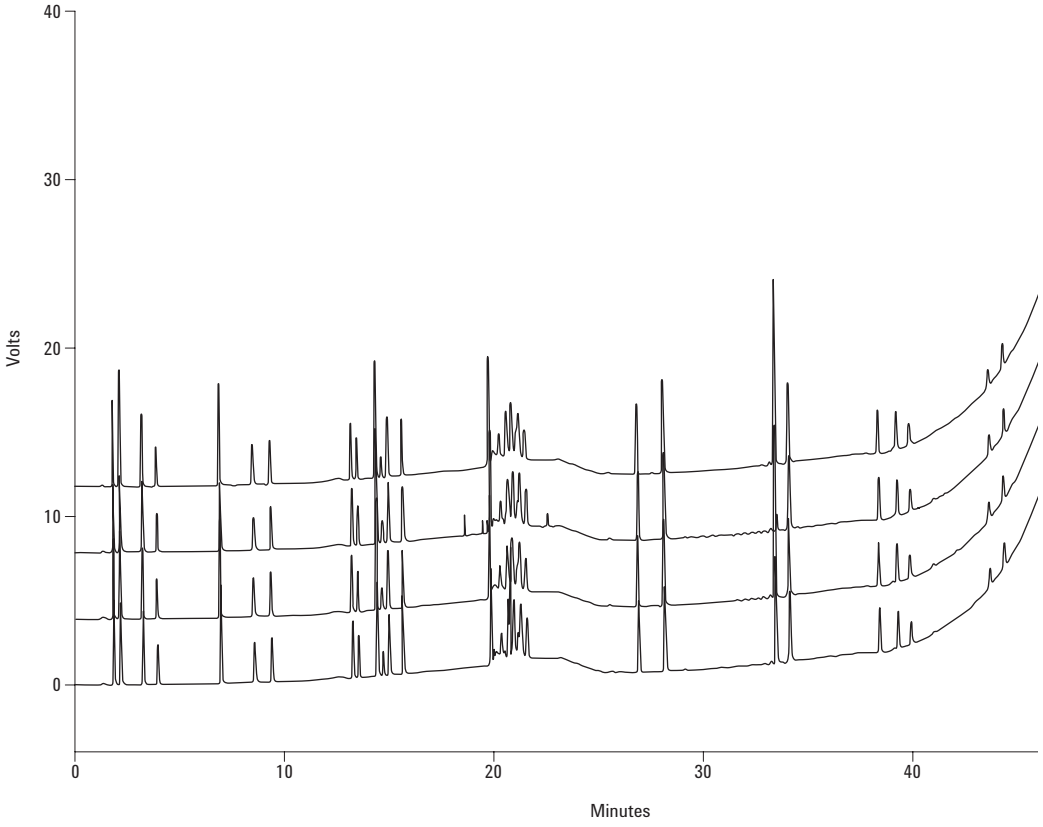

Figure 3. Repeat analyses of 200 mL gas standard run before 5-day field monitoring study.

Suburban Air Monitoring

Analyzer performance for an unattended field operation was evaluated during a 5-day trial at one of Europe's leading centers for standardization in environmental monitoring. Figure 4 shows a sequence of ambient air profiles running from before dawn through the height of the rush hour in a suburban environment. These data were collected at the end of the trial and show that good analytical performance was maintained. No user intervention was required during the 5-day trial. Detection limits in this relatively clean environment were also satisfactory.

Figure 5 describes a two-column configuration suitable for GC-FID detection and quantitation of low molecular weight hydrocarbons.

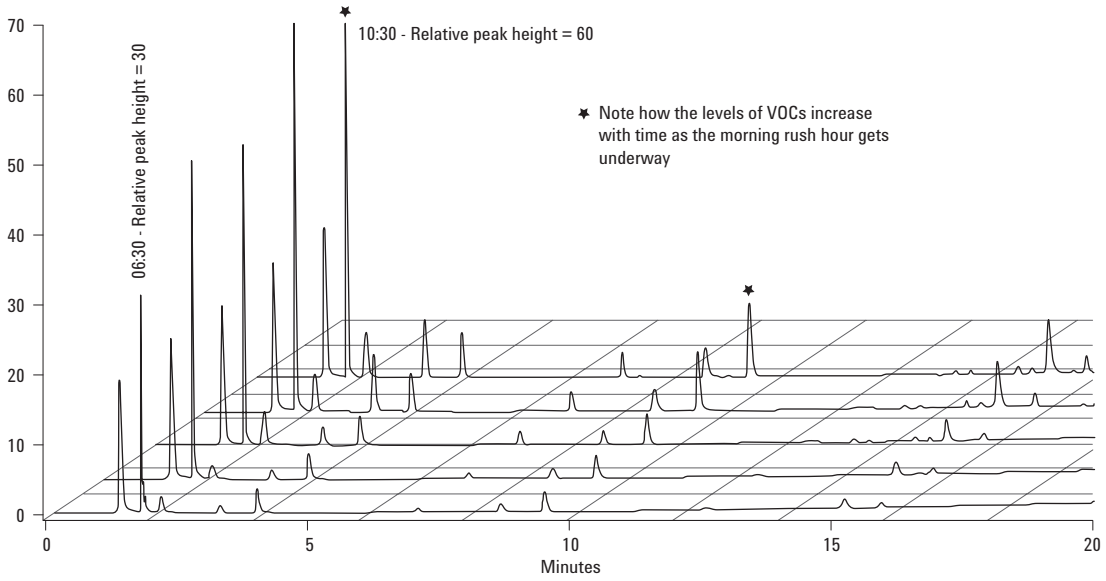

Figure 4. A series of suburban air profiles from 06:30 to 10:30 on 24th January 2000.

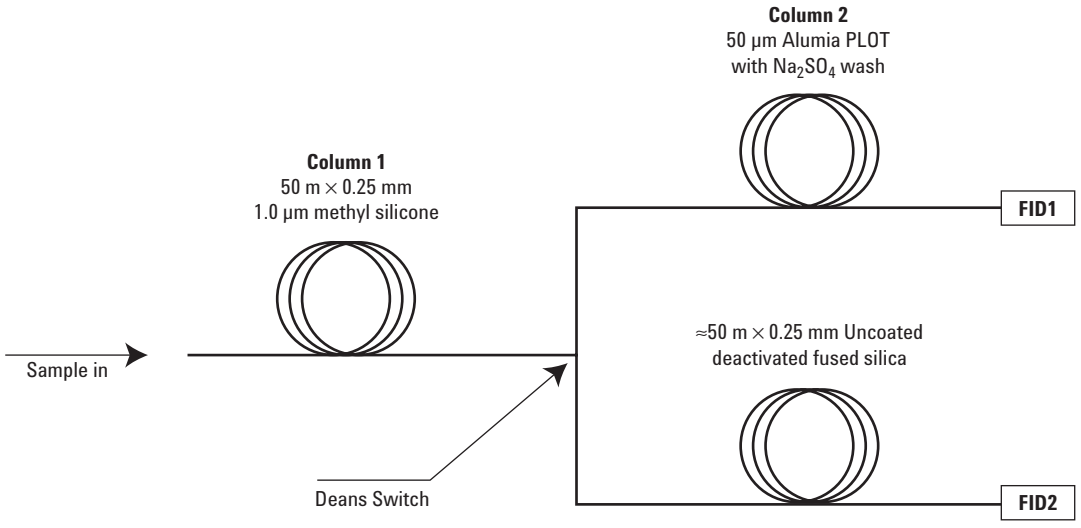

Figure 5. Schematic representation of the two-column ozone precursor analytical system.

Figures 6 and 7 show chromatograms obtained using the 30- and 56-component calibration gas standards respectively, using the described two-column GC system. Peak identifications are given in Tables 1 and 2 in the Appendix. This configuration makes it possible to separate all of the components in these two standard mixtures.

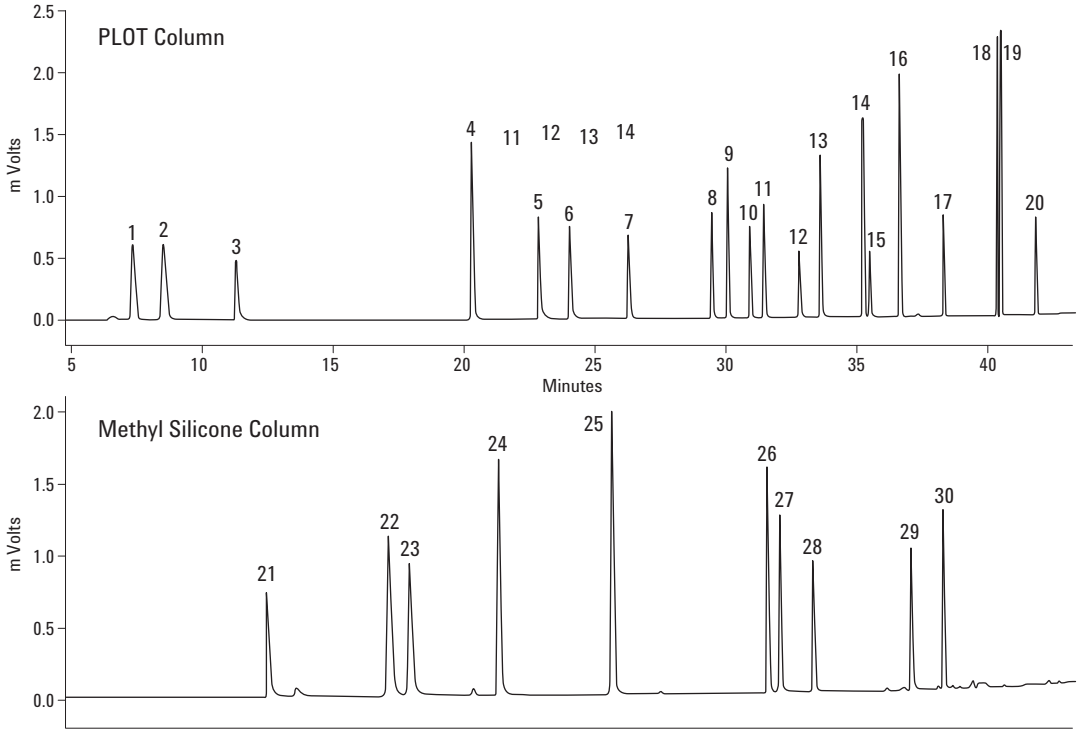

Figure 6. Thirty-component calibration gas injection on two-column analytical system.

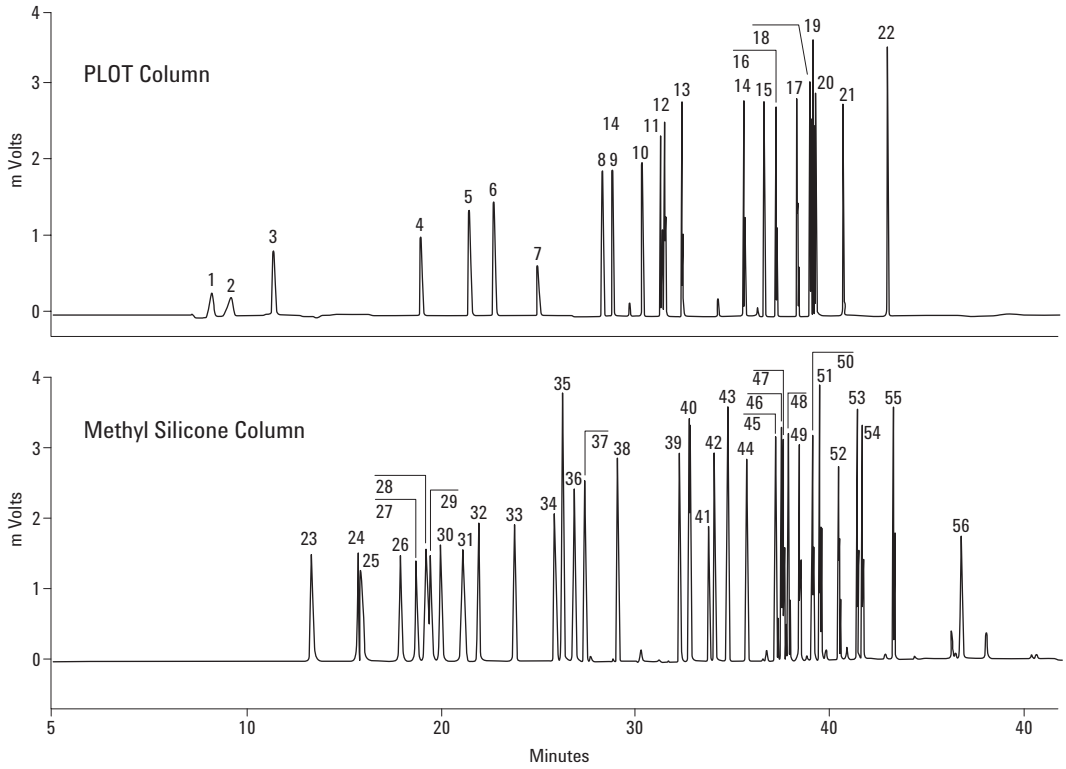

Figure 7. Fifty six-component calibration gas injection on two-column analytical system.

Figures 8 and 9 show linearity plots for five selected compounds.

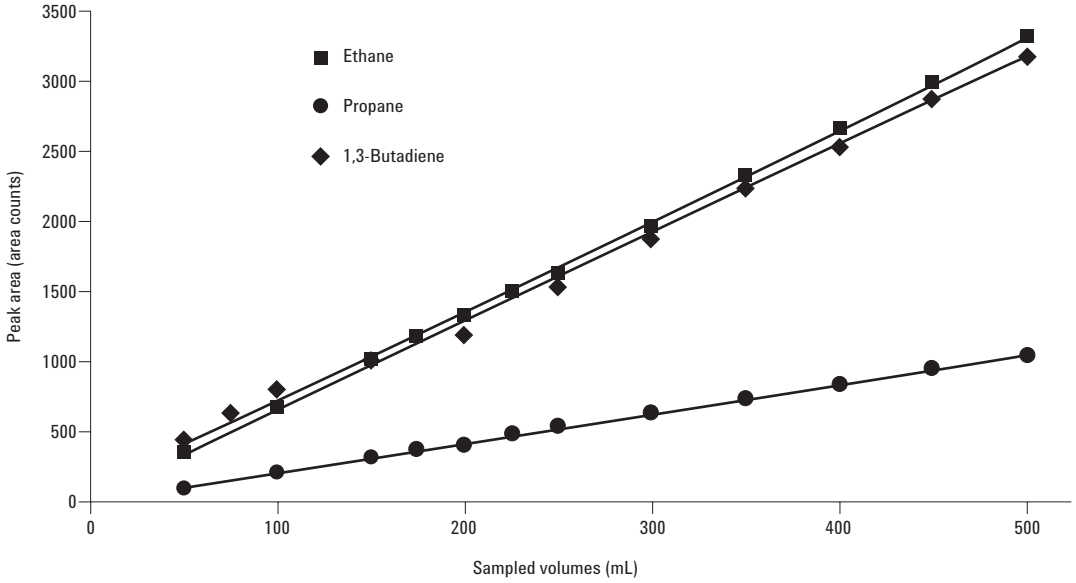

Figure 8. Detector response vs. sampled volume for ethene, propane, and 1,3-butadiene.

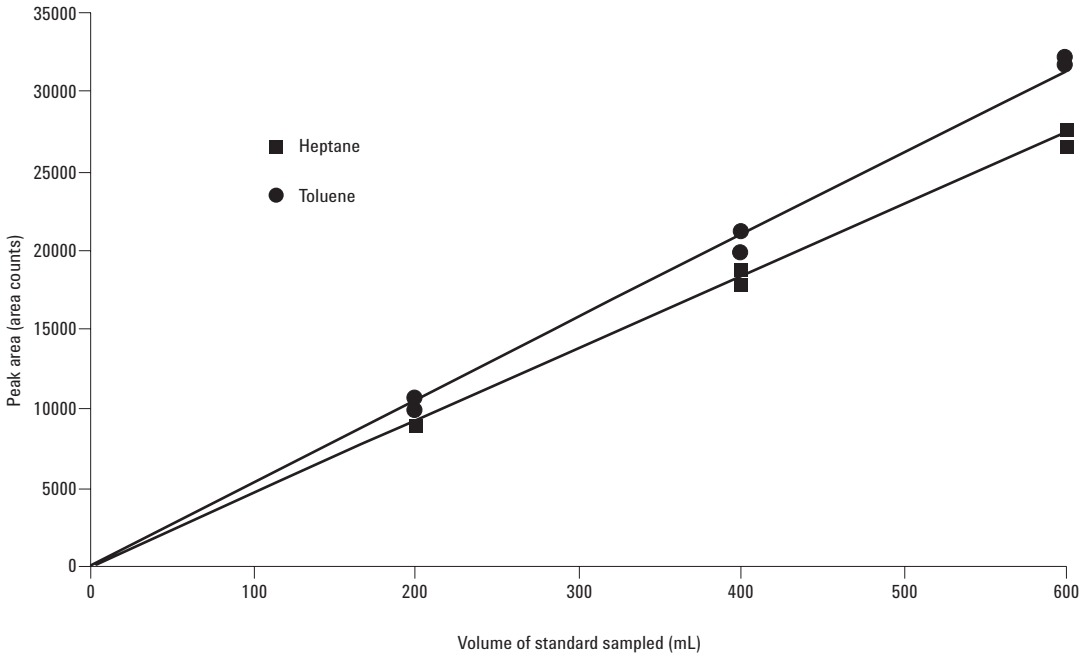

Figure 9. Detector response vs. sampled volume for heptane and toluene.

Appendix

Table 1. Details of ppb-Level 30-Component Gas Standard

Compound	Concentration (mole fraction by ppb)	Uncertainty (mole fraction by ppb)
Ethane (1)	5.94	±0.15
Ethene (2)	9.31	±0.20
Ethyne (7)	7.75	±0.20
Propane (3)	2.25	±0.05
Propene (4)	5.86	±0.15
Propyne (15)	2.53	±0.05
n-Butane (6)	2.27	±0.05
iso-Butane (5)	2.63	±0.05
iso-Butene (10)	2.49	±0.05
1-Butene (9)	2.91	±0.05
trans-2-Butene (8)	1.94	±0.05
cis-2-butene (11)	2.08	±0.05
1,3-Butadiene (14)	4.66	±0.10
n-Pentane (13)	2.32	±0.05
i-Pentane (12)	1.04	±0.02
trans-2-Pentene (16)	3.54	±0.10
cis-2-Pentene (17)	1.35	±0.03
Isoprene (20)	1.61	±0.04
2-Methylpentane (18)	2.78	±0.05
3-Methylpentane (19)	3.18	±0.05
Cyclohexane (23)	2.92	±0.05
n-hexane (21)	1.55	±0.04
Benzene (22)	3.00	±0.05
n-Heptane (24)	2.43	±0.05
Toluene (25)	2.82	±0.05
Ethylbenzene (26)	1.55	±0.04
o-Xylene (28)	0.88	±0.02
m-Xylene (27)	1.23	±0.03
1,2,4-Trimethylbenzene (30)	0.99	±0.02
1,3,5-Trimethylbenzene (29)	0.81	±0.02

Table 2. Details of ppb-Level 56-Component Gas Standard

Peak number	Compound
1	Ethane
2	Ethylene
3	Propane
4	Propylene
5	*iso*-Butane
6	n-Butane
7	Acetylene
8	*trans*-2-Butene
9	1-Butene
10	*cis*-2-Butene
11	Cyclopentane
12	Isopentane
13	n-Pentane
14	*trans*-2-Pentene
15	1-Pentene
16	*cis*-2-pentene
17	2,2-Dimethylbutane
18	2,3-Dimethylbutane
19	2-Methylpentane
20	3-Methylpentane
21	Isoprene
22	2-Methyl-1-Pentene
23	Hexane
24	Methylcyclopentane
25	2,4-Dimethylpentane
26	Benzene
27	Cyclohexane
28	2-Methylhexane
29	2,3-Dimethylpentane
30	3-Methylhexane
31	2,2,4-Trimethylpentane
32	n-Heptane
33	Methylcyclohexane
34	2,3,4-Trimethylpentane
35	Toluene
36	2-Methylheptane
37	3-Methylheptane
38	n-Octane
39	Ethylbenzene
40	m/p-Xylene
41	Styrene
42	o-Xylene
43	n-Nonane
44	Isopropylbenzene
45	n-Propylbenzene
46	m-Ethyltoluene
47	p-Ethyltoluene
48	1,3,5-Trimethylbenzene
49	o-Ethyltoluene
50	1,2,4-Trimethylbenzene
51	n-Decane
52	1,2,3-Trimethylbenzene
53	m-Diethylbenzene
54	p-Diethylbenzene
55	n-Undecane
56	n-Dodecane

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Printed in the USA
April 24, 2003
5988-9254EN

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MARKES international LIMITED

Application of SecureTD™ for Re-collection and Repeat Analysis of Desorbed Samples

Overcoming the one-shot limitation of thermal desorption

Technical Overview

Introduction

Thermal desorption (TD) has a number of very significant advantages versus conventional solvent extraction methods. These include:

- Increased sensitivity
  - Detection limits enhanced by a factor of 10^3 to 10^4.
  - Higher sample recovery. A 95% or better desorption efficiency for all volatile organic compounds (VOCs), including polar compounds, vs. 30% to 80% for most solvent extraction methods.
- Cost savings
  - No manual sample preparation required, thus reducing time and cost per analysis.
  - Reusable TD tubes (100 to 200 times).
- No solvent required
  - No masking of peaks of interest by the solvent.
  - No introduction of artifacts/impurities from the solvent.
  - Improved laboratory working environment (with elimination of a health hazard). Carbon disulfide (CS_2), the most commonly used extraction solvent, is very toxic.
  - No solvent disposal costs or expensive air extraction equipment required.

However, once a sample has been thermally desorbed (that is, heated in a flow of carrier gas), no sample remains for repeat analysis. In contrast to this, CS_2 extracts from charcoal tubes can be injected many times, as long as they are kept refrigerated. In some cases this can be a significant consideration, overriding the many other advantages of TD. Markes International TD systems, including UNITY™ (single tube thermal desorber) and ULTRA-UNITY™ (100-tube automated thermal desorber), are the only thermal desorbers with SecureTD™. SecureTD is designed to overcome the one-shot limitation of conventional TD by using quantitative re-collection for repeat analysis.

SecureTD: Split Re-collection for Repeat Analysis

UNITY, The Markes International platform thermal desorber, was specifically designed to overcome the one-shot limitation of conventional analytical TD by harnessing the idea of split re-collection pioneered by Dr Jan Kristensson [1]. Using any of Markes International TD systems, samples may be split as they are transferred from the primary sample tube to the focusing trap and/or during subsequent transfer from the focusing trap to the analyzer. The split flow is directed to either a tube filled with charcoal (to scrub the effluent stream), or to a conditioned sorbent tube for sample re-collection.

The same conditioned sorbent tube is used to collect the flow whether splitting on the inlet to the trap (primary desorption), outlet to the trap (secondary desorption), or both (see Figures 1 and 2).

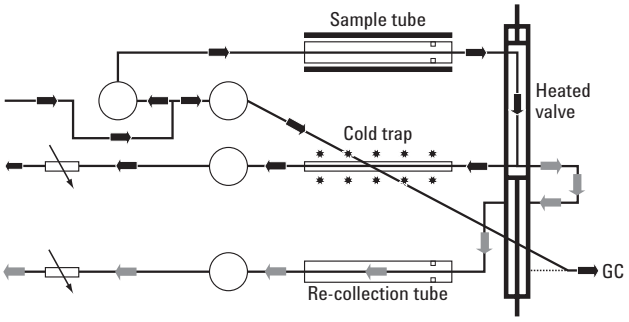

Figure 1. Re-collection during primary (tube) desorption.

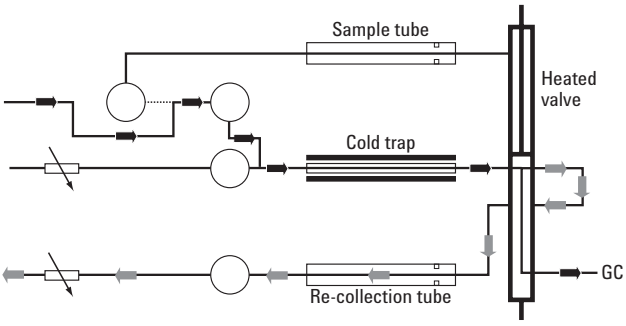

Figure 2. Re-collection during secondary (trap) desorption.

TD offers such a large enhancement in sensitivity versus solvent extraction that it is invariably possible to redirect a portion of the sample for re-collection without compromising method detection limits. The short length of the UNITY flow path leading to the split re-collection tube is constructed of inert Silcosteel™ tubing, heated to prevent analyte condensation or degradation. A steep temperature gradient inside the re-collection tube ensures quantitative trapping of target analytes over the relatively short re-collection period without condensation or breakthrough. UNITY control software allows exchange of the split re-collection tube in between samples without interrupting gas flow to the analyzer.

An automated ULTRA-UNITY system may use manual SecureTD for method development/validation or re-collection of critical samples. If automatic re-collection is required for every sample, then the SecureTD function may be automated using an AutoSecure™ system. See Figure 3.

Figure 3. AutoSecure system.

Laboratory Test of Re-collection Performance

The performance of SecureTD was tested with a high loading (~1 µg) of toluene. To prepare the standard, 1 µL of a 0.1% (v/v) toluene standard in methanol was introduced to a conditioned Tenax TA tube in stream of pure nitrogen via the standard loading rig (C-CSLR).

Analytical conditions:

Tenax tube	
Tube desorb:	280 °C for 5 min
Flow path:	120 °C
Cold trap packed with Tenax and Carbopack	
Cold trap low:	–10 °C,
Cold trap high:	300 °C for 2 min
Helium carrier gas:	14 psi (giving a column flow of 1.5 mL/min)
Desorb flow:	15 mL/min, Split flow: 40 mL/min giving a split ratio of 99:1
GC column:	30 m × 0.32 mm × 1 mm film methyl silicone

The sample was re-collected and re-analyzed four times.

Recovery data are presented in Table 1. Figure 4 shows a chromatogram from a recovered sample and a bar chart for the toluene recoveries over the four re-collection and reanalysis steps.

Table 1. Analysis of Toluene Using Re-collection with a 98.9 : 1 Split Ratio

Analysis number	Area counts	Data point as a % of previous	Data point as % of original
1	643952		100.0
2	638144	99.1	99.1
3	630494	98.8	97.9
4	623338	98.9	96.8
5	616320	98.9	95.7

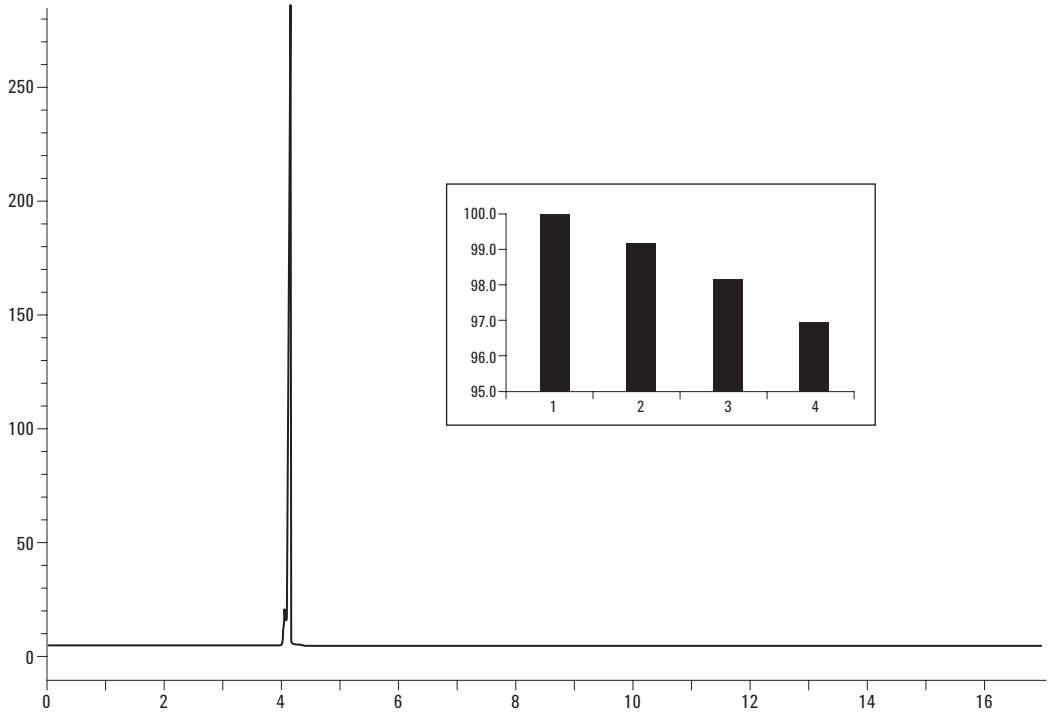

Figure 4. Chromatogram and bar chart of relative peak area % on subsequent "saved" samples.

SecureTD performance was also tested with a low concentration (approximately 170 ng/µL) benzene, toluene, o-xylene (BTX) solution. Two µL of the solution was introduced onto a conditioned Tenax tube, as above, and analyzed under similar conditions - this time using a split ratio of 21:1. Six re-collection, repeat-analyses were carried out and showed good correlation between the expected and observed decay. See Figure 5.

SecureTD: Why Re-Collect?

There are a number of situations where re-collection of a portion of the sample is advantageous.

- Method development/validation
- Erroneous GC parameters, for example, co-elution, detector problems, premature completion of the GC run, etc.
- Incorrect split conditions, including too little or too much sample passed onto column
- Identification of unknowns
- Troubleshooting
- Sample archiving - for critical one-off samples or samples taken for regulatory compliance
- Unique samples, for example, re-collection from online/headspace samples

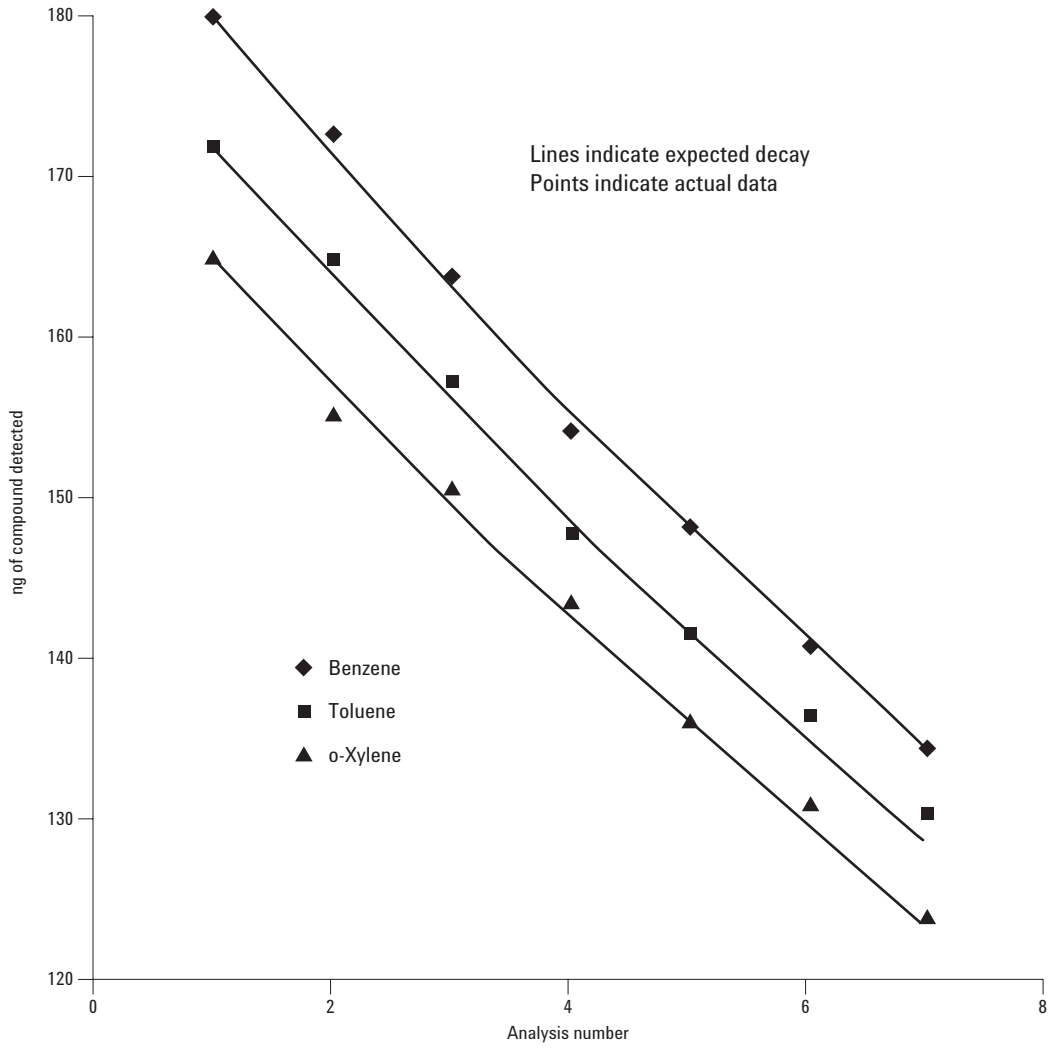

Figure 5. Re-collection and re-analyses of BTX solution.

Method Validation - Validation of Quantitative Recovery of High Boiling Compounds

A solution of the following phthalates (high boiling plasticizer compounds) was analyzed with re-collection:

DEP Diethyl phthalate
DMPP Dimethyl propyl phthalate
DBP Dibutyl phthalate
DEHP Diethyl hexyl phthalate
DOP Dioctyl phthalate
DNP Dinonyl phthalate

Figure 6 shows how SecureTD re-collection was used to validate the quantitative recovery of high boiling compounds such as dioctyl and dinonyl phthalate. No bias was observed throughout the sequence of primary and repeat analyses. Blanks run between each of the repeat analyses demonstrated no carryover.

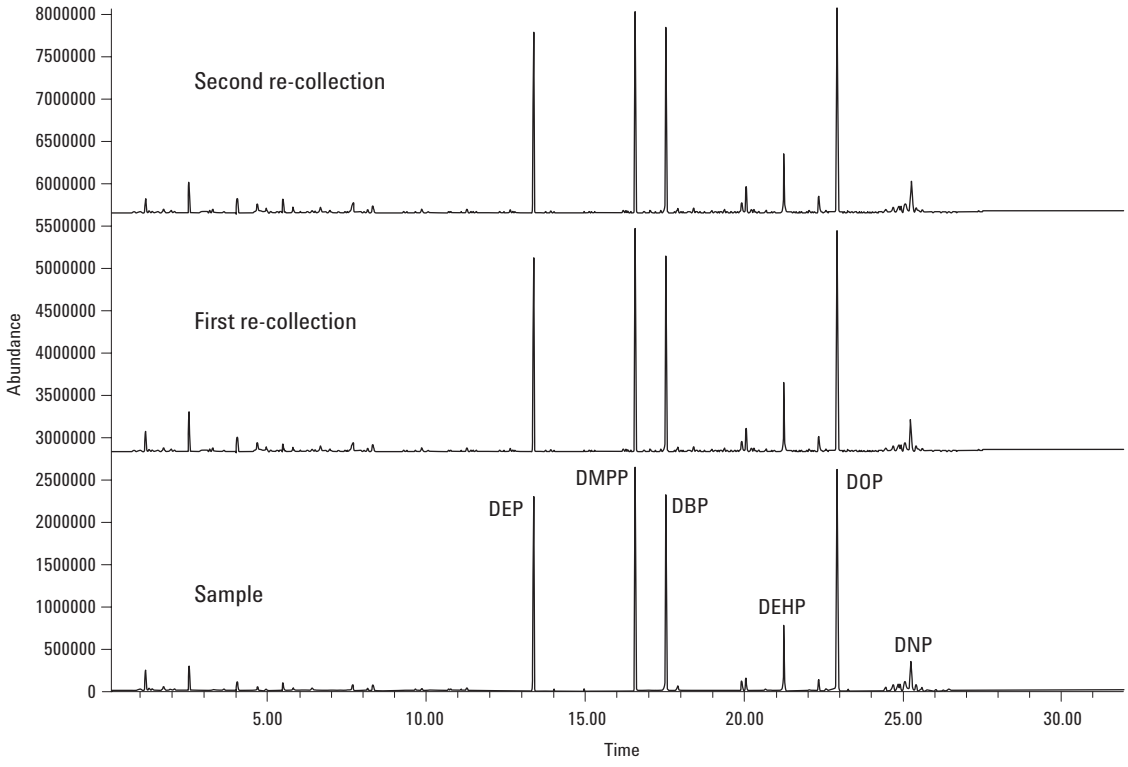

Figure 6. Re-collection of high boiling compounds.

Erroneous GC Parameters - Evaluation of Repeat Analysis for Labile, High Boiling Analytes

To test the repeat analysis capability for other demanding applications, a Tenax TA tube was loaded with low µg levels of a series of labile, high boiling organic amines. See Table 2. The loaded tube was prepared in the South Wales laboratory of Solutia UK Ltd. using direct injection of a liquid standard. A blank tube was also analyzed. Split effluent from the sample was re-collected on a conditioned Tenax TA tube and re-analyzed. During the first analysis of the standard, the GC run finished prematurely, half-way through elution of 4A. Its relative concentration, however, was determined from analysis of the re-collected sample. Relevant chromatograms are shown in Figures 7 to 9.

Analytical conditions were set as follows:

Tube desorb:	320 °C for 10 min
Flowpath:	200 °C
Cold trap packed with Tenax TA	
Cold trap low:	–10 °C,
Cold trap high:	300 °C for 5 min
Helium carrier gas at	15 psig giving a column flow of ~1.5 mL/min
Desorb flow:	15 mL/min, split flow (inlet and outlet) 47 mL/min giving an overall split ratio of ~130:1
GC column:	30 m × 0.25 mm × 0.25 mm film methyl silicone
GC oven:	50 °C for 2 min, 30 °C/min to 250 °C for 3.5 min, 15 °C/min to 280 °C for 0 min (run 1) or 1 min (subsequent analyses)

Table 2. Repeat Analysis of Amines

Compound name	Abbr	Peak area Run 1	Peak area Repeat analysis
Para-nitrochlorobenzene	PNCB	3225	3583
Formaninlide	FAN	4177	4352
N-isopropyl, N'-phenyl paraphenylenediamine	1PPD	4729	4950
4-Nitrodipheylamine	4N	3104	3274
4-Aminodiphenylamine	4A	4967*	5283

*Extrapolated from rpt analysis

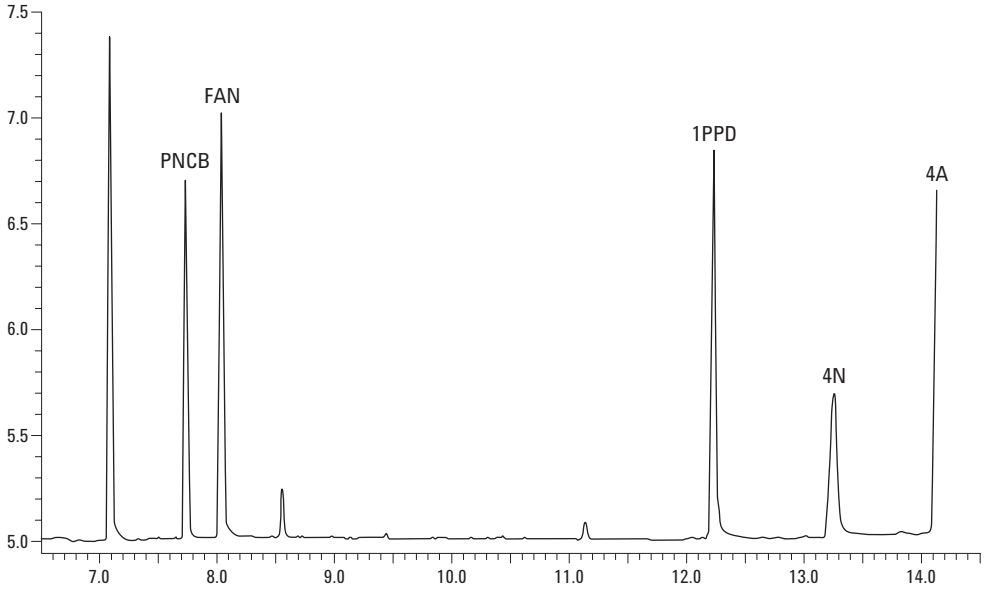

Figure 7. Chromatogram showing the first desorption of a liquid standard of a series of labile, high boiling amines.

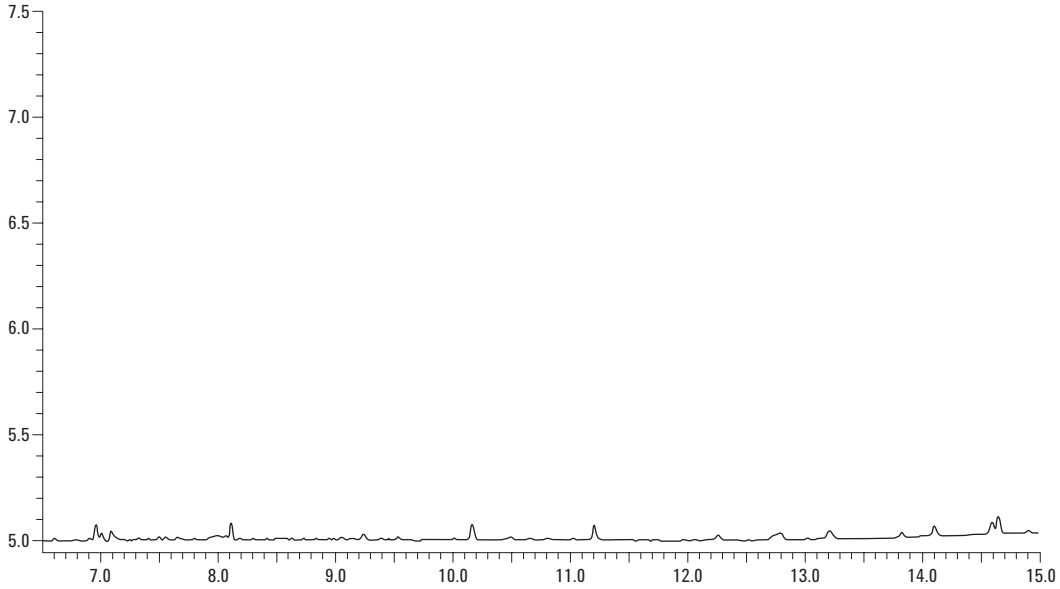

Figure 8. Chromatogram of blank tube desorbed after liquid standard - showing no system carryover.

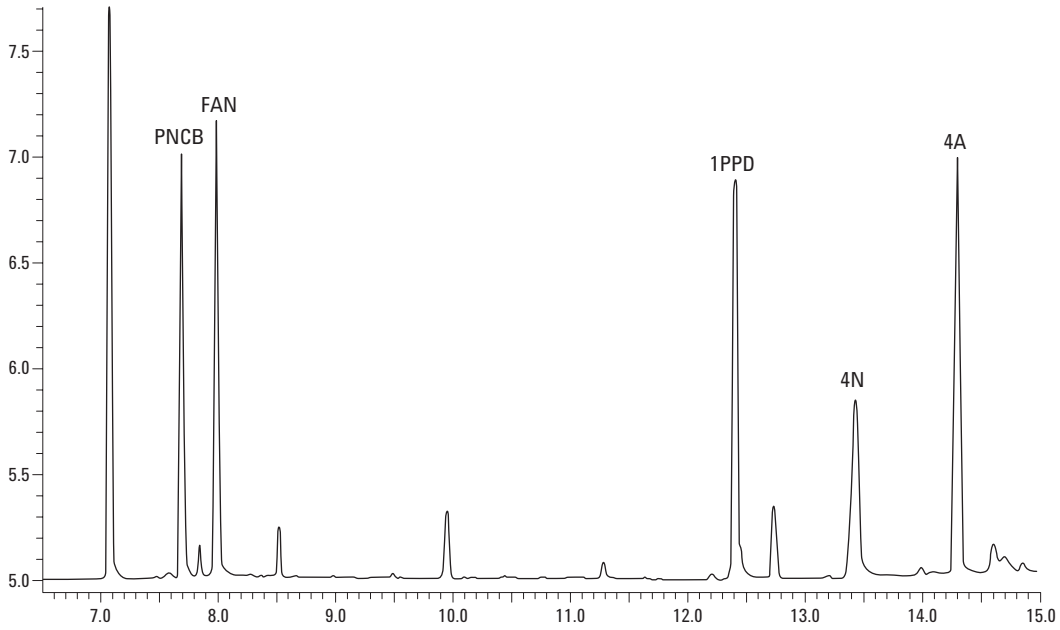

Figure 9. Chromatogram of re-collected split sample.

Troubleshooting

A solution of high molecular weight hydrocarbons (C28, C32, C36, and C40) was loaded onto pre-conditioned sorbent tubes packed with quartz wool and Tenax TA, then analyzed.

Each compound was nominally present at a similar concentration; however, the C36 and C40 peak were much smaller than expected. It was unclear at first whether this was an instrumentation problem or an issue with the sample solution. The sample was re-collected and reanalyzed three times and no bias, that is, no loss of n-C36 or n-C40, was observed. This showed that higher boiling components were in fact at a lower concentration than the more volatile species, and it was later determined that the high boilers were dropping out of solution before they could be loaded onto the primary sorbent tube. See Figure 10.

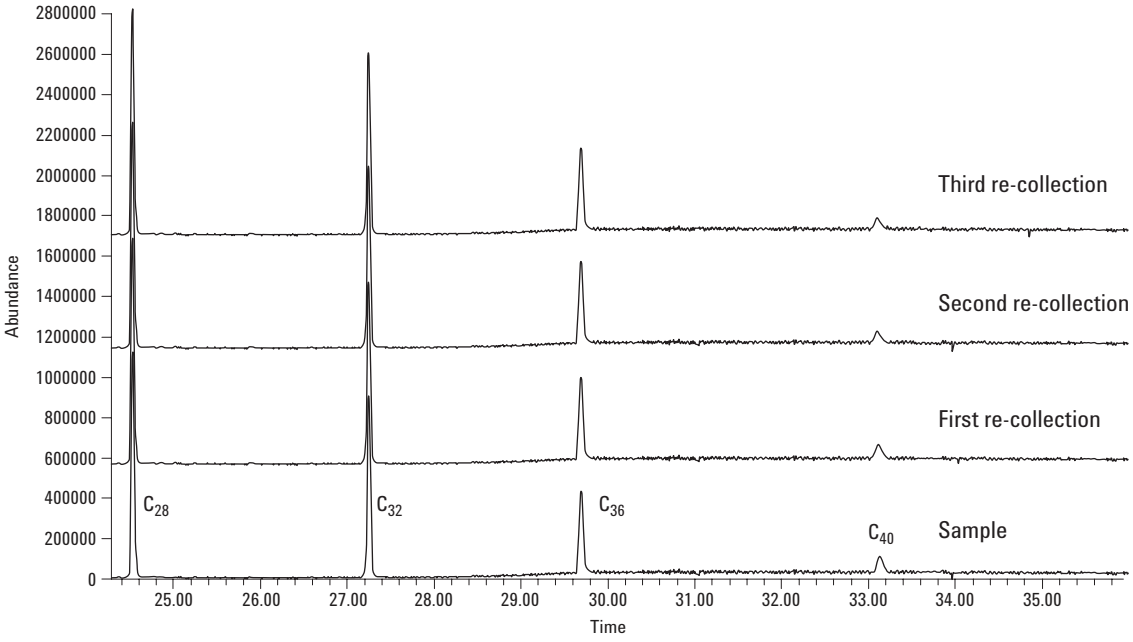

Figure 10. Stacked chromatograms of successively re-collected high molecular weight hydrocarbons.

Summary

This work illustrates the significant benefits of SecureTD, both for overcoming the one-shot limitation of traditional TD, and as a powerful tool for method development and validation. This innovation should allow TD, with all its inherent advantages of cost, sensitivity, and safety, to be used for all relevant environmental health and safety applications.

Acknowledgement

The evaluation entitled Erroneous GC Parameters was carried out in collaboration with Solutia UK Ltd. and Flexsys Ltd. We gratefully acknowledge their contribution to the work.

Reference

1. J. Kristensson, Thermal desorption: A multi-shot technique, Stockholm Sweden: University of Stockholm; 1987.

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Printed in the USA
April 24, 2003
5988-9253EN

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Optimizing Analytical Performance and Extending the Application Range of Thermal Desorption for Monitoring Air Indoors and Inside Vehicle Cabins

Technical Overview

Introduction

Thermal desorption (TD) is a readily automated gas extraction technology based on standard gas chromatography parameters. It provides an efficient, high-sensitivity alternative to conventional solvent extraction. The process of TD involves the extraction of volatile or semivolatile organic compounds from a sorbent or material by heating the sample in a flow of inert gas. The extracted analytes are then transferred in the flow of carrier gas to the analyzer [typically a gas chromatograph (GC) or a gas chromatograph/mass spectrometer (GC/MS)] as a small, discreet, and concentrated volume of vapor. The thermal desorber becomes a multipurpose, standalone GC injector. Concentration factors as high as 10^5 to 10^6 can be achieved using modern systems with analytes collected from tens to hundreds of liters of air being delivered to the analyzer in as little as 200 µL of gas.

Though inherently simple, many factors contribute to the performance and efficiency of the TD process, which determines the ultimate sensitivity and reliability of a TD-based analytical method. These factors include retention efficiency (during sampling/focusing), desorption efficiency, artifacts, band broadening, and analyte/system stability. This overview describes optimization of all of these parameters during the development and validation of TD procedures. Examples of optimum method performance in terms of precision, linearity, and sensitivity are presented. A novel approach to overcoming the traditional one-shot limitation of TD is also described.

Analytical TD — The Process

Analytical TD is a gas-phase introduction technique for vapor-phase analytical systems such as GC and GC/MS. It combines many pre-analytical procedures including sample preparation/collection, selective concentration, analyte extraction, and injection into one labor-saving automated operation. It is used for the measurement of trace volatile organic compounds (VOCs); however, the range of sample types and applications is very diverse:

- Air can be sampled and analyzed online on a semicontinuous basis for real-time studies. Examples include diurnal variation of indoor air pollution, real-time tracer gas studies, etc.
- Building materials and furniture are large contributors to indoor air pollution. The volatile content of solid or liquid samples such as paints or textiles can be measured by weighing the material into empty sampling tubes for extraction and quantitative analysis by direct TD-GC/MS.
- In other cases, vapor phase samples can be collected offline into containers (canisters, bags, etc.) or sorbent tubes. Relevant applications for collection in sorbent tubes include exhaust from materials emission tests, indoor air pollution profiling, studies of building ventilation using tracer gases, and the characterization of odors.

Regardless of the primary sampling device used, volatiles are ultimately swept by the carrier gas into a secondary focusing device inside the thermal desorber where target analytes are selectively retained. Once all the compounds of interest have been transferred to the focusing device and all unwanted volatiles (water, for example) have been swept to vent, the focusing device is thermally desorbed by rapid heating in a reverse flow of inert gas. This process 'injects' target compounds into the analyzer in a tiny, concentrated 'slug' of vapor.

Sampling Options

Containers – Canisters and Bags

Containers, such as passivated canisters or Tedlar™ bags, are the best air sampling option for ultravolatile chemicals such as C2 hydrocarbons. Though expensive, evacuated canisters provide the simplest of all air sampling options with 'grab' sample collection via release of a single valve. However, Tedlar bags offer limited storage stability (<24 hours) for many common VOCs [1]. Canisters are similarly prone to poor recovery of less volatile or more polar species [2] when used for higher concentration atmospheres. Many polar or less volatile species tend to stick to the internal walls of containers and cannot be quantitatively recovered. Humidity can also cause problems. If liquid water condenses inside the container, organic compounds, particularly the more polar species, will partition between the aqueous and vapor phases, giving unreproducible results. While Tedlar bags are typically used only once, canisters can be reused indefinitely. However, they require stringent cleaning by repeated evacuation and purging between uses.

Vapor Sampling onto Sorbent Tubes

While no single sampling method suits all indoor applications, TD sample tubes may provide the most versatile option. Used either empty for desorbing volatiles from materials (see below), or packed with sorbent for retaining vapor-phase organics, they are compatible with all but the most volatile species (for example, acetylene, ethylene, and some freons). Typically, a known volume of air is pulled through the tube at around 50 mL/min using a standard pump. Alternatively, industry-standard steel or coated steel tubes, which have a well-defined, fixed-air gap between the end of the tube and the sorbent sampling surface, can also be used as diffusive (passive) samplers. In this mode, tubes are simply left open at the sampling end, allowing analytes to migrate from the air to the sorbent at a rate controlled by the diffusion gradient according to Fick's first law.

Many of the limiting factors dictating the performance of sorbent tube based air sampling methods (pumped or diffusive) relate to sorbent selection and preparation.

Optimizing Analytical Performance for Sorbent Tube-Based Methods

Sorbent Selection

Sorbent strength – Analytical sensitivity and precision are largely determined by sampling efficiency, desorption efficiency, and the level of interferences (see section on artifacts below). The sorbent(s) selected must be sufficiently strong enough to retain target analytes during sampling/concentration, but weak enough to release them efficiently during the TD phase.

Concentration enhancement potential – Depending on the retentive strength (breakthrough volume) of the sorbent tube selected for the analytes in question, as much as 100–200 L of air can be pumped through a sorbent tube during sampling. During primary (tube) desorption the compounds of interest can be eluted in as little as 100–200 mL of carrier gas and transferred to the focusing trap. Using new, state-of-the-art, fast desorption traps, analytes can subsequently be desorbed from the trap and transferred to the analyzer, splitless, in as little as 200 µL of gas. This produces an overall concentration enhancement of 10^6. Exceptional detection limits can be achieved, even with a conventional Flame Ionization Detector (FID) (Figure 1).

A wide range of sorbents is now commercially available. These can be classified generally as weak, medium, or strong. Less volatile analytes should be trapped on weaker sorbents, while more volatile analytes should be trapped on stronger sorbents. If a wide volatility range of compounds is being monitored, it is often necessary to pack the tube with more than one sorbent material and to arrange them in order of increasing strength, starting from the sampling end. At ambient

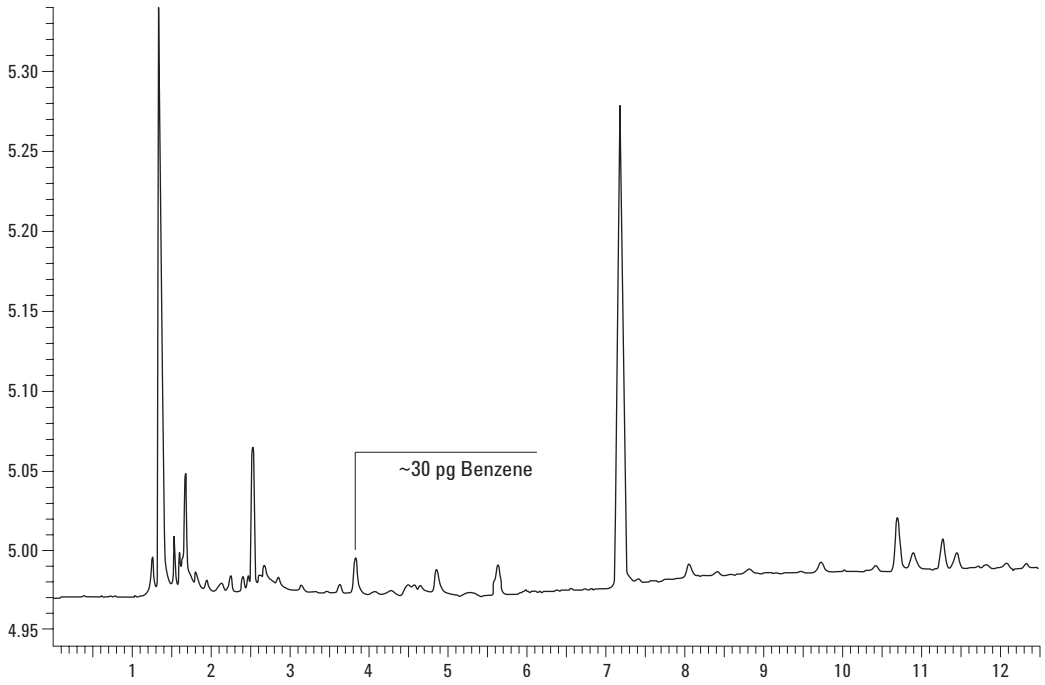

Figure 1. Thirty pg of benzene from a sorbent tube. Equivalent to 10 ppt in 1 L of air.

temperatures, sorbents can be used to retain quantitatively compounds as volatile as vinyl chloride monomer (VCM) and propane. Electrically-cooled sorbent focusing traps can concentrate the most volatile freons and components as volatile as acetylene without additional cooling from liquid cryogen.

Other key considerations when selecting sorbents include:

- **Inertness** – Some sorbents are contaminated by chemically active materials, such as trace metals, from the production process. This is especially true of carbon blacks, many of which derive originally from natural charcoals.
- **Hydrophobicity** – Most common weak and medium strength sorbents are very hydrophobic; their sorbent strength is not compromised even when sampling at high (>90%) humidity. However, most strong sorbents are comprised of some sort of carbonized molecular sieve, and their sorbent strength can be reduced at very high humidity by as much as a factor of 10. If a large amount of water is retained on the tube, this can adversely affect the analysis; however, most modern desorption systems incorporate one or more methods for selectively eliminating water.
- **Artifacts** – Sorbents vary significantly with respect to inherent artifact levels. Some porous polymers, such as the Chromosorb Century series and Poropaks, have relatively high artifacts, with several peaks at 5–10 ng levels. Tenax TA™ is better with minimum levels between 0.1 and 1 ng for well-conditioned materials. Both carbon blacks and carbonized molecular sieves are excellent with respect to inherent artifacts, between 0.01 and 0.1 ng, if well conditioned. However, the carbonized molecular sieves require extended conditioning at steadily increasing temperatures, and when new, can continue to show a high background of inorganic gases for several days.
- **Temperature stability** – Most sorbents, including Tenax TA, are stable up to 350 °C, and many of the carbon sorbents can be taken much higher. Care must be taken with most of the other porous polymers, Chromosorbs and Poropaks, which typically have temperature limits at or below 225 °C. This means that they cannot be packed into mixed-bed tubes with more stable sorbents. If this is done, it is not possible to adequately condition the higher temperature materials without overheating the polymers.

- **Mechanical strength** – Carbon blacks are extremely friable and prone to the formation of fines. Care should be taken not to over compress these sorbents during tube packing and to avoid sharp knocks to the tubes once they are packed. As the carbon packing ages, the formation of fines may increase tube impedance beyond the limit of some pumps. Most other sorbents are mechanically strong, though Tenax TA can have a high percentage of fines when new and may require sieving before use. Generally speaking, recommended mesh sizes for sorbents in standard 4–5 mm bore sampling tubes range from 30–80 mesh. A selection of the most common sorbents and their associated characteristics is presented in Table 1.

Pumped Monitoring/Active Sampling Through Sorbent Tubes

Pumped monitoring is the most versatile sampling option for the compatibility of packed tubes with both single and multibed sorbents. It is specified by a number of international standard methods relating to indoor air. These include prENV 13419 and ISO DIS 16000 for testing emissions from building materials and US EPA Method TO-17, ISO 16017 Pt. 1, and ASTM D6196-97 for general monitoring of VOCs in indoor air. Industry standard ¼-inch od by 3.5-inch long tubes can be sampled efficiently at rates ranging from 10 to 200 mL/min, with the optimum being 50 mL/min [3].

'Universal' tubes – There is no such thing as a universal tube. However, perhaps the most useful combination of sorbents that can be packed into a single tube for pumped monitoring of uncharacterized atmospheres is Tenax TA backed up by Carbopack B™ (Carbograph 1™), in turn backed up by Spherocarb™ (Unicarb™) or Carboxen 1000™. The main limitation of this sorbent combination is that the middle strength carbon black sorbent is not completely inert and may cause degradation of labile analytes such as nitrogen, sulphur-containing compounds, and some monoterpenes. The ultimate 'train' of tubes for monitoring uncharacterized areas consists of three inert Silcosteel tubes connected together in series using inert, nonemitting fittings. The front tube is packed with Tenax TA, the middle one is packed with Chromosorb 106™, and the back one is packed with Unicarb. Whenever using these or any multisorbent combination of tubes, sampling must always take place through the weaker sorbent first. Higher boiling analytes are thus retained by and desorbed from the weak sorbent without coming into contact with the stronger sorbents.

Table 1. Key Features of the Most Common Sorbents

Sorbent	Strength	Features
Tenax TA	Weak	Inert, hydrophobic, individual artifacts below 1 ng, max temperature: 350 °C, sieve to remove fines
Carbograph 1	Weak-Medium	Not inert, hydrophobic, individual artifacts below 0.1 ng, max temperature: >400 °C, prone to fines formation
Chromosorb 106	Medium	Inert, hydrophobic, individual artifacts up to 10 ng, max temperature: 225 °C, precondition to shrink before use
Unicarb/Spherocarb	Strong	Inert, not hydrophobic, individual artifacts below 0.1 ng, max temperature: >350 °C, condition slowly - increasing the temperature stepwise, purge thoroughly to remove O_2 before heating
Carboxen 1000	Ultrastrong	Inert, not hydrophobic, individual artifacts below 0.1 ng, max temperature: >350 °C, condition slowly - increasing the temperature stepwise, purge thoroughly to remove O_2 before heating

Diffusive sampling

Axial samplers – Single-bed, ¼-inch od, 5 mm id stainless steel or Silcosteel sorbent tubes with a 15-mm air gap between the surface of the sorbent and the sampling surface are used as standard for pumped monitoring (see above). However, these tubes were designed as long ago as 1979 [4] to be used as axial format diffusive samplers. The uptake rate of many common solvents is already well validated for these tubes. Diffusive sampling eliminates the expense and relative complexity of sampling pumps and facilitates large-scale air monitoring campaigns at affordable cost. The diffusive sampling rate is a constant function of atmospheric concentration, as predicted by Fick's law, provided the concentration at the surface of the sampler remains at zero (Figure 2).

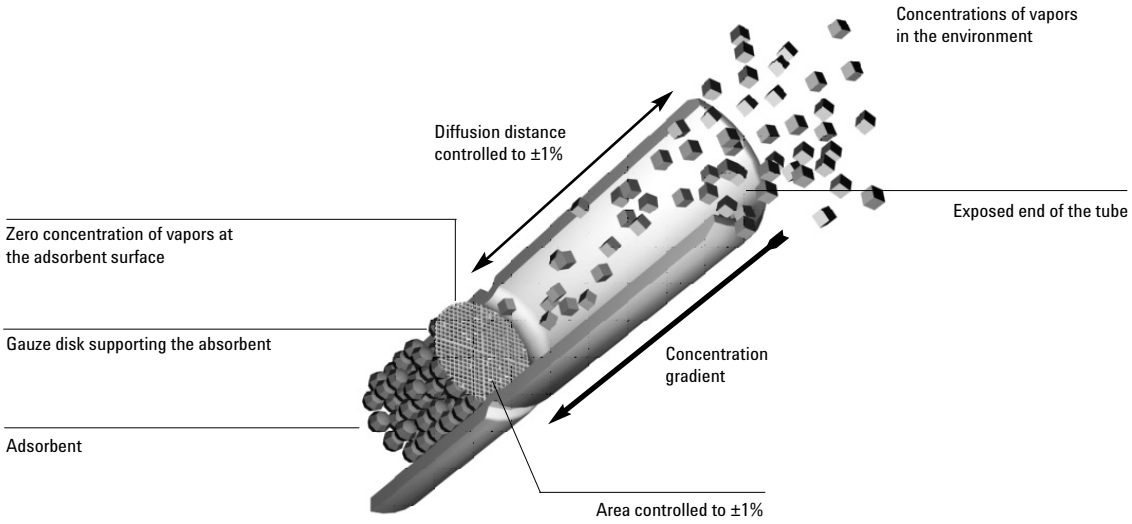

Figure 2. Illustration of diffusive sampling on axial sorbent tubes.

For use as diffusive samplers, the tubes are capped with special diffusion caps at the sampling end and kept sealed at the nonsampling end. The diffusion caps simply have a gauze surface to stop macroparticles from entering the tube and to mask the sorptive surface.

Typical sampling rates on axial diffusive tubes are quoted at around 2 ng/ppm/min (2 pg/ppb/min), which is equivalent to a pumped flow of between 0.5 and 1 mL/min. Standard sorbent tubes may be used in diffusive mode for both short term monitoring (1–8 hours) in high concentration areas and long term (3 days to 4 weeks) monitoring of 'typical' indoor and ambient air.

Radial diffusive samplers – New radial diffusive samplers consist of a sorbent sampling cartridge housed in a porous polymer body; this allows sampling along and around the whole cylindrical surface of the sampler (Figure 3). These devices sample at a rate equivalent to 50–100 mL/min, but saturate quickly. They can only be used for short term 0.5 to 6-hour air monitoring and at ambient/indoor (low ppb) levels. They are a useful complement to the axial diffusive tubes. After sampling, the sorbent cartridge is simply slipped from its porous polymer housing and placed into an empty 'carrier' tube for analysis by TD-GC/MS. The sampling cartridge is an impedance fit inside the middle of the carrier tube to ensure gas passes through the body of the cartridge during desorption. The cartridge may be reused as many times as a standard sorbent tube.

Diffusive sampling is specified by a number of international standard methods relating to indoor air. These include prEN 13528 and ISO 16017 Pt. 2 for general monitoring of VOCs in indoor air and the Dutch standard for ventilation testing using perfluorocarbon tracer gases [5].

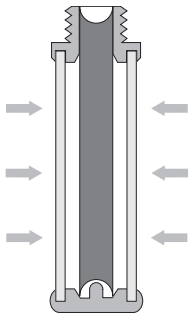

Figure 3. Radial diffusive samplers.

Conditioning and Storage of Sorbent Tubes

To clean them before use, sorbents invariably require stringent conditioning at high temperatures in a flow of inert gas. Many of the porous polymer-type sorbents also require preconditioning in bulk before they are used to pack tubes. This is because as much as 10%–15% of sorbent mass may be lost during the first conditioning cycle. It is rare for any form of solvent washing to be required, but conditions used for tube cleaning should be more stringent (in terms of flow and temperature) than those to be used subsequently for analytical TD.

Conditioned and sampled tubes should be stored using long-term ¼-inch screw caps fitted with combined PTFE ferrules. Tubes capped and stored in this way are reported to be stable for up to 27 months [6], provided the compounds concerned are not chemically active.

Desorption and Analysis

Advice on optimizing and validating the TD and GC/MS analysis process has been described in the literature [7] and is outlined in many of the international standard methods listed above for pumped and diffusive sampling. In summary, analytical desorption temperatures should be kept below those used for tube conditioning with a carrier gas flow of 20-30 mL/min. All air (O_2) should be purged from the tubes before heat is applied, and system flow paths should be kept short, inert, and uniformly heated. TD methods should readily facilitate better than 95% recovery in a single desorption.

The linearity of TD-GC/MS methods should be the same as those achieved using GC/MS with conventional liquid inlets. The precision of TD methods is typically limited to 1%–2% by the manual introduction of standards to sorbent tubes during calibration. However, this is insignificant relative to the overall variability of the complete sampling and analysis procedure for indoor or ambient air. Most standard methods quote this at 15%–30%.

As demanded by international standard methods, TD instrumentation should feature automatic leak testing and tubes that are sealed before and after analysis to maintain data integrity.

SecureTD™ Repeat Analysis for TD

Given its enormous advantages over solvent extraction of adsorbents (in terms of sensitivity, reusable tubes, reproducibility, and environmental acceptability), it is sometimes surprising that TD has not universally replaced solvent extraction for all air monitoring applications. The reason that solvent extraction is still used, especially for some industrial applications, is that more than one analysis can be carried out on each extracted sample. TD, on the other hand, has traditionally been a one-shot technique; once a sample has been thermally desorbed (heated in a flow of inert gas), it is gone. No sample remains for repeat analysis. The latest commercial TD technology overcomes this limitation by offering quantitative re-collection of the split effluent for repeat analysis. In all but the lowest (ppt) level applications, a split can be used. In some cases, when determining the solvent content of coatings or adhesives for example, a large split is often necessary for optimum analytical performance. The latest commercial TD apparatus facilitates quantitative split re-collection for repeat analysis. In these systems, the normal charcoal filter is designed to be the same size as a standard sorbent tube and is easily interchanged. The flowpath leading up to the split point is also uniformly heated and inert. For sample re-collection, the charcoal tube is simply replaced with a conditioned sorbent tube. A steep temperature gradient along the first portion of the re-collection tube ensures good retention efficiency.

The re-collected sample can be archived for analysis by a third party lab or re-analyzed immediately under the same or different analytical conditions as required. Excellent precision can be obtained (Figure 4).

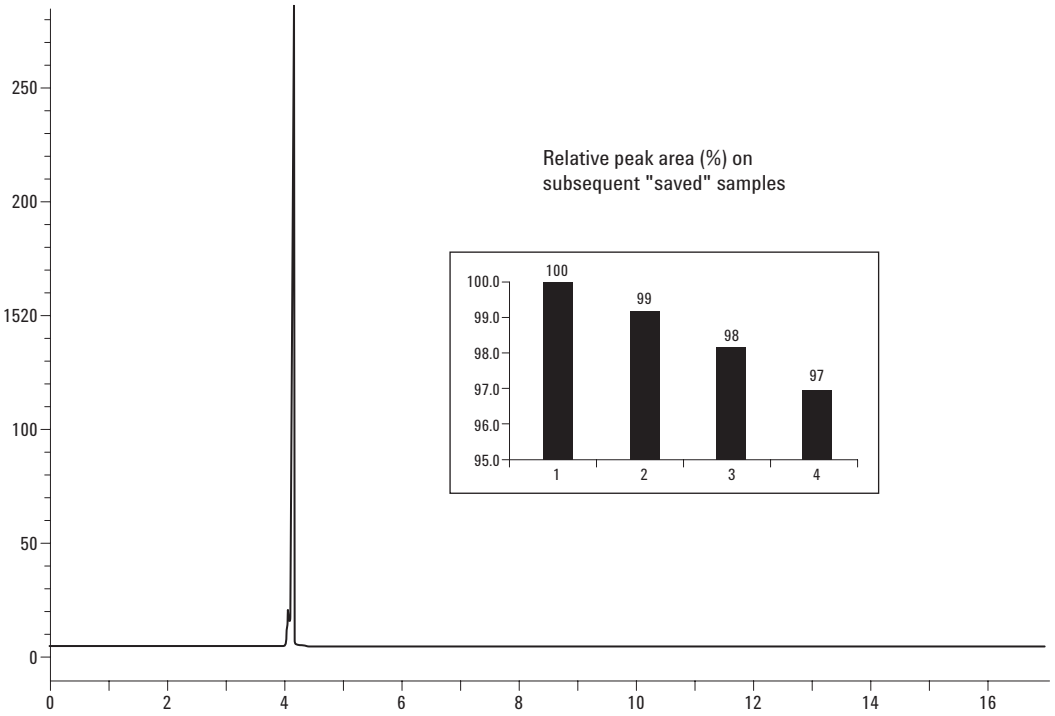

Figure 4. Re-collection and repeat analysis of desorbed toluene.

The Field and Laboratory Emissions Chamber (FLEC)

The FLEC (Figure 5) is a specialized piece of sampling apparatus for testing VOC emissions from construction products and other materials used indoors. It is a simple, portable materials emissions chamber that is shaped like the mouth of a trumpet. It is placed onto the surface of a planar material and air is passed uniformly over the surface. Exhaust gases are collected onto one or two sorbent tubes and then analyzed using standard TD-GC/MS techniques.

Figure 5. Field and laboratory emission cell (FLEC) for emission testing.

The FLEC complies with Section 2 of the new European standard for testing VOC emissions - prENV 13419. FLEC applications include emissions testing from applied wall coverings, floor coverings, adhesives, sealant materials, paints, and coatings.

Breath Sampling as a Tool for Investigating Biological Exposure

The Bio-VOC Breath Sampler (Figure 6) is a disposable device that collects a 100-mL sample of end-tidal air and transfers it to a sorbent tube [8]. Several breath samples from the same individual can be loaded onto the same sample tube if required. Analysis is typically done by conventional TD-GC/MS.

Figure 6. Monitoring biological exposure via alveolar air collected using the Bio-VOC breath sampler.

Indoor air-related applications for the Bio-VOC Breath sampler include chronic personal exposure monitoring, particularly for individuals living near local emission sources (for example, above a dry cleaning shop).

Direct Desorption

Direct TD provides a convenient and high-sensitivity alternative to purge and trap or solvent extraction for some relatively homogeneous materials. Samples such as powders, film, fibers, granules, resin, or even droplets of liquid can be weighed directly into empty tubes or special PTFE tube inserts.

The sample is then heated in a stream of inert carrier gas that strips volatiles from the sample and transfers them to the focusing trap. In this mode, TD becomes a dynamic headspace procedure.

It is used for complete and quantitative extraction of residual volatiles to determine the solvent or volatile content of a sample. Examples of building materials suitable for this approach include printed polymers/papers, carpet, water based paint, wood varnish, adhesives, etc.

For many quality control and trouble-shooting applications, direct TD eliminates hours of conventional sample preparation. In many cases, a 3-way separation can be achieved. Solids are left in the sample tube and prevented from contaminating the analytical system, and unwanted interferents such as water or ethanol may be eliminated during the focusing process. This leaves only the target organics to be collected in the focusing trap and transferred to the analyzer.

Samples may be weighed directly into empty tubes supported by two glass wool plugs or placed into inert tube inserts such as PTFE liners to prevent contamination of the inner surface of the tube. If complete, quantitative extraction is required, samples should have a relatively high surface area to mass ratio. Examples of such samples include powder, granules, liquid droplets, or fibers. Resins should be smeared inside PTFE inserts or onto glass fiber 'boats' to prevent contamination of the inside of the tube. Similarly, liquids (emulsions, solutions, etc.) can be introduced as droplets on glass wool plugs inside PTFE liners. It is important to make sure the sample does not block the sample

tube; this will stop the gas flow and prevent complete TD. In addition, make sure that the sample is not taken above its decomposition temperature. An example of paint analysis by direct TD-GC/MS is shown in Figure 8.

Summary of Applications for TD in Indoor Air Monitoring

TD methods provide a high sensitivity and robust analytical option for a wide range of indoor air monitoring and related applications. A summary of some key applications is given below, along with useful references. Factors affecting method optimization were described and many key applications relating to indoor air were referenced. A summary of these and other relevant TD applications is listed below with key references:

- Testing VOC emissions from building materials and furnishings [9, 10]
- Indoor air profiling [11]
- Ventilation testing [5]
- VOC content of materials [12]
- Identifying indoor mold/fungal contamination via VOC profiling [13]
- Biological exposure testing [14]
- Real-time air profiling for diurnal variation studies [15]

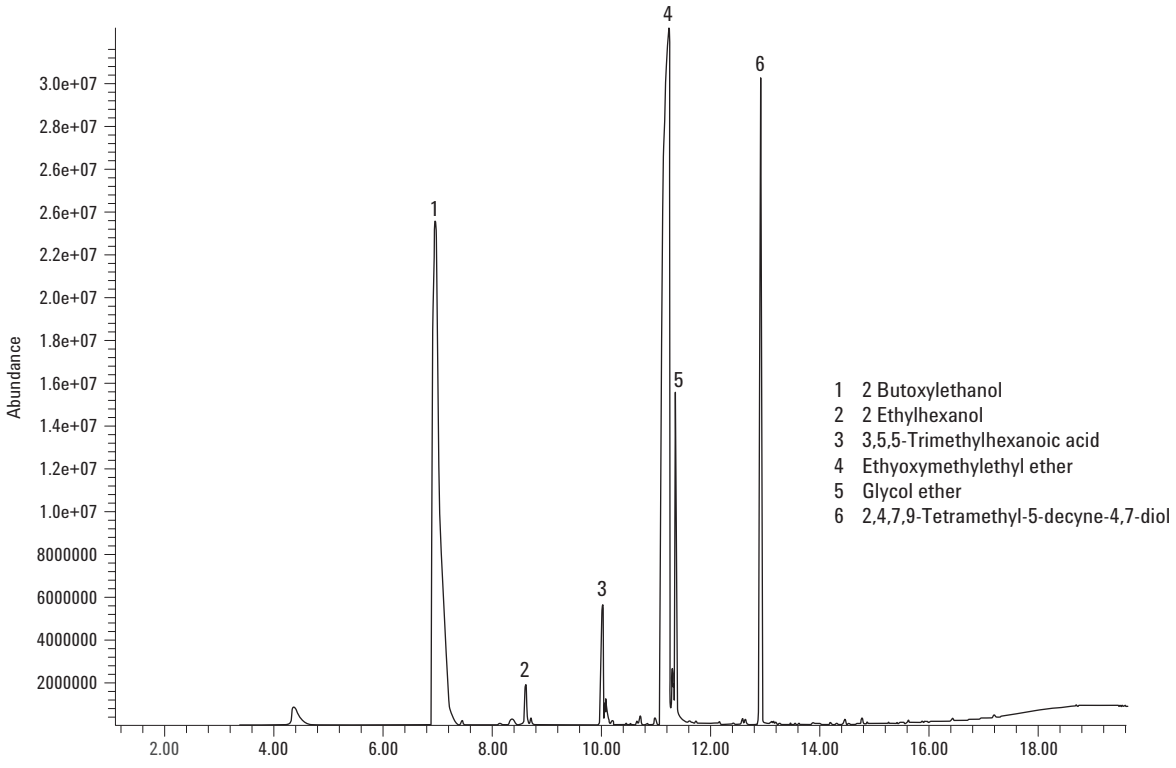

Figure 8. Direct desorption of volatile and semi-volatile organics from paint.

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Printed in the USA
April 21, 2003
5988-9255EN

Agilent Technologies

MARKES international LIMITED

The Benefits of Setting Up a UNITYe-Based Thermal Desorber Using an Agilent 6890 GC's Electronic Pneumatic Control

Technical Overview

Introduction

Electronic Pneumatic Control (EPC) offers numerous advantages for gas chromatographic (GC) methods including: electronic control of all gas flows and pressures, maintenance of constant flow or pressure throughout a run, flow or pressure programming, and independent regulation of column and split flows. With EPC, flow rates may be stored and recalled with each individual GC method. GCs equipped with EPC allow reproducible results that are independent of operator, laboratory environment, or column.

The precise control of the Agilent GC column flows has allowed the development of Retention Time Locking (RTL) software. RTL allows one to match retention times between different Agilent 6890 systems independent of the inlet or detector. This has substantial cost and time saving benefits and leads to more accurate peak identification.

Though desirable for enhanced analytical performance, it has previously proved difficult and expensive to incorporate EPC into method-compliant thermal desorption (TD) systems. This is because of the many valve and carrier gas flow path changes that occur during the analytical sequence (for example, stop-flow leak testing, dry-purging, prepurging, tube desorption, and backflush trap desorption). However, after a collaborative development program between Agilent Technologies, Inc. and Markes International, Ltd., backpressure regulated EPC has now been successfully and cost-effectively incorporated into the UNITY™ TD platform. This development significantly improves analysis using coupled thermal desorption-gas chromatography (TD-GC), particularly for complex sets of target analytes.

Implementation of EPC with UNITY - UNITYe

Back-pressure regulated EPC control is implemented on UNITY using the standard EPC module supplied with the 6890 GC split/splitless (S/S) inlet (Figure 1). Some modifications are incorporated on a standard UNITY system to make it an EPC-compatible UNITYe. The most important modification involves inserting a tee into the carrier gas bypass line, close to the connection point with the fused silica transfer line. The tee is connected to a convenient bulkhead fitting on Unity, allowing easy connection to the septum purge port of the Agilent split/splitless EPC module. This provides accurate monitoring and closed-loop control of column head pressure, regardless of the stage of TD operation and the required flow. Use of a low-volume, 3-way valve on each of the two gas connection lines (not shown in Figure 1) would allow the EPC module to be connected interchangeably between the UNITYe and the split/splitless GC inlet. Once configured, a UNITYe-based TD system coupled to a 6890 GC or gas chromatograph/mass spectrometer (GC/MS) offers all the performance enhancements associated with electronic pressure and flow control on standard Agilent 6890 liquid injection systems.

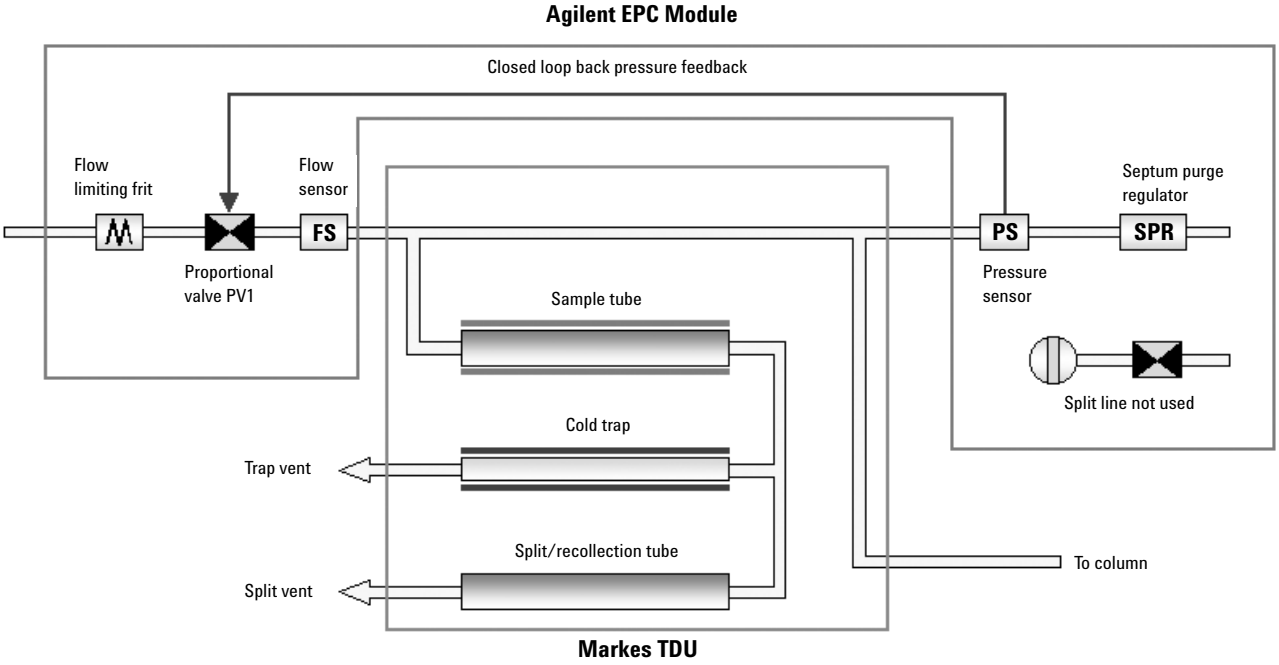


Figure 1. Schematic of UNITYe showing primary desorption step.

Stable Retention Times with Different Split Flow Settings

Using conventional pressure pneumatics, the column flow and, therefore, analyte retention times shift every time the TD split flow is adjusted. This shift makes it difficult to calculate split ratios exactly and prevents the same data processing method and compound list being used for both high and low concentration applications. With EPC, carrier gas pressure at the head of the column is continuously monitored and maintained. Retention times remain steady despite split flow changes (Figure 2). EPC control of the GC and TD flows is extremely stable over time. For example, there was no change in the retention times for the benzene, toluene, and xylene peaks over the 15-hour sequence shown in Figure 3.

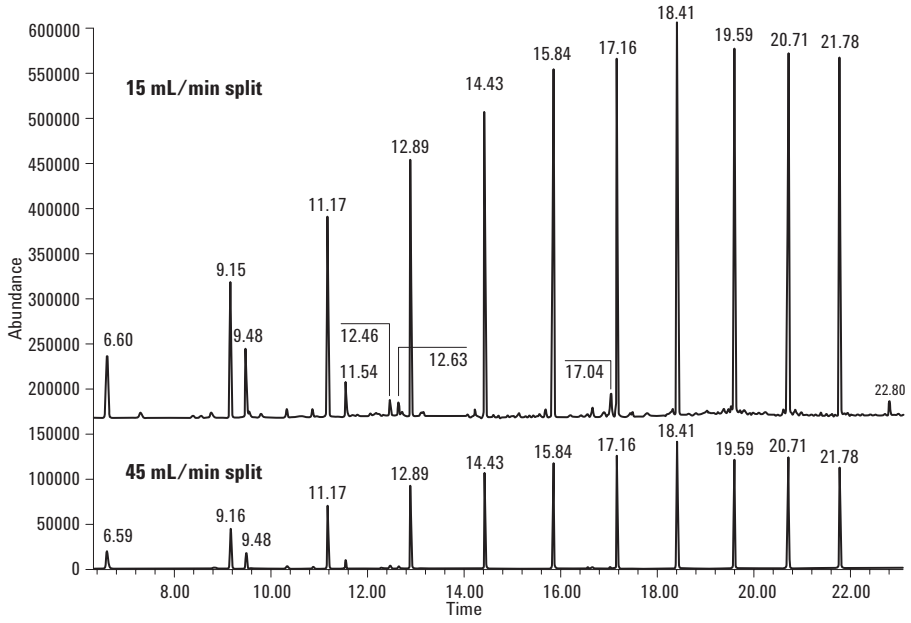


Figure 2. Retention times stable to two decimal places under significantly different split flows.

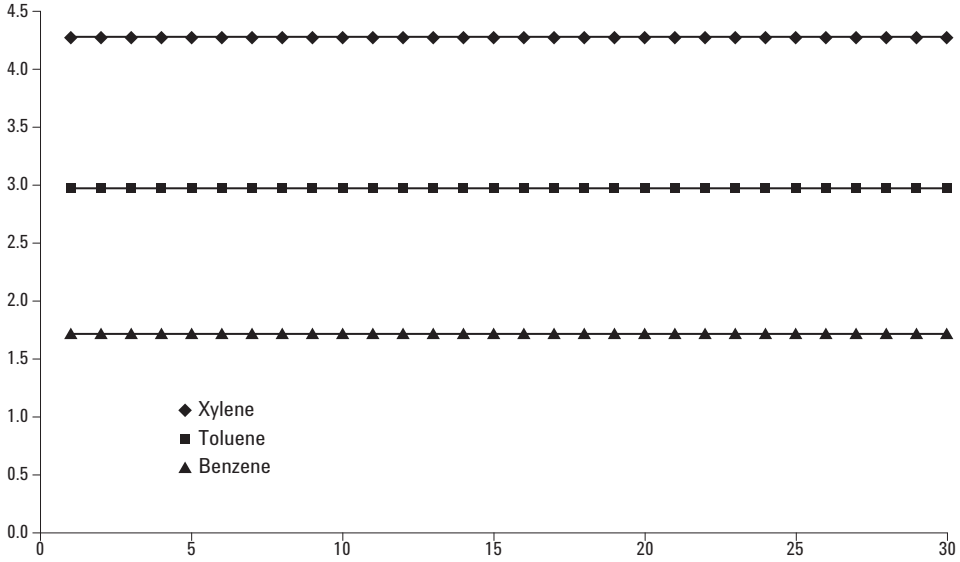


Figure 3. Retention time stability for 30 TD/GC/MS analyses of benzene, toluene and xylene over a 15-hour period.

Retention Time Locking (RTL) and Compound Databases

RTL allows retention times to be fixed; they can be re-established precisely after column maintenance or replacement. This means that calibration tables, developed in data handling software to identify and quantify peaks, never need to be adjusted. It also allows methods to be transferred and chromatograms to be reproduced on any other UNITYe-Agilent 6890 TD/GC (or TD/GC/MS) system using the same method and configured with a column of the same nominal dimensions.

In fact, RTL has rendered retention times so stable that it is now possible to create searchable databases (libraries) of component retention times.

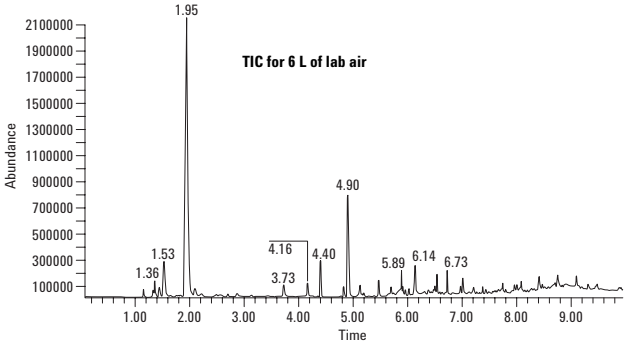
RTL databases for use on GC/MS systems include the full spectrum for each compound, its locked retention time, and a table of key ions for use by the ChemStation screener software. The Agilent screener software searches for every compound in the RTL database in a fully automated post-run data processing operation (Figure 4).

A user-generated RTL mass spectral database was used to screen the laboratory air sample shown in Figure 1a. Figure 1b gives the initial report generated by the RTL screener software with numerous target compounds identified. Figure 1c shows the extracted ion chromatogram for *m/z* 91 which is common to several of the identified peaks. Agilent's results screener software makes it convenient to confirm peak identities.

Electronic Read-Out of Total System Flow

Another practical benefit of EPC with UNITYe-based thermal desorbers is the ability to monitor carrier gas flow through the system in real-time. Total gas flow [column flow plus cold trap flow, when applicable, plus split flow] is displayed when accessed via the convenient keyboard and display unit on the 6890 GC or via ChemStation PC software. This eliminates the need for flow meters and provides a convenient confirmation of long-term system stability and leak-tight gas supply connections into the system.

4a



4b

Cpd#	Compound Name	Status	EXpRt	Delta	Target *m/z*	Qualifiers	Out of Range	XCR
14	MTBE methyl-t-butyl-ether	?	1.702	-0.021	73	114	57, 41, 43	
34	Chloropicrin	?	3.888	0.004	117	84	119, 82, 47	
37	Tetrachloroethene	?	4.247	0.014	166	1018	164, 131	0.6
40	Ethylbenzene	x	4.821	0.005	91	47633		0.99
41	m-Xylene	x	4.902	0.001	91	397628		0.99
42	p-Xylene	x	4.904	-0.001	91	397628		0.99
44	Styrene	x	5.11	-0.005	104	9886		0.97
45	o-Xylene	x	5.129	-0.005	91	41866		0.99
48	Isopropylbenzene	x	5.404	-0.010	105	2085		0.91
50	2-Chlorotoluene	?	5.626	-0.001	91	4338	126, 89	0.84
51	n-Propylbenzene	x	5.639	-0.014	91	4338		0.97
53	1,3,5-Trimethylbenzene	x	5.746	-0.015	105	5157		0.94
55	1,2,4-Trimethylbenzene	x	5.928	-0.014	105	17919		0.99
56	1,3-Dichlorobenzene	?	6.021	-0.017	146	194	111, 75	0.62
59	p-Isopropyltoluene	x	6.127	-0.014	119	5234		0.67
61	n-Butylbenzene	x	6.32	-0.015	91	2638		0.60
63	1,2,4-Trichlorobenzene	?	6.981	-0.024	180	534	182, 184	0.61

4c

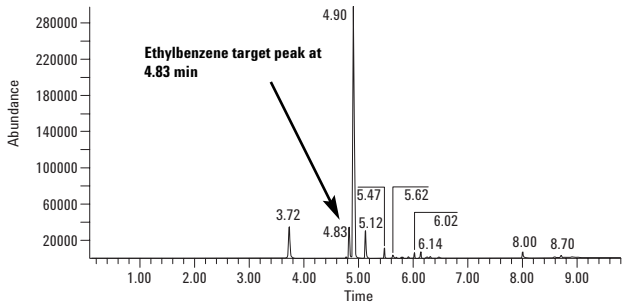


Figure 4. Use of RTL database searching to identify compounds in a 6-L sample of laboratory air. a) Total ion chromatogram (TIC) from TD/GC/MS analysis. b) RTL database search report generated during post-run data analysis. Compounds marked with an "X" are likely hits; compounds marked with a "?" require further review. c) Extracted ion chromatogram of *m/z* 91 showing ethylbenzene, one of the compounds identified by RTL database searching.

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Printed in the USA
March 31, 2003
5988-9252EN

HPLC Analysis of Formaldehyde in Indoor Air

Hiroki Kumagai

Environmental

Abstract

It was recently discovered that some volatile organic compounds cause the sick building syndrome. Formaldehyde is such a typical compound. It was analyzed by HPLC using 2,4-dinitorophenylhydorazine (DNPH) as the derivatization reagent. The silica gel cartridge, which was impregnated with DNPH (DNPH cartridge) is commonly used for sampling and concentrating aldehydes in air.

In this Application Brief we describe HPLC analysis of formaldehyde in houses using the DNPH cartridge.

Analyzed compounds

Formaldehyde and acetaldehyde of indoor air were analyzed as DNPH derivatives.

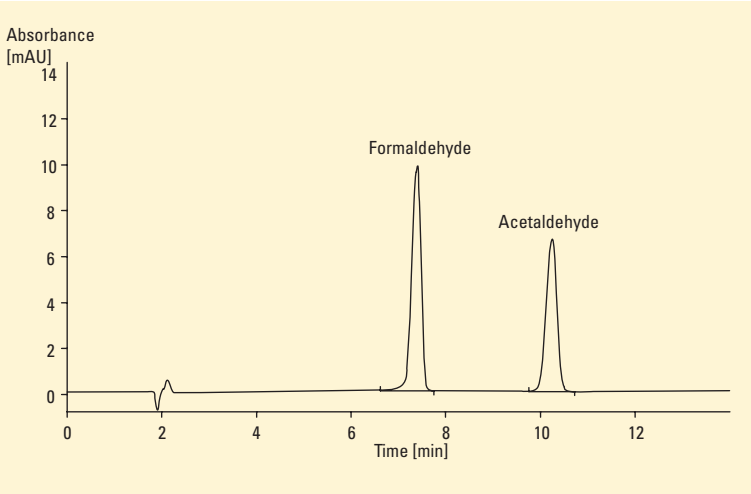

Figure 1
Chromatogram of formaldehyde and acetaldehyde (standard)

Conditions

Column:
250 x 4.6 mm
ZORBAX Eclipse XDB-C18
(Agilent part number 990967-902)
Mobile phase:
CH_3CN/H_2O = 45/55
Column compartment:
40 °C
Injection vol:
25 µl
Detector:
diode-array detector
wavelength 365/16 nm
reference: off

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Sample preparation

Indoor air of newly built houses was taken as sample. Sampling was performed by sucking air through DNPH cartridges with the pump. An ozone scrubber was inserted before the DNPH cartridge. The actual sampling volume was 5 - 20 l.

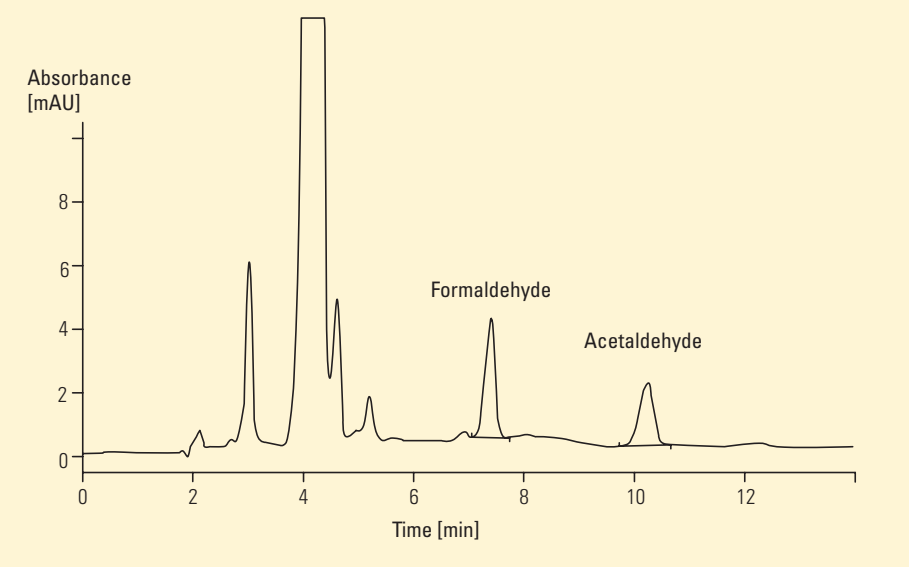

Figure 2
Chromatogram of formaldehyde and acetaldehyde (DNPH derivative) of indoor air of newly-built house A.

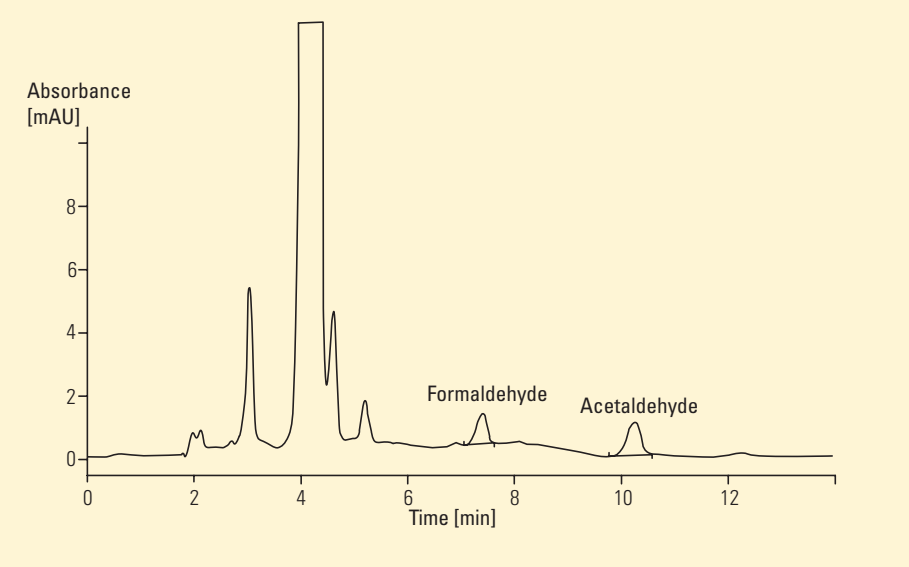

Figure 3
Chromatogram of formaldehyde and acetaldehyde (DNPH derivative) of indoor air of newly-built house B.

Equipment

Agilent 1100 Series
- vacuum degasser
- quaternary pump
- autosampler
- thermostatted column compartment
- diode array detector, Agilent ChemStation + software

HPLC method performance

Limit of detection:
formaldehyde 0.25 µg/m3,
acetaldehyde 0.35 µg/m3
(calculated from 3 s of blank values)
Repeatability:
of RT over 6 runs
<0.1 %
of areas over 6 runs
<0.5 % %

Hiroki Kumagai is application chemist at Yokogawa Analytical Systems Inc., Tokyo, Japan

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Released 04/98
Publication Number 5967-5598E

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Analysis of Formaldehyde and Acetaldehyde in Air by HPLC using DNPH Cartridge

Noriko Shimoi and Hiroki Kumagai

Environment

Abstract

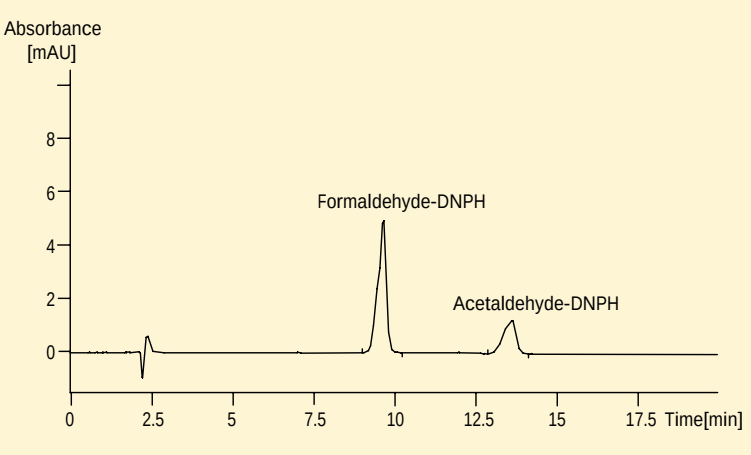
The monitoring of aldehydes, especially formaldehyde and acetaldehyde, is important for the monitoring of air pollution and acid rain problems. These aldehydes are analyzed by HPLC using 2,4-dinitorophenylhydorazine (DNPH) as the derivatization reagent. The cartridge of silica gel that was impregnated with DNPH (DNPH cartridge) is commonly used for the sampling and concentrating of aldehydes in air.
This application brief describes the analysis of formaldehyde and acetaldehyde in the air using DNPH cartridge.

Analyzed Compounds

Formaldehyde and acetaldehyde in air as DNPH derivatives.

Sample

Air of some location in Japan.



Conditions

Column
250 mm ˘ 4.6 mm i.d. Inertsil ODS 80A
Mobile Phase
CH_3CN/H_2O = 50/50
Temperature
40 °C
Injection vol
25 µl
Diode array detector
A—365/8 nm, reference off

Figure 1
Chromatogram of DNPH derivatives of formaldehyde and acetaldehyde

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Sample Preparation

Sampling was performed by sucking air through the DNPH cartridge (ozone scrubber was inserted before DNPH cartridge) with a pump. Sampling time was 24 hours at a flow rate of 0.1 l/min. The actual sampling volume was measured by the flow meter.

Method performance

Limit of Detection: formaldehyde 0.25 µg/m^3, acetaldehyde 0.35 µg/m3 (calculated from 3σ of blank values)
Repeatability of RT over 6 runs < 0.1 %
Repeatability of area over 6 runs < 0.5 %

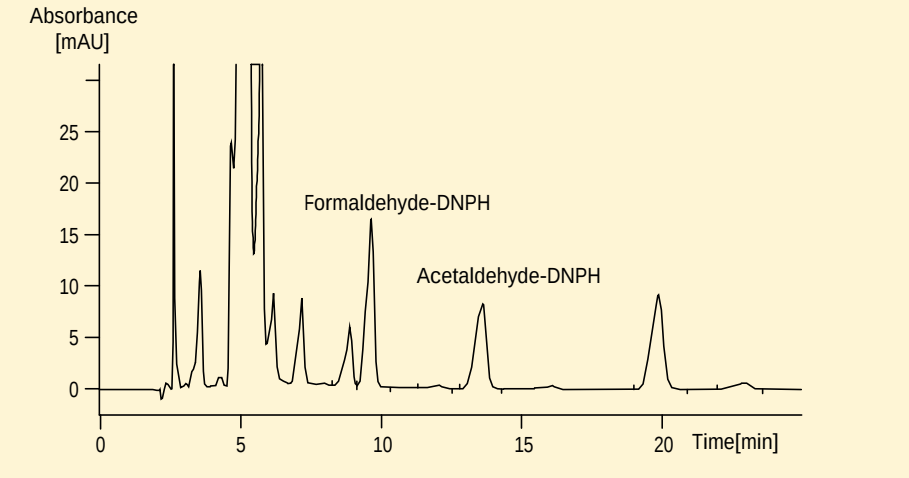


Figure 2
Chromatogram of aldehydes in the air of city A (Japan)

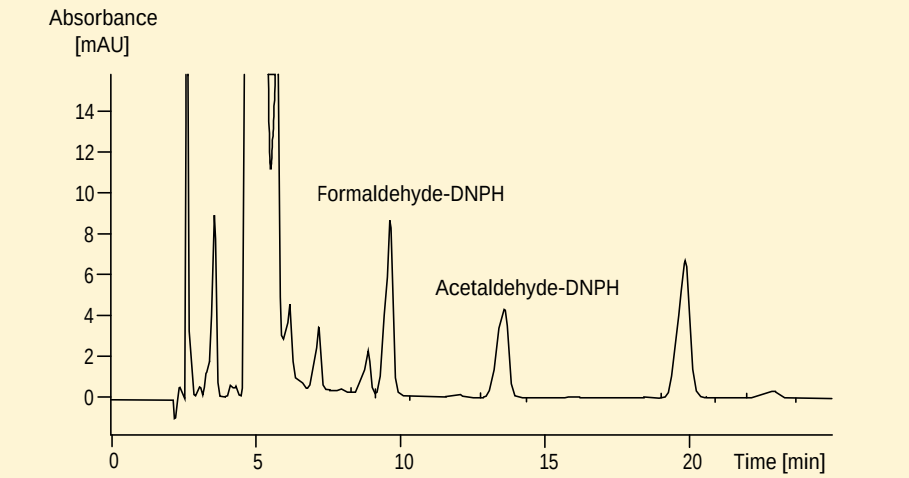
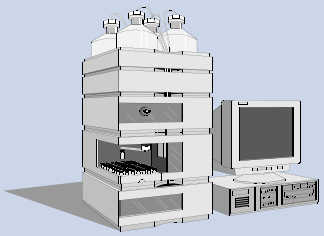


Figure 3
Chromatogram of aldehydes in the air of city B (Japan)

Equipment

Agilent 1100 Series
- degasser
- binary pump
- autosampler
- thermostatted column compartment
- diode array detector

Agilent ChemStation + software



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Released 06/97
Publication Number 5965-9796E

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