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

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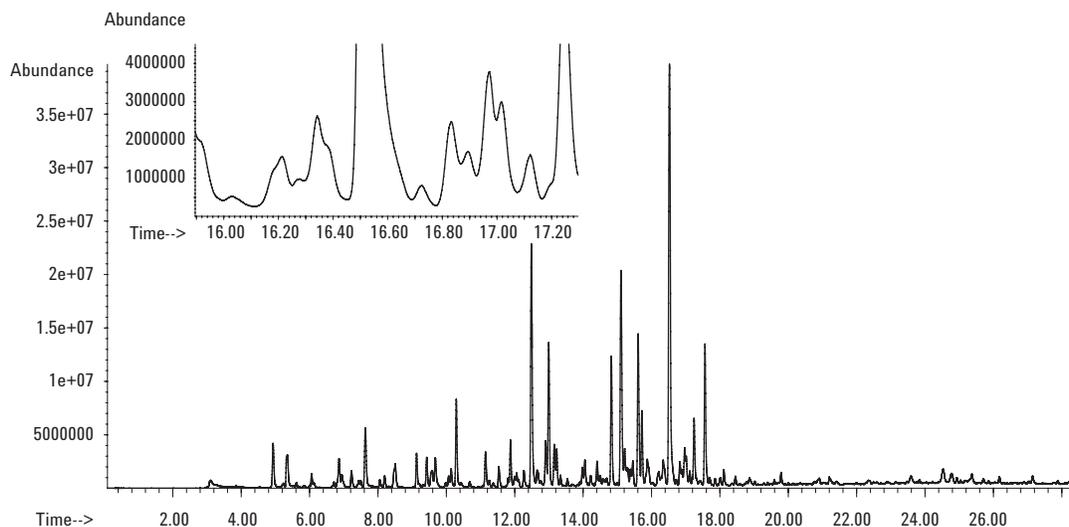
Figure 1.   TD/GC/MS chromatogram of an air sample collected in an office building. The inset shows that many peaks are poorly resolved and could be difficult to identify with normal GC/MS data analysis.

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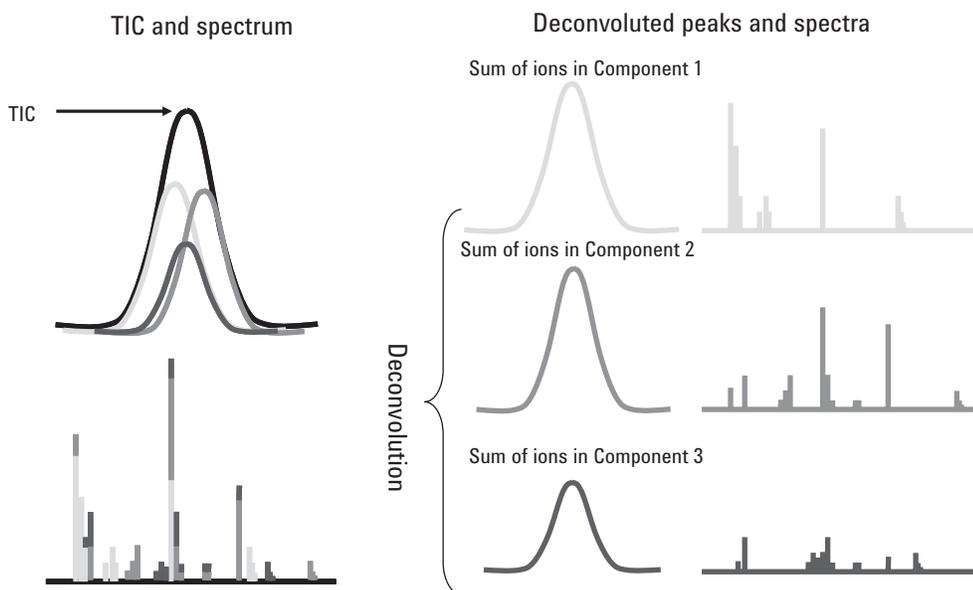
Figure 2. An illustration showing how AMDIS deconvolution software can extract "clean" spectra from unresolved chromatographic peaks. The deconvoluted spectra can be searched against normal mass spectral libraries with a high probability of finding a good match.

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.

R.T.	Cas #	Compound Name	Agilent ChemStation Amount (ng)	AMDIS Match	R.T. Diff sec.	NIST 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.
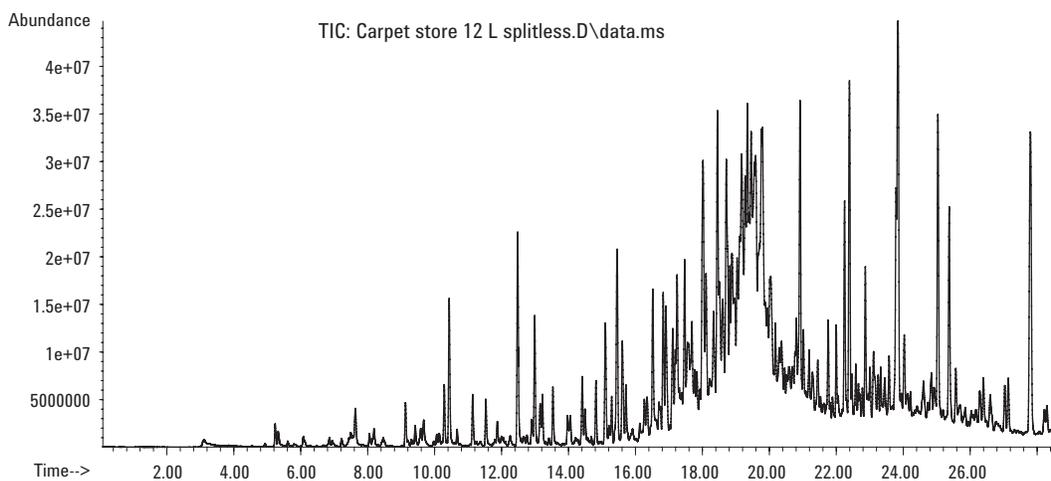
Figure 4. TD/GC/MS chromatogram of a 12-L air sample collected in a carpet store using a Tenax TA TD tube. Figure 5 shows the DRS report for this sample.

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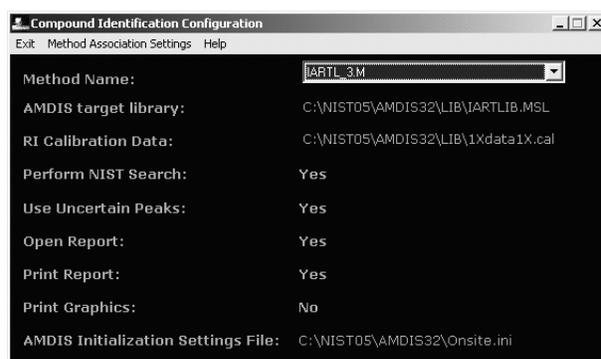
Figure 6. Compound Identification Configuration window in the DRS software. Users can edit these setpoints under Method Association Settings. One of the choices is whether or not to use uncertain peaks when searching the NIST'05 mass spectral library.

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 Chem-Station	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.

A

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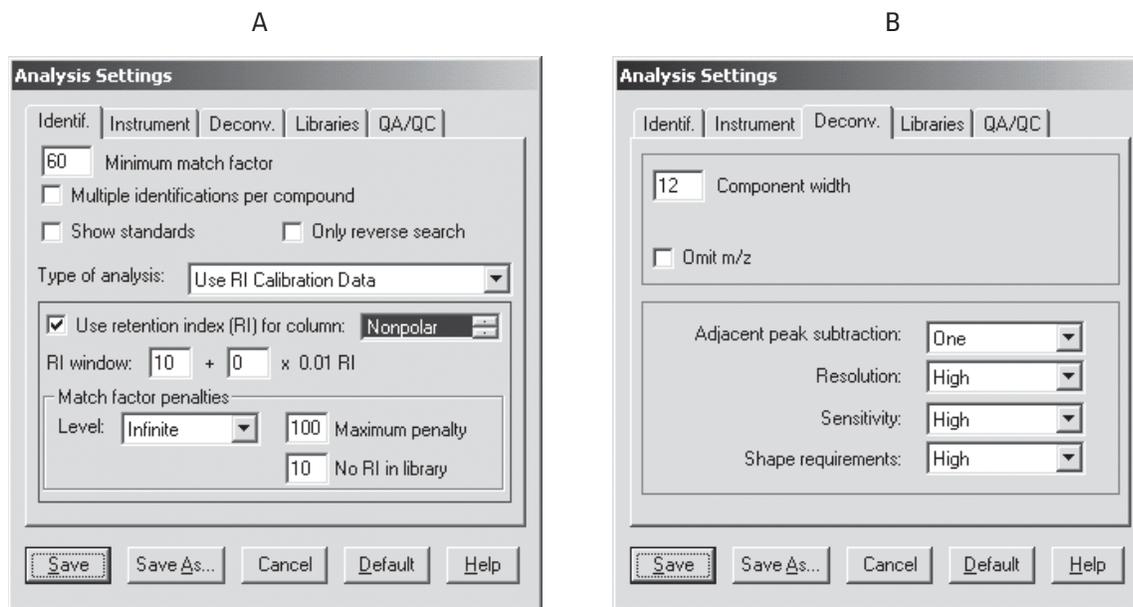
Figure 7. Two windows from the AMDIS software showing the deconvolution setpoints used for these analyses. These windows are accessed within the AMDIS software under the "Analyze/Settings" drop-down menu item.

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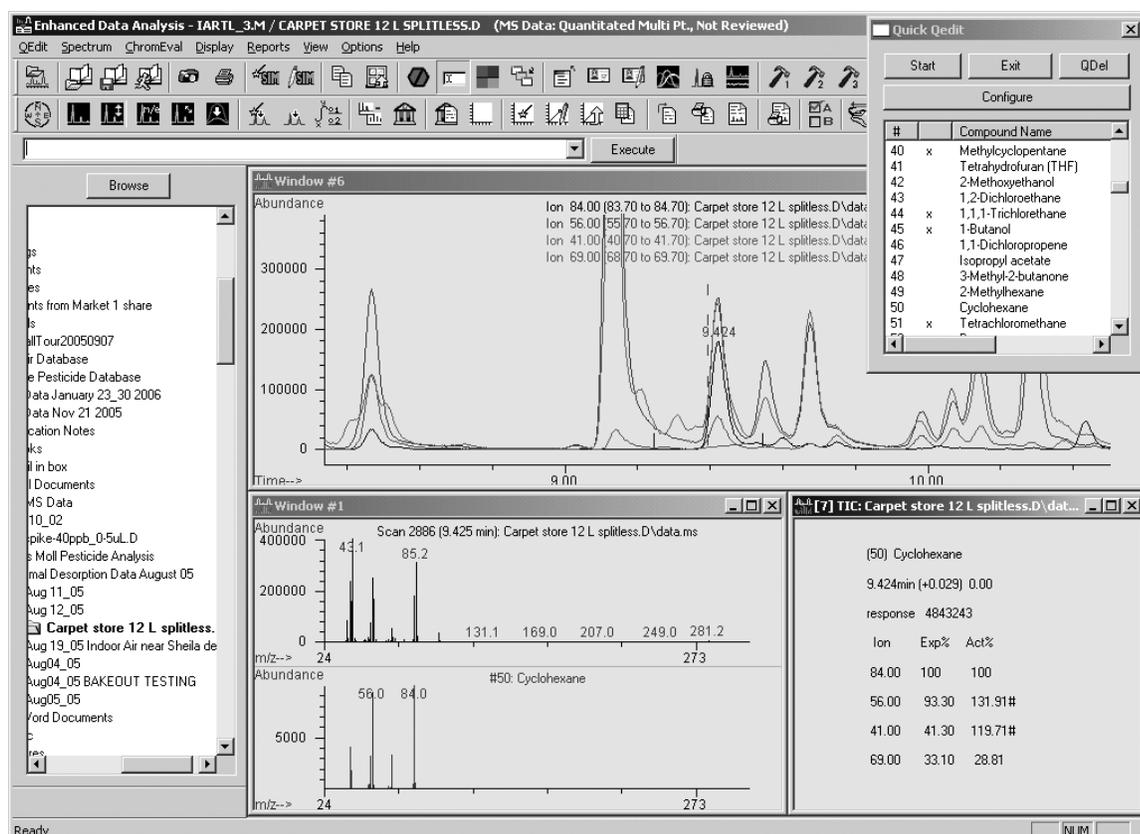
Figure 8. In this QEdit window, the user can verify integrations and integrate peaks that were initially missed by the ChemStation but identified by AMDIS as part of the DRS software.

"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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