Application Note

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Confident Characterization of Organic Components in Stripper Using HPLC/UV, GC/MS, and LC/MS Technologies

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Abstract

This application note presents a method for characterizing stripper using high-performance liquid chromatography with ultraviolet detection (HPLC/UV), gas chromatography/mass spectrometry (GC/MS), and liquid chromatography/mass spectrometry (LC/MS) techniques. HPLC/UV is a routine method for product quality control that is useful for the preliminary characterization of UV-absorbing components in the sample. GC/MS and LC/MS can detect trace compounds without UV-absorbing functional groups and enable qualitative and quantitative analysis, making the techniques suitable for stripper impurity studies and formulation profiling.

Introduction

Photolithography is a precision machining process that applies features onto a thin film or substrate (also known as a "wafer"). The technology uses light to transfer geometric patterns from a photomask onto a photosensitive photoresist attached to the substrate. The exposed pattern is then etched into the material through a series of chemical processes or new material is deposited on the material beneath the photoresist in the desired pattern. Photolithography is the core step in chip fabrication. Not only photoresist but also other chemicals such as developers, etchants, and strippers are used in the entire photolithography process. Stripper, as one of the key steps in photolithography aims to completely remove the photoresist from the substrate without corroding the substrate itself.

There are many types of photoresists, which are usually divided into two categories: positive and negative photoresists. Different photoresists are used for different photolithography processes. To effectively remove the photoresist from the substrate, it is essential to select a stripper tailored to the type and structural characteristics of the photoresist. There is a wide variety of stripper available, including positive PR stripper (water- or organic-based), stripper for Al process, and stripper for Cu process, etc.. For example, for the UV photoresists whose main components are phenolic resin and photosensitizer (exposure wavelength 465 nm/365 nm), the stripping process mainly involves: 1) alkanolamine attack of the photoresist, breaking its molecular chains into smaller molecular-weight fragments, 2) organic solvent penetration into the interior of the fragments, causing swelling, 3) glycol ether dissolution of the swollen photoresist fragments, and finally 4) detachment of photoresist fragments from the substrate surface via a spray liquid and water rinse.[2]

The main components of the stripper include alcohols, organic amines, and ethers.[1-4] To protect the substrate from corrosion, aromatic compounds, hydroxyl compounds, benzotriazole compounds[5], amino acids, and organic acids or acid anhydrides[1] may be added to the stripper. There are few reports on its composition analysis. In this application note, the stripper was comprehensively characterized using high-performance liquid chromatography with ultraviolet detection (HPLC/UV), gas chromatography/mass spectrometry (GC/MS), and liquid chromatography/mass spectrometry (LC/MS) techniques. HPLC is a routine method for the analysis of stripper, while GC/MS and LC/MS are the preferred methods for research applications due to their high sensitivity and capability of identifing the compounds based on the mass information. In addition, as shown in this application note, the identification results of organic amines and ethers by both GC/MS and LC/MS corroborate each other.

Experiment

Reagents and samples

All reagents were HPLC grade or higher. MS grade acetonitrile was purchased from Merck (Darmstadt, Germany). MS grade formic acid (part number G2453-85060) was from Agilent Technologies. LC grade phosphoric acid was purchased from ANPEL Laboratory Technologies (Shanghai) Inc. (Shanghai, China). The water was high-purity deionized water prepared by the EMD Millipore Milli-Q Integral system (Darmstadt, Germany).

The stripper sample was provided by an Agilent customer.

Instrumentation

HPLC/UV system

The Agilent 1290 Infinity II LC system was equipped with an Agilent High-Speed Pump (G7120A), Agilent Multisampler (G7167B), Agilent Multicolumn Thermostat (G7116B), and Agilent Diode Array Detector (G7117B). The system was controlled by Agilent OpenLab CDS 2.8.

GC/MS system

The Agilent 8890-5977C GC/MSD system was equipped with an Agilent 7693 Automatic Liquid Sampler and controlled by Agilent MassHunter Acquisition software for GC/MS revision 13.

HPLC/MS system

The Agilent 1290 Infinity II LC system was equipped with an Agilent High-Speed Pump (G7120A), Agilent Multisampler (G7167B), Agilent Multicolumn Thermostat (G7116B), and Agilent Diode Array Detector (G7117B). The Agilent 1290 Infinity II LC system was coupled with the Agilent Revident quadrupole time-of-flight mass spectrometer (LC/Q-TOF) equipped with an Agilent Dual Jet Stream Technology Ion Source (AJS). The system was controlled by MassHunter Acquisition software for LC/MS systems revision 12.1.

Sample preparation

For HPLC/UV analysis, the sample was diluted 10-fold with water. For GC/MS analysis, no dilution was performed prior to direct analysis. For LC/MS analysis, the sample was diluted 1000-fold with water.

Instrument conditions

The operating conditions for the HPLC/UV, GC/MS and LC/MS systems are shown in Tables 1, 2, and 3, respectively.

Table 1. HPLC/UV conditions.

LC Conditions	
Column	Agilent Zorbax SB-C18, 2.1 × 100 mm, 2.7 µm (p/n 858700-902)
Column Temperature	20 °C
Injection Volume	0.2 µL
Detection Wavelength	210 nm
Mobile Phase	A = Water (containing 0.1% HCOOH)
	B = ACN
Run Time	12 min
Post Time	3 min
Flow Rate	0.4 mL/min
Gradient Program	Time (min) B (%) 0.0 0 1.0 0 10.0 50 12.0 50

Table 2. GC/MS conditions.

GC Conditions	
Column	Agilent HP-5 MS UI, 30 m × 0.25 µm × 0.25 mm (p/n 19091S-433UI)
Injection Port Temperature	280 °C
Injection Volume	0.5 µL and 0.1 µL
Split	50:1 and 100:1
Run Time	35 min
Transfer Line Temperature	280 °C
Column Flow Rate	1 mL/min
Temperature Ramp Program	50 °C (3 min), then increase to 300 °C (7 min) at a rate of 10 °C/min
MS Conditions	
Ion Source	EI
Ion Source Temperature	280 °C
Quadrupole Temperature	150 °C
Solvent Delay	0.1 min
Full Scan Range	35-500 AMU

Table 3. LC/MS conditions.

LC Conditions	
Column	Agilent Zorbax SB-C18, 2.1 × 50 mm, 1.8 µm (p/n 857700-902)
Column Temperature	40 °C
Injection Volume	2.0 µL
Detection Wavelength	210 nm
Mobile phase	A = Water (containing 0.1% HCOOH)
	B = ACN (containing 0.1% HCOOH)
Run Time	13 min
Post Time	3 min
Flow Rate	0.4 mL/min
Gradient Program	Time (min) B (%) 0.0 0 1.0 0 10.0 30 11.0 50 11.1 95 13.0 95
MS Conditions	
Ionization Mode	Positive ion mode
Scan Mode	Q-TOF scanning, auto MS/MS scanning
Scan Range	50-1000 *m/z*
Sheath Gas Temperature	350 °C
Sheath Gas Flow	11 L/min
Drying Gas Temperature	280 °C
Drying Gas Flow Rate	8 L/min
Nebulizer Pressure	30 psi
Capillary Voltage	3500 V
Fragmentor Voltage	150 V
Nozzle Voltage	0 V

Results and discussion

HPLC/UV results

The HPLC/UV chromatogram (Figure 1) shows that the sample containing UV-absorbing compounds were well separated on the Zorbax SB-C18 column. OpenLab CDS software provides the peak height, peak area and the percentage of each peak. The results show that HPLC/UV is an ideal routine testing method for stripper.

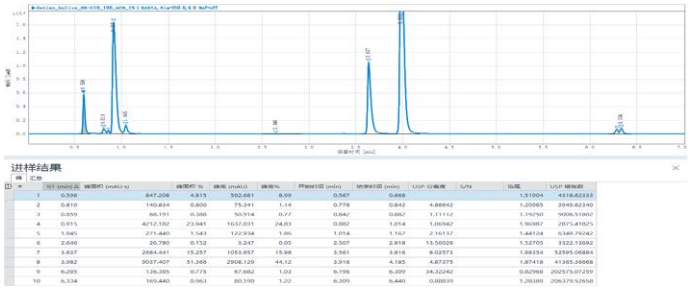

Figure 1. Top: HPLC/UV chromatogram of the stripper sample (detection wavelength: 210 nm). Bottom: The peak results in OpenLab CDS table.

GC/MS results

Figure 2 shows the GC/MS full scan chromatograms of the stripper collected at two different injection volumes and split ratios.

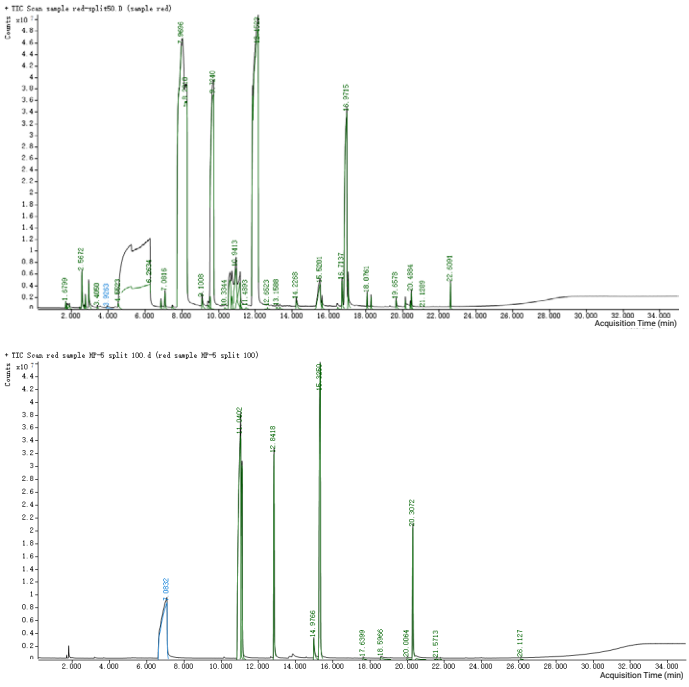

Figure 2. GC/MS full scan chromatogram of the stripper. Top: injection volume 0.5 µL, split ratio 50:1. Bottom: injection volume 0.1 µL, split ratio 100:1.

From figure 2, lower-level components were detected in the stripper if under the GC-MS parameters of 0.5 µL and a split ratio of 50:1. However, when an injection volume of 0.1 µL and a split ratio of 100:1 were used instead, while better peak shape and resolution for the main components were obtained if under the GC-MS parameters of 0.1 µL and a split ratio of 100:1.

The numerous peaks in Figure 2 indicate that the composition of the stripper was complex. One of the challenges for data-processing is to quickly and accurately identify the compounds from the numerous peaks in a full-scan chromatogram. Manual data analysis is usually time-consuming and unable to resolve the co-eluting components, leading to inaccurate results or not reporting the presence of minor or trace components. Deconvolution is a mathematical algorithm that resolves co-eluting components by extracting the extracted ion chromatograms (EICs) of all *m/z* by retention time and abundance. This process resolves complex multicomponent mass spectra into "clean" mass spectra for the individual components. The data analysis workflow is shown in Figure 3.

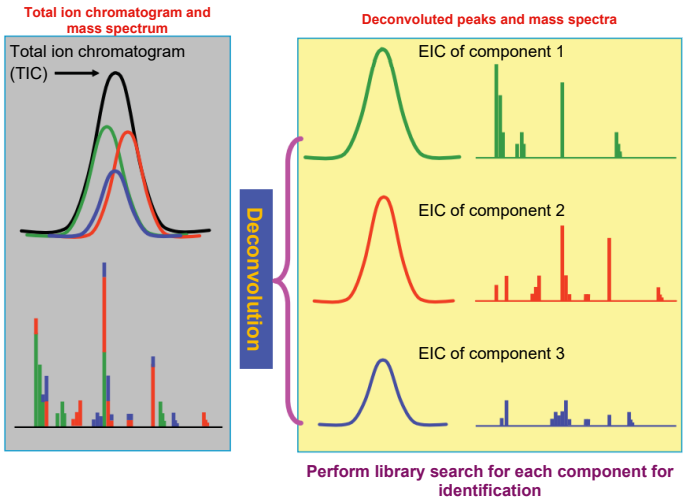

Figure 3. Schematic of the deconvolution workflow.

By using deconvolution algorithms, the "clean" mass spectrum of the co-eluent components can be obtained. These "clean" spectrum was compared against the ones in spectral libraries to achieve accurate analytical results.

The Agilent MassHunter Unknowns Analysis software features a built-in deconvolution algorithm, enabling fully automated deconvolution and library searching for rapid and accurate identification of components in full scan chromatograms. Figure 4 shows data-processing interface of MassHunter Unknowns Analysis software, which is intuitive and easy-to-use.

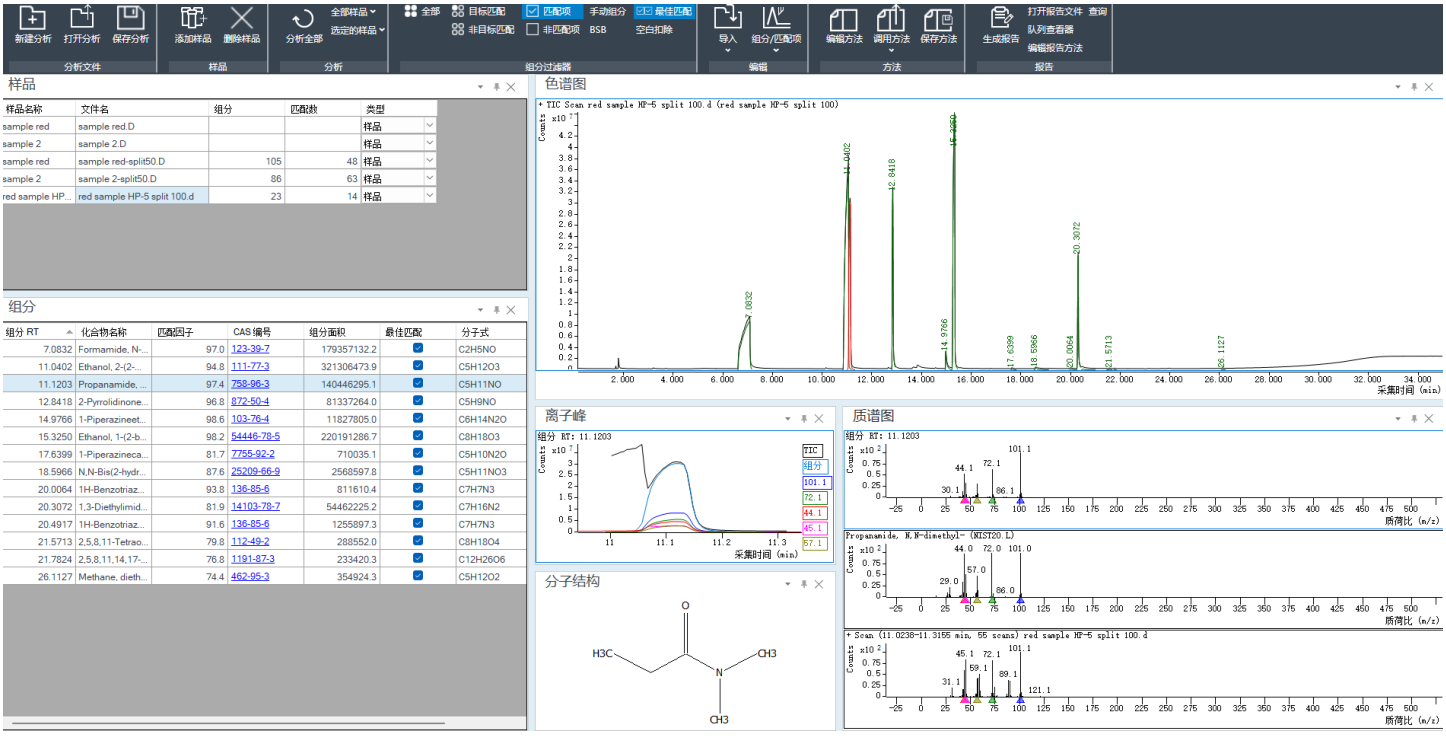

Figure 4. The data-processing interface of Agilent MassHunter Unknowns Analysis software.

In the GC/MS experiment, N,N-dimethylpropionamide and 2-(2-methoxyethoxy)ethanol were not completely separated on the HP-5MS column. However, using the deconvolution function of the MassHunter Unknowns Analysis software, the two components were accurately identified (Figure 5).

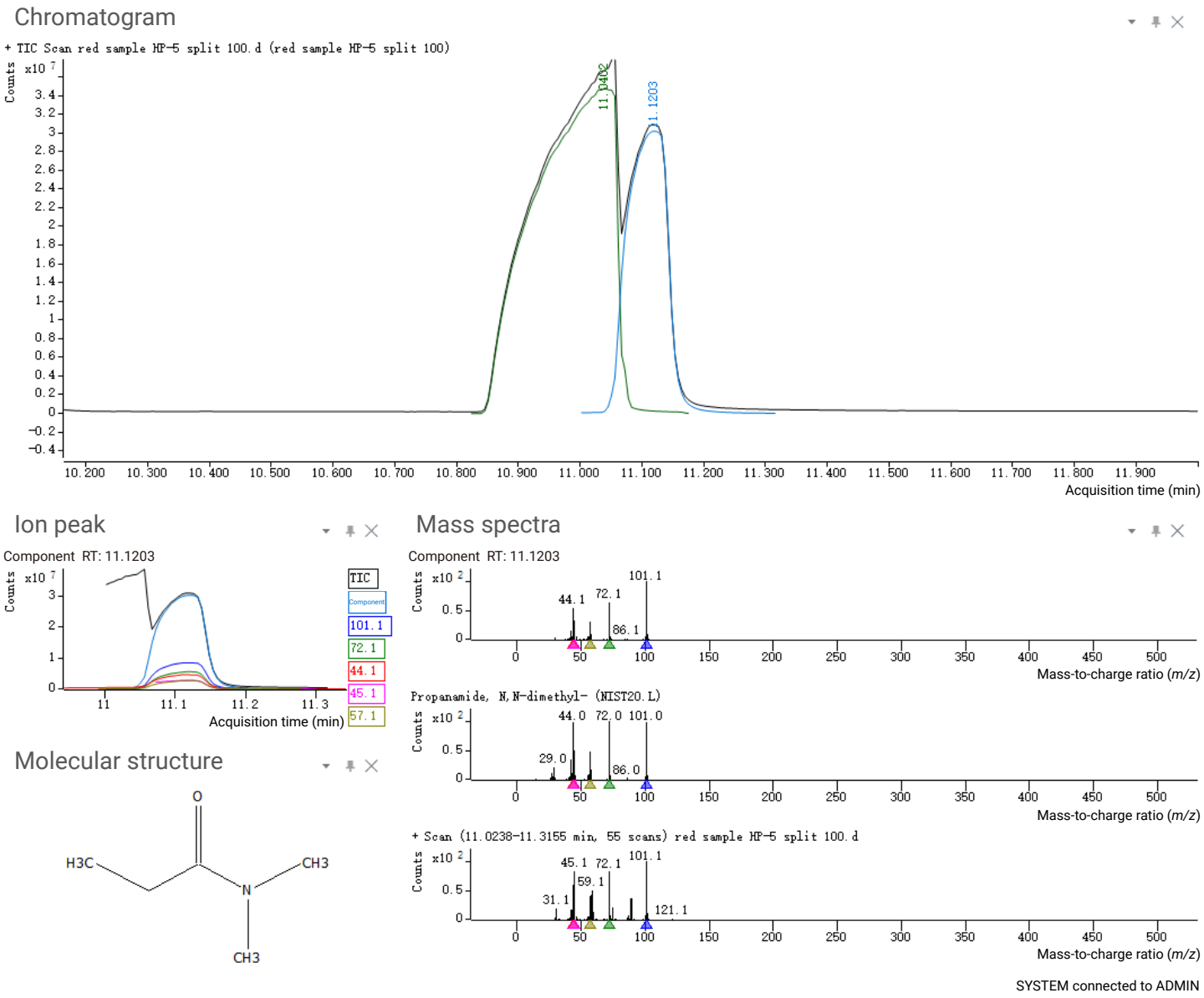

Figure 5. N,N-dimethylpropionamide and 2-(2-methoxyethoxy)ethanol were resolved using the deconvolution function of Agilent MassHunter Unknowns Analysis software.

The main GC/MS chromatographic peaks in the stripper were analyzed using the deconvolution and library search and comparison capabilities of MassHunter Unknowns Analysis software. Compounds with a match score above 80 are listed in Table 4 (injection volume: 0.1 µL, split ratio: 100:1).

Table 4. Compounds in the stripper sample identified GC/MS.

No.	Retention Time	Compound	Match Score	CAS Number	Formula
1	7.083	Formamide, N-methyl-	97.0	123-39-7	C_2H_5NO
2	11.040	Ethanol, 2-(2-methoxyethoxy)-	94.8	111-77-3	$C_5H_{12}O_3$
3	11.120	Propanamide, N,N-dimethyl-	97.4	758-96-3	$C_5H_{11}NO$
4	12.842	2-Pyrrolidinone, 1-methyl-	96.8	872-50-4	C_5H_9NO
5	14.977	1-Piperazineethanol	98.6	103-76-4	$C_6H_{14}N_2O$
6	15.325	Ethanol, 1-(2-butoxyethoxy)-	98.2	54446-78-5	$C_8H_{18}O_3$
7	17.640	1-Piperazinecarboxaldehyde	81.7	7755-92-2	$C_5H_{10}N_2O$
8	18.597	N,N-Bis(2-hydroxyethyl)formamide	87.6	25209-66-9	$C_5H_{11}NO_3$
9	20.006	1H-Benzotriazole, 5-methyl-	93.8	136-85-6	$C_7H_7N_3$
10	20.307	1,3-Diethylimidazolidine	81.9	14103-78-7	$C_7H_{16}N_2$
11	20.492	1H-Benzotriazole, 5-methyl-	91.6	136-85-6	$C_7H_7N_3$

LC/MS results

The Total Ion Chromatogram (TIC) obtained by LC/MS (Figure 6A) contains significantly more peaks than the ones by UV chromatogram (Figure 6B), indicating that MS provides higher sensitivity and more comprehensive characterization on the organic compounds in the stripper. High-resolution MS data provides the accurate masses and isotope patterns that can be translated into a proposed elemental composition. High-resolution MS/MS data also can provide information on the compound structures and search against the previously acquired MS/MS data in the application-specific Agilent Personal Compound Database and Libraries (PCDL).

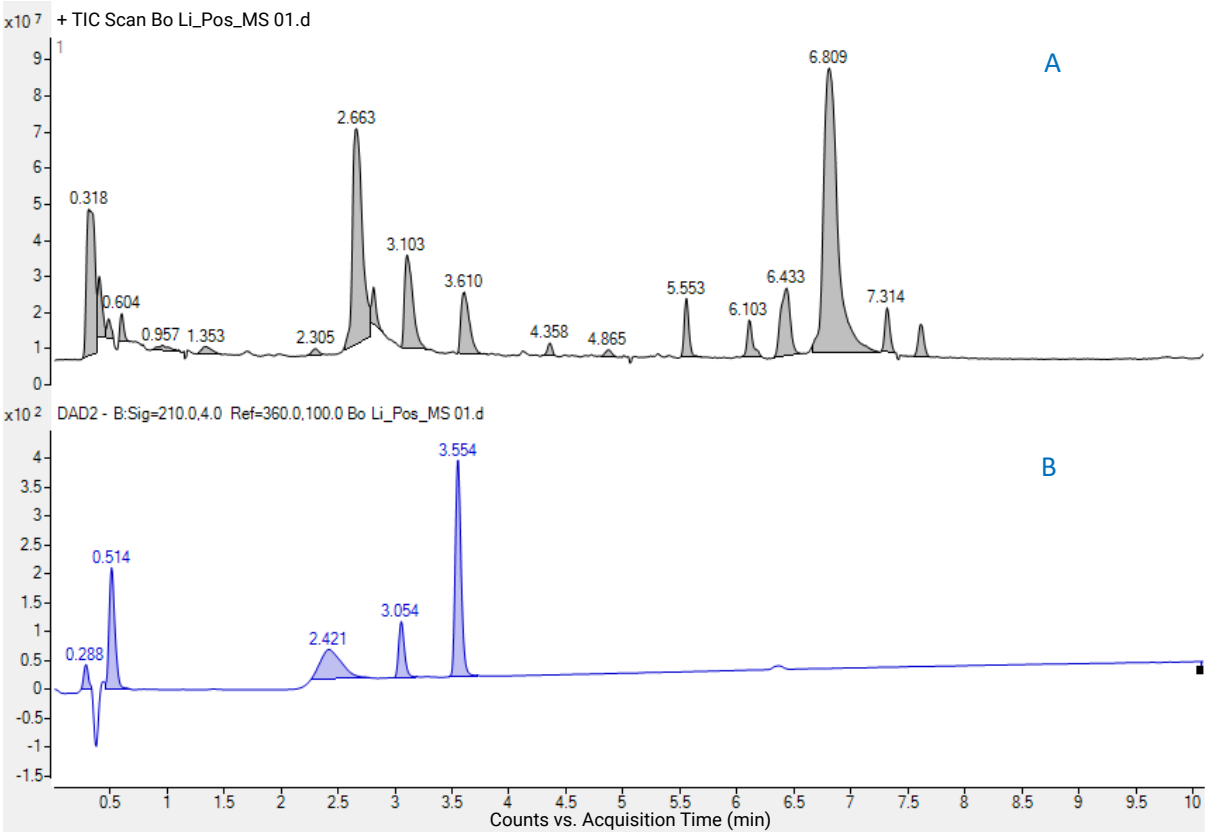

Figure 6. LC/MS spectrum of the stripper sample: A. Total ion chromatogram; B. UV chromatogram at 210 nm.

For example, the chromatographic peak at 7.50 min was identified as triethylene glycol monobutyl ether, with an MS1 match score of 99.71. This indicates that its accurate mass, isotopic abundance, and isotopic spacing were close to the theoretical values for the compound (Figure 7). The MS/MS (MS2) spectrum obtained at a collision energy of 20 V perfectly matched the spectrum in the PCDL, and the mirror image comparison clearly showed the differences between the experimental and reference spectrum (Figure 8). The compounds identified by LC/MS are listed in Table 5.

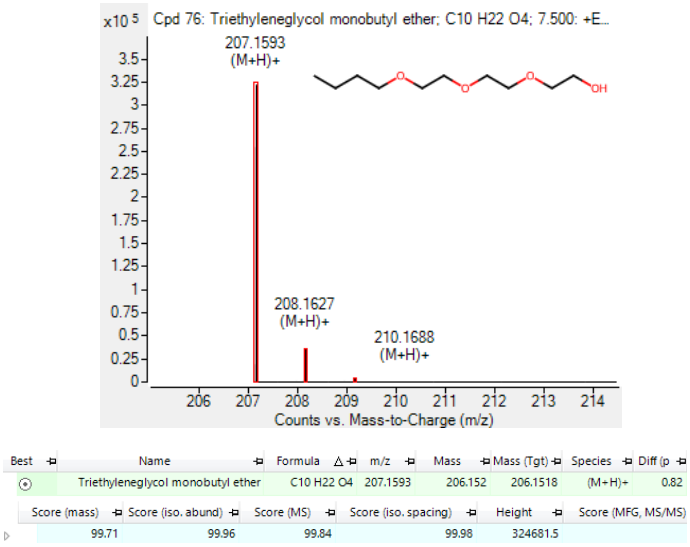

Figure 7. MS1 spectrum. The experimental isotope pattern matched the theoretical isotope pattern (red boxes) with the mass measurement error of 0.82 ppm for triethylene glycol monobutyl ether.

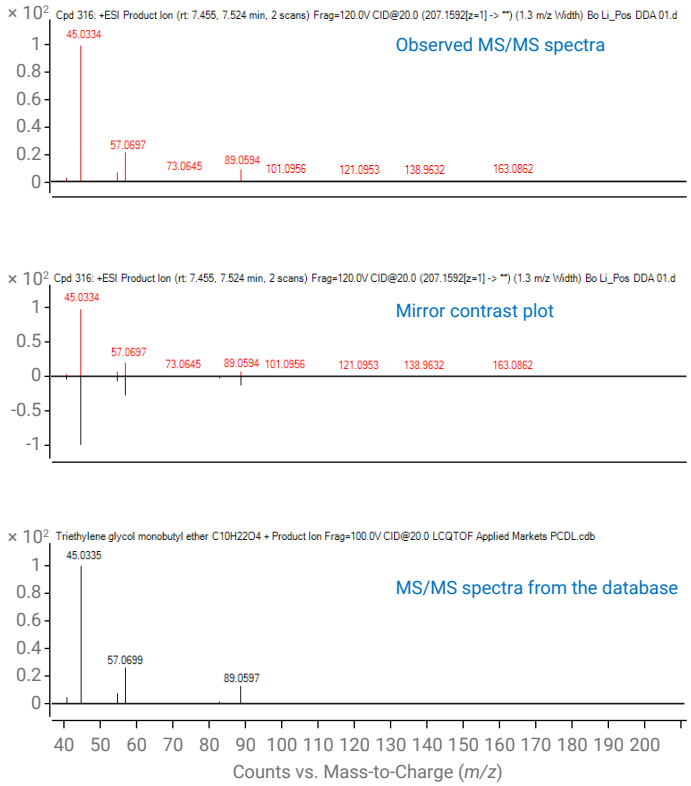

Figure 8. Mirror image comparison of the MS/MS spectrum and the reference mass spectrum in the PCDL for triethylene glycol monobutyl ether.

Table 5. Compounds in the stripper by using LC/MS data with the Agilent PDCL.

No.	Compound	Formula	Mass	Retention time (min)	Mass-to-charge Ratio (*m/z*)	Mass Deviation (ppm)	Match Score
1	Pentylurea	$C_6H_{14}N_2O$	130.1107	0.191	131.1179	0.68	98.85
2	Diethanolamine	$C_4H_{11}NO_2$	105.079	0.224	128.0682	0.31	92.43
3	1,3-Dimethyl-2-imidazolinone	$C_5H_{10}N_2O$	114.0794	0.328	115.0866	0.62	99.07
4	Alanine	$C_3H_7NO_2$	89.0476	0.378	90.0549	-0.78	94.99
5	N-methylformamide	C_2H_5NO	59.037	0.46	60.0443	-1.75	99.63
6	N,N-Bis(2-hydroxyethyl)formamide	$C_5H_{11}NO_3$	133.074	0.493	134.0812	0.43	96.07
7	Amylnitrate	$C_5H_{11}NO_3$	133.074	0.967	134.0812	0.63	92.71
8	2-(2-Methoxy-acetylamino)-4,5-dimethyl-thiophene-3-carboxylic acid ethyl ester	$C_5H_{10}O_4$	134.0579	2.31	135.0652	-0.13	98.75
9	Ethanol, 2-(2-methoxyethoxy)-	$C_5H_{12}O_3$	120.0787	2.546	121.086	0.41	98.55
10	PropyleneOxide	C_3H_6O	58.0418	2.552	59.049	-1.84	99.88
11	Ethylene glycol methyl ether	$C_3H_8O_2$	76.0523	2.568	77.0596	-2.04	99.72
12	N-Methylpyrrolidone (NMP)	C_5H_9NO	99.0684	3.003	100.0756	-0.38	93.85
13	N-ethylpropanimidate	$C_5H_{11}NO$	101.084	3.499	102.0912	-0.9	94.44
14	Triethylene glycol dimethyl ether	$C_8H_{18}O_4$	178.1204	3.669	201.1097	-0.51	94.51
15	Caprolactam	$C_6H_{11}NO$	113.0841	4.011	114.0913	0.1	93.55
16	Pentaethyleneglycol	$C_{10}H_{22}O_6$	238.1418	4.137	239.1491	0.55	93.48

No.	Compound	Formula	Mass	Retention time (min)	Mass-to-charge ratio (*m/z*)	Mass deviation (ppm)	Match score
17	2-[2-(2-Ethoxyethoxy)ethoxy]ethanol	$C_8H_{18}O_4$	178.1206	4.374	179.1278	0.38	92.87
18	2-[2-(2-Propoxyethoxy)ethoxy]ethanol	$C_9H_{20}O_4$	192.1362	5.442	193.1434	0.19	97.85
19	5-Methylbenzotriazole (5-Tolyltriazole)	$C_7H_7N_3$	133.0641	6.317	134.0713	0.69	91.57
20	Benzylamine	C_7H_9N	107.0735	6.328	108.0807	-0.05	94.98
21	Diethylene glycol monobutyl ether	$C_8H_{18}O_3$	162.1257	6.708	185.1149	0.41	99.96
22	Triethylene glycol monobutyl ether	$C_{10}H_{22}O_4$	206.152	7.501	207.1593	0.81	93.7

Conclusion

Agilent's GC/MS and LC/MS systems, with the high sensitivity and excellent qualitative analytical capabilities, can characterize the stripper samples quickly and effectively. GC/MS identified glycol ethers, ethers, amides, and pyrrolidones, while LC/MS identified ethers, amines, and pyrrolidones. Ether and amines were identified using both GC/MS and LC/MS. Alcohols are difficult to ionize on LC/MS, but can be detected by GC/MS very well. Therefore, combining GC/MS and LC/MS techniques enables more efficient and comprehensive analysis and characterization of organic compounds in stripper. After characterization using MS techniques, HPLC/UV can be used for routine quality control of stripper products.

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