



## LC/DAD/MS Analysis of Carbonyl (2,4-Dinitrophenyl)hydrazones

*Eric Grosjean and Daniel Grosjean,*  
DGA, Inc., Ventura, CA

*Peter G. Green,* Environmental Analysis Center,  
Environmental Engineering Science, California  
Institute of Technology, Pasadena, CA

*John M. Hughes,* Agilent Technologies,  
Pleasanton, CA

### Abstract

A simple and sensitive LC/MS method has been developed for the analysis of carbonyl compounds derivatized with (2,4-dinitrophenyl)hydrazine (DNPH) using the Agilent 1100 LC/MSD system. Detection is carried out simultaneously with the diode-array detector and the LC/MSD using negative ion atmospheric pressure chemical ionization (APCI).<sup>1</sup> The method was applied to 78 carbonyls including 1-alkanals (from formaldehyde to octadecanal), saturated and unsaturated aliphatic aldehydes and ketones, aromatic carbonyls (including hydroxy- and/or methoxy-substituted compounds), aliphatic dicarbonyls, and aliphatic carbonyl esters.

### Introduction

The ability to identify carbonyls and to measure their concentrations at levels of parts per billion (ppb) or lower in complex mixtures is important in many areas, including biomedical research and environmental chemistry—especially air pollution. A well-established method utilizing UV detection of the DNPHs of both simple and multifunctional carbonyl compounds<sup>2, 3</sup> has been extended to include simultaneous MS detection using APCI in negative ion mode. Concentration of the compounds

of interest from ambient air samples and subsequent derivatization is simplified by the use of C18 SPE cartridges impregnated with the derivatizing reagent. The combined methodology has been applied to several studies involving air pollution phenomena.<sup>1</sup>

### Experimental

The system included an Agilent 1100 Series binary pump, vacuum degasser, autosampler, thermostatted column compartment, diode-array detector, and an LC/MSD. The LC/MSD was used with the APCI source. Complete system control and data evaluation were carried out using the Agilent ChemStation for LC/MS.

### Sample Collection and Preparation

Carbonyl-DNPH standards were synthesized in our laboratory as described previously.<sup>2, 3</sup> Carbonyls were purchased from commercial suppliers (Aldrich Chemical Co., Lancaster Synthesis, Wiley Organics, Fluka Chemical Corp.) or were prepared as described in previous work.<sup>2, 3</sup>

Air samples were collected by drawing air at 1 liter/minute through C18 Sep-Pak cartridges (Waters Corporation) impregnated with (2,4-dinitrophenyl)hydrazine/phosphoric acid.<sup>4</sup> Collected carbonyl compounds were derivatized to (2,4-dinitrophenyl)hydrazones on the cartridge, and were then eluted with 2 mL of acetonitrile. The eluate was analyzed directly by LC/MS. The sample can be concentrated for the analysis of the higher molecular weight carbonyls, which are present at lower levels in ambient air.

## Results and Discussion

DNPH derivatives are used to analyze carbonyl compounds by liquid chromatography to maximize detection of small, polar molecules, many of which cannot be analyzed using gas chromatography. The original LC/UV method for the analysis of DNPH derivatives of carbonyls was first improved by the use of a diode-array detector and HP particle beam LC/MS interface to provide positive identification of about 40 carbonyls at ppb levels in laboratory studies of air pollution chemistry<sup>5</sup> and in urban air.<sup>6</sup> The mass spectrometer provided extra dimensions of information to the already-rich data of the diode-array LC method, allowing the quantitation of coeluting analytes and the identification of unknowns for which standards were not initially available. However, the particle beam interface could not provide the detection limits necessary for measurement of carbonyls in ambient air, due to the significant percentage of water in the LC gradient required for the separation of the more complex mixtures.

To overcome this limitation, API-LC/MS was evaluated for this application. Both electrospray (ESI) and APCI in positive ion and negative ion modes were evaluated. APCI negative ion detection was found to provide the most sensitive and specific information about these compounds, giving 1–2 orders of magnitude better sensitivity than either ESI positive or negative ion or APCI positive ion detection.

Parameters for the acquisition of mass spectral data were automatically optimized by carrying out multiple injections of a standard mixture of 13 carbonyl-DNPH derivatives, using the system's Flow Injection Analysis Series capability. A fragmentor setting was chosen to obtain maximum  $[M-H]^-$  for all 13 compounds present in the test mixture. Further optimization of the fragmentor voltage for specific compounds could be carried out to obtain distinct fragments, as the fragmentor voltage is time-programmable during acquisition. Those compounds which required a high percentage of acetonitrile for elution (eluting after 33 minutes) were found to have much better response with a corona current of 10  $\mu$ A versus 4  $\mu$ A for the smaller, early-eluting analytes. The scan range can be lowered

to 50 amu if significant fragment ions below 125 amu are generated by in-source collision-induced dissociation (CID); the chemical noise, especially in the TIC, is lower when starting the scan at 125 amu.

Mobile phases containing acetonitrile often do not give optimal response in APCI compared to methanol/water eluents, and acetonitrile seems to form carbon on the corona needle more quickly than methanol. However, for this analysis, adequate separation of carbonyls in a reasonable analysis time could not be achieved using methanol/water instead of acetonitrile/water, even trying a variety of columns. Nonetheless, maintenance of the APCI spray chamber after extended use with high flow rates of acetonitrile/water only required cleaning of the corona needle and spray shield with mild abrasive cloth and solvent.

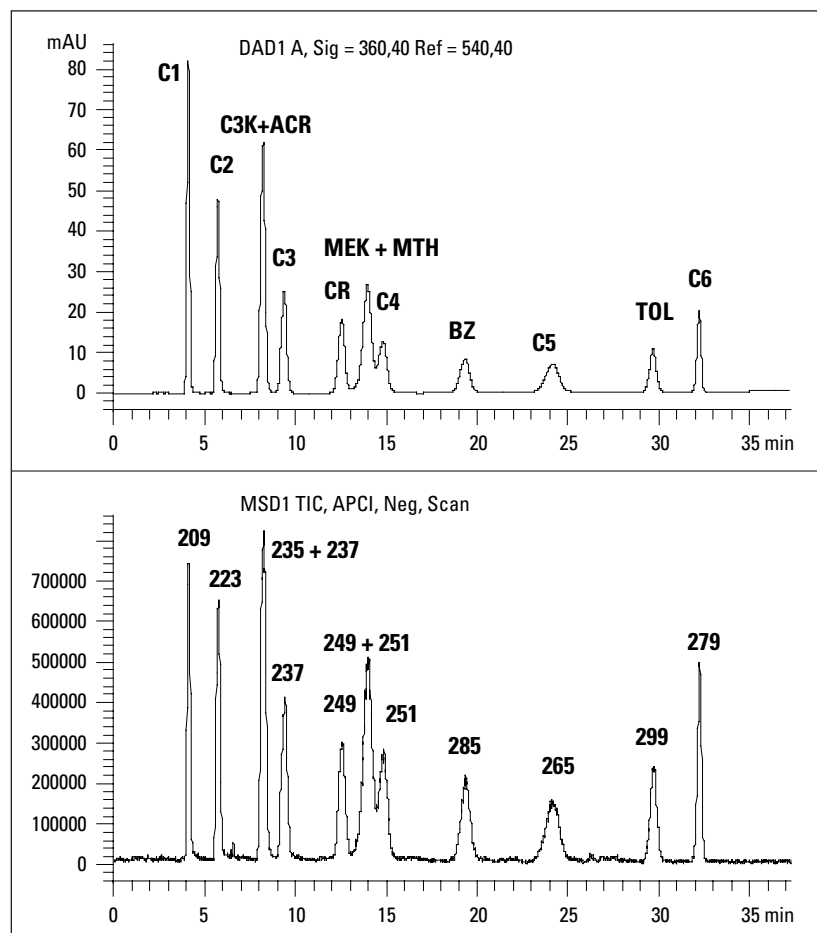
Early work with this method was carried out using a similar column but with dimensions of 4.6 mm i.d.  $\times$  150 cm at a flow rate of 1.4 mL/min, with results comparable to those obtained on the 3mm i.d. column. An additional gradient has also been developed utilizing THF as a mobile phase modifier. This gradient method is capable of better separation of C3 and C4 carbonyl compounds which co-elute using the acetonitrile/water gradient.

Tables 1–6 (shown on pages 9–14) list the first 78 carbonyl compounds that have been analyzed with this method, along with chromatographic and spectral details. The method has been used for more than 140 carbonyl compounds, including several with molecular weights of approximately 650 Da.

Figure 1 shows the 360 nm and MS total ion chromatograms of a mixture of the DNPH derivatives of 13 carbonyls. The amount injected per component is 60 ng (as carbonyl). The UV chromatogram is labeled with the identity of the peaks and the MS chromatogram with the mass of the base peak in the spectrum ( $[M-H]^-$  anion).

Figure 2 shows extracted ion chromatograms from the data in Figure 1, illustrating how the specificity of the MS detector can help with coelution, sometimes even allowing quantitation of coeluting peaks.

## LC/DAD/MS Analysis of Carbonyl (2,4-Dinitrophenyl)hydrazones



### Chromatographic Conditions

Column: Nucleosil 100-5 C18 HD 5  $\mu$ m,  
3  $\times$  250 mm  
Guard column: Phenomenex Security Guard C18,  
3 mm i.d.  $\times$  4 mm  
Mobile phase: A = water  
B = acetonitrile  
Gradient: Start with 49% B  
at 26 min 49% B  
at 40 min 100% B  
Post-time: 5 minutes  
Flow rate: 1.0 ml/min  
Column temp: 38°C  
Injection vol: 20  $\mu$ l  
Diode-array detector: Signal: 360, 40; 385, 40; 430, 40 nm  
Reference: 540, 40 nm

### MS Conditions

Source: APCI  
Ionization mode: Negative  
Vcap: 1500 V  
Corona current: 10  $\mu$ A  
Nebulizer: 60 psig  
Drying gas flow: 4 l/min  
Drying gas temp: 350°C  
Vaporizer temp: 500°C  
Scan: 125–600 amu,  
Threshold: 150 counts  
Gain: 5  
Step size: 0.1 amu  
Peak width: 0.1 min  
Time filter: 0n  
Fragmentor: 50 V

**Figure 1. Liquid chromatography analysis of a mixture of the DNPH derivatives of 13 carbonyls by ultraviolet absorption at 360 nm (diode array detector, top) and by atmospheric pressure negative chemical ionization mass spectrometry (total ion current, bottom): C1, formaldehyde; C2, acetaldehyde; C3K, acetone; ACR, acrolein; C3, propanal; CR, crotonaldehyde; MEK, 2-butanone; MTH, methacrolein; C4, butanal; BZ, benzaldehyde; C5, pentanal; TOL, *m*-tolualdehyde; C6, hexanal.**

LC/DAD/MS Analysis of Carbonyl  
(2,4-Dinitrophenyl)hydrazones

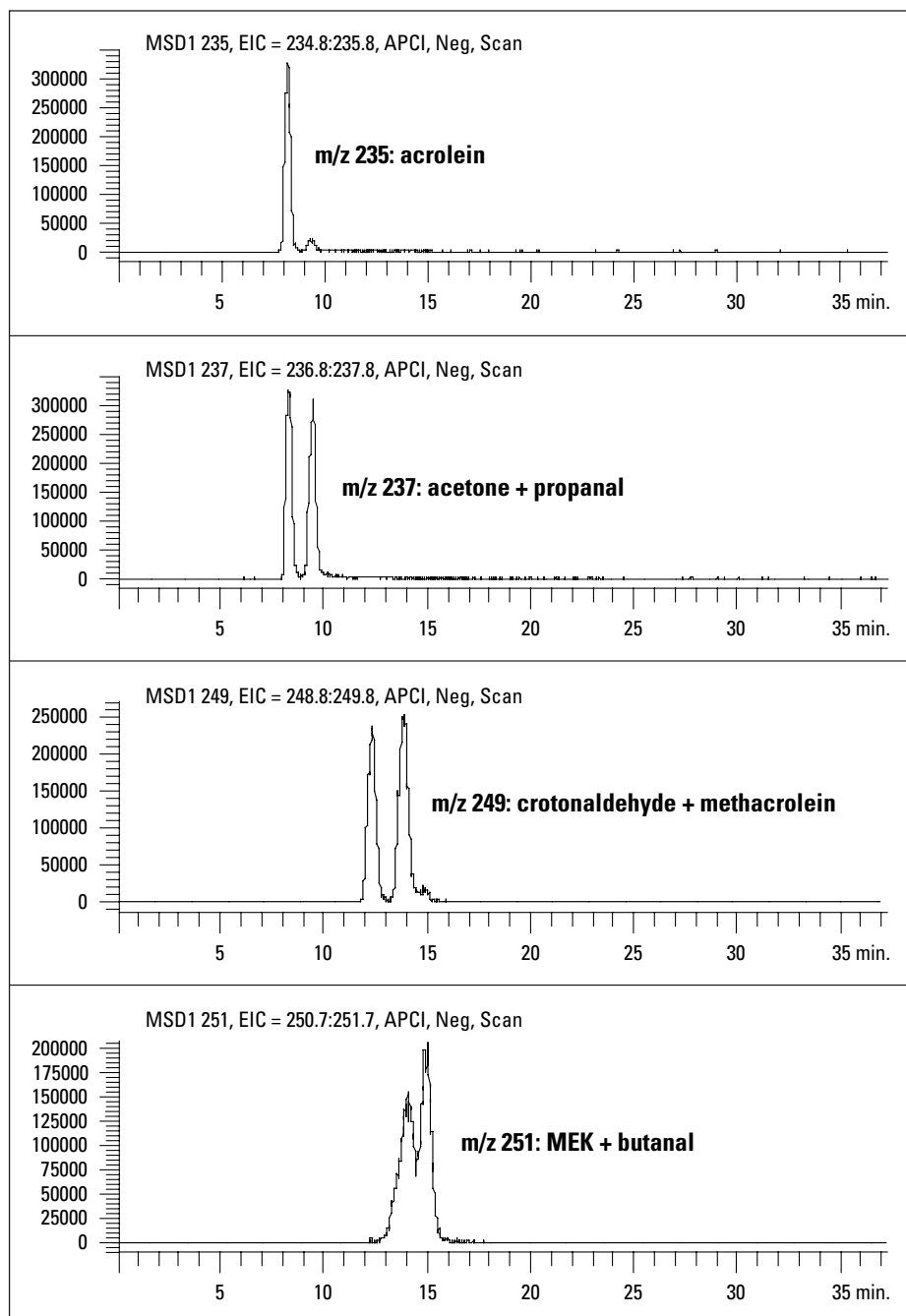


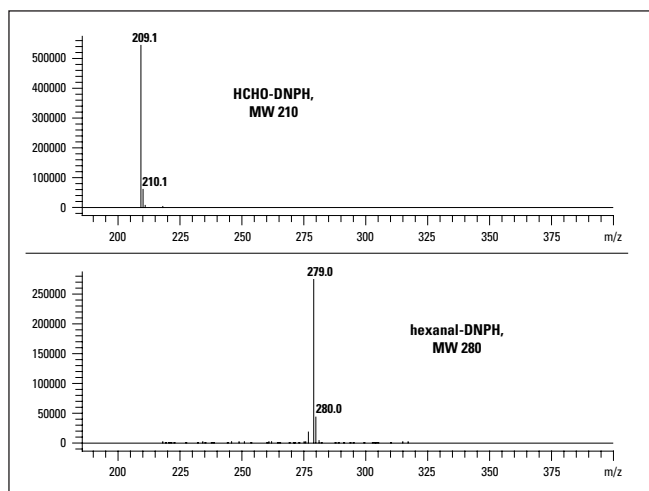
Figure 2. Extracted ion chromatograms for the region of Figure 1 containing acrolein ( $m/z$  235), acetone and propanal ( $m/z$  237), crotonaldehyde and methacrolein ( $m/z$  249), and MEK (2-butanone) and butanal ( $m/z$  251).

## LC/DAD/MS Analysis of Carbonyl (2,4-Dinitrophenyl)hydrazones

Figure 3 shows mass spectra of two carbonyl DNPHs from the data in Figure 1: formaldehyde DNPH and hexanal DNPH. Using conditions optimized for best detection of the  $[M-H]^-$  ion, these spectra show little fragmentation even with the high vaporizer temperature ( $500^\circ\text{C}$ ) found to be optimal for the method.

Figure 4a shows the MS total ion chromatogram of a sample taken from a study of the reaction of the unsaturated ketone 4-hexen-3-one with ozone in a laboratory smog chamber. The LC/MS analysis allows the identification of unreacted 4-hexen-3-one,

and of the carbonyl reaction products acetaldehyde, 2-oxobutanal, formaldehyde, glyoxal, and cyclohexanone (the latter a product of oxidation of cyclohexane, added to scavenge any OH radical which may form as a side product of the ozone-unsaturated ketone reaction). Figure 4b shows the mass spectra of the DNPH derivatives of cyclohexanone and of the dicarbonyl compound 2-oxobutanal. The spectra contain the ion  $m/z$  182, which is characteristic of many carbonyl DNPHs and can be used to help locate and identify carbonyl DNPHs in complex mixtures.



**Figure 3. Atmospheric pressure negative chemical ionization mass spectra of analytes in Figure 1: (top) formaldehyde DNPH, (bottom) hexanal DNPH.**

LC/DAD/MS Analysis of Carbonyl  
(2,4-Dinitrophenyl)hydrazones

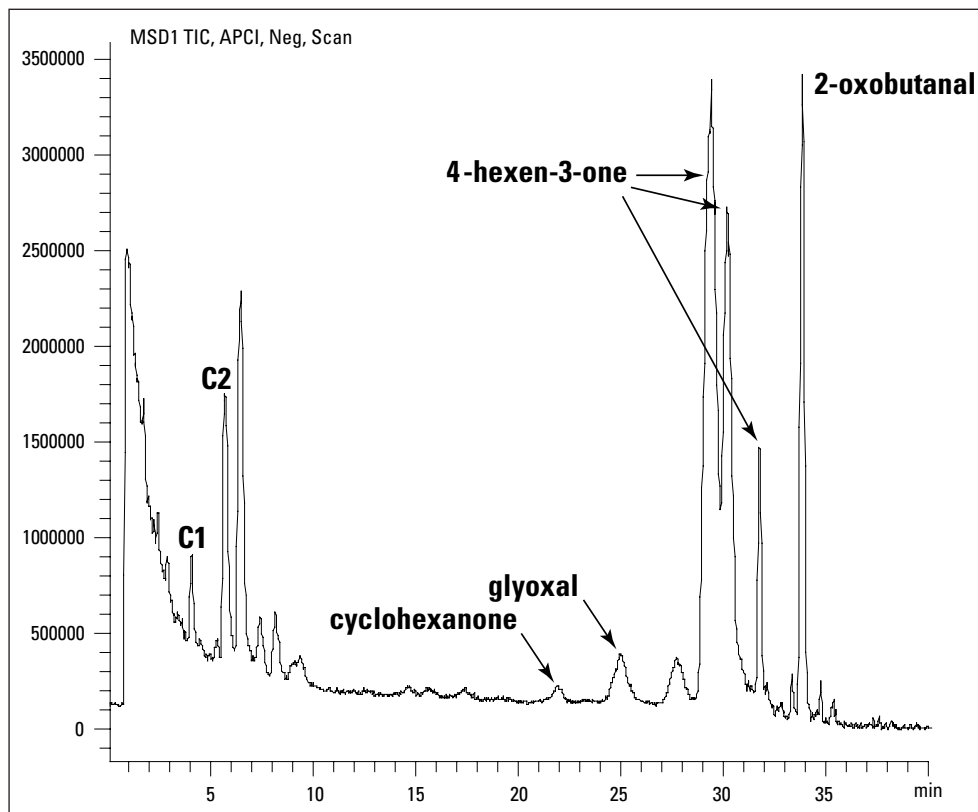


Figure 4a. Atmospheric pressure negative chemical ionization mass spectrometry analysis of the carbonyl products of the reaction of ppb levels of ozone with 4-hexen-3-one in the presence of cyclohexane: (a) total ion current chromatogram with DNPH derivatives of unreacted 4-hexen-3-one (three peaks due to syn/anti isomers of DNPH) and of the reaction products formaldehyde (C1), acetaldehyde (C2), cyclohexanone, glyoxal, and 2-oxobutanal.

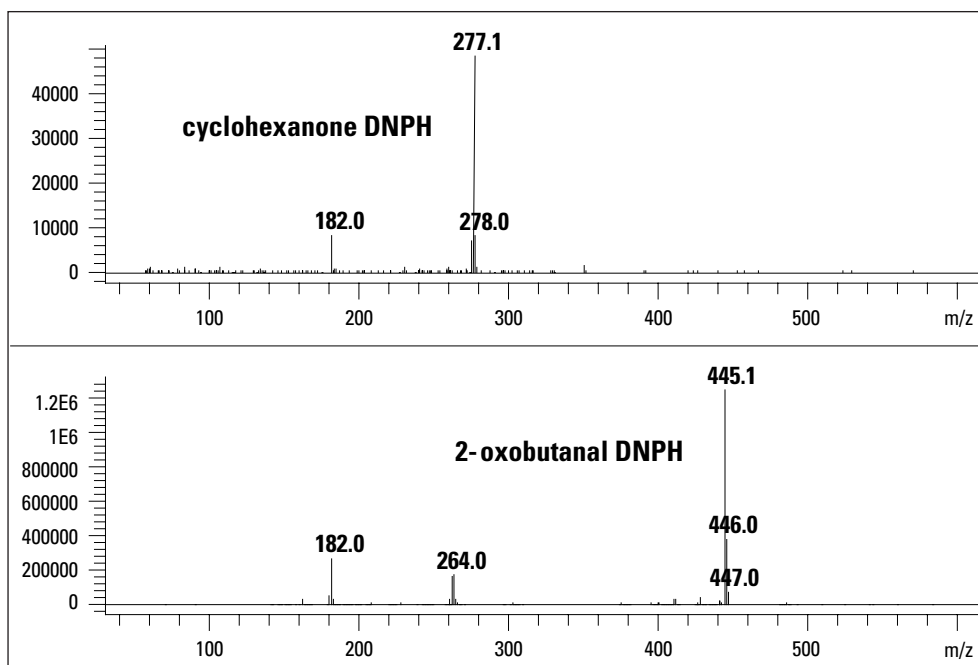
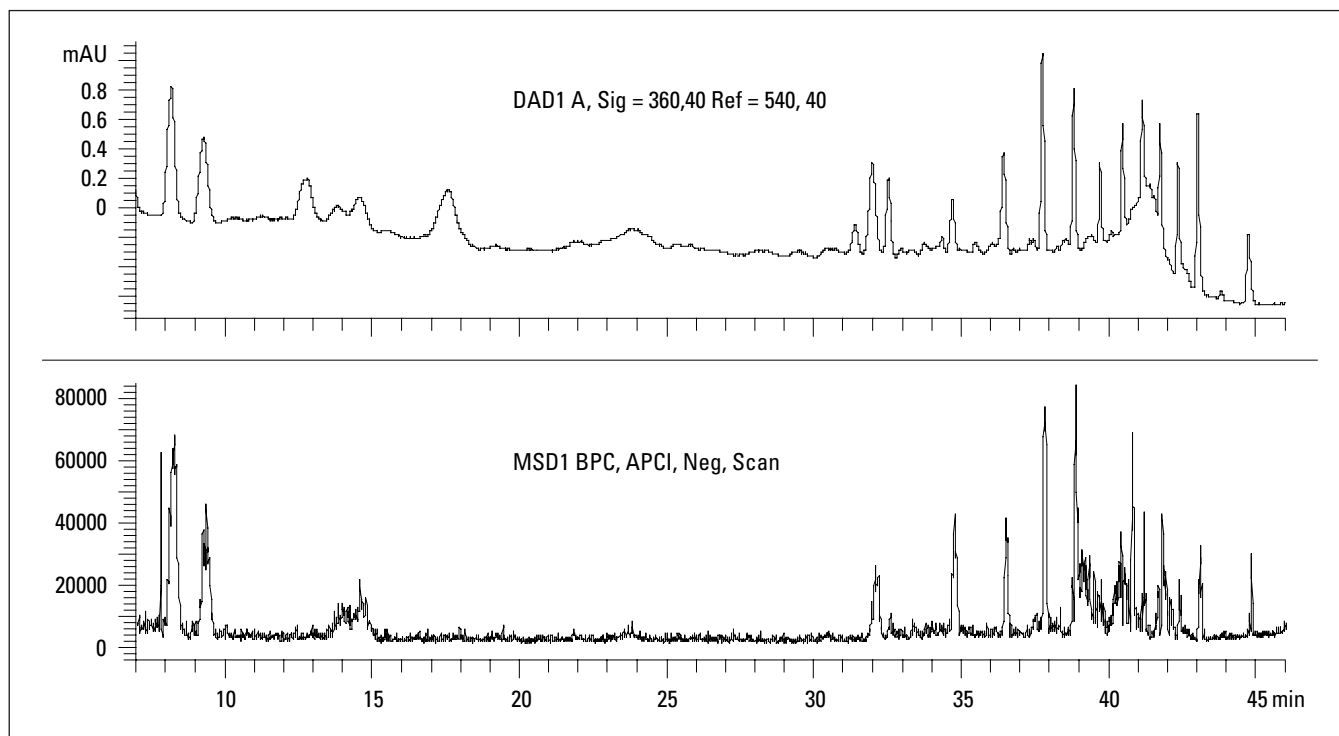


Figure 4b. Atmospheric pressure negative chemical ionization mass spectra of DNPHs of cyclohexanone and 2-oxobutanal.

## LC/DAD/MS Analysis of Carbonyl (2,4-Dinitrophenyl)hydrazones

Figure 5a shows the UV and MS chromatograms from the LC/MS analysis of an ambient air sample collected during early morning peak traffic in Porto Alegre, Brazil, where the mixture of vehicle fuels is unique in the world.<sup>7</sup> The MS data is shown using the base peak chromatogram (BPC), a very useful tool for helping to filter noise from the MS data. The BPC reconstructs an MS chromatogram using only the most intense ion (the base peak) from each spectrum, rather than adding up the abundances of all ions in each spectrum as does the total ion chromatogram (TIC).

Figure 5b shows an expanded view of the region of the UV and MS chromatograms, in which the C6 to C18 straight-chain alkanals elute. In Figure 5c, the extracted ion chromatograms for specific compounds show the distinctive masses of the  $[M-H]^-$  ions, which confirm and/or identify the peaks detected with the UV detector.



**Figure 5a.** LC/MS analysis of an ambient air sample collected in Porto Alegre, Brazil, during early morning peak traffic: (top) UV 360 nm chromatogram; (bottom) APCI negative ion base peak chromatogram (BPC).

LC/DAD/MS Analysis of Carbonyl  
(2,4-Dinitrophenyl)hydrazones

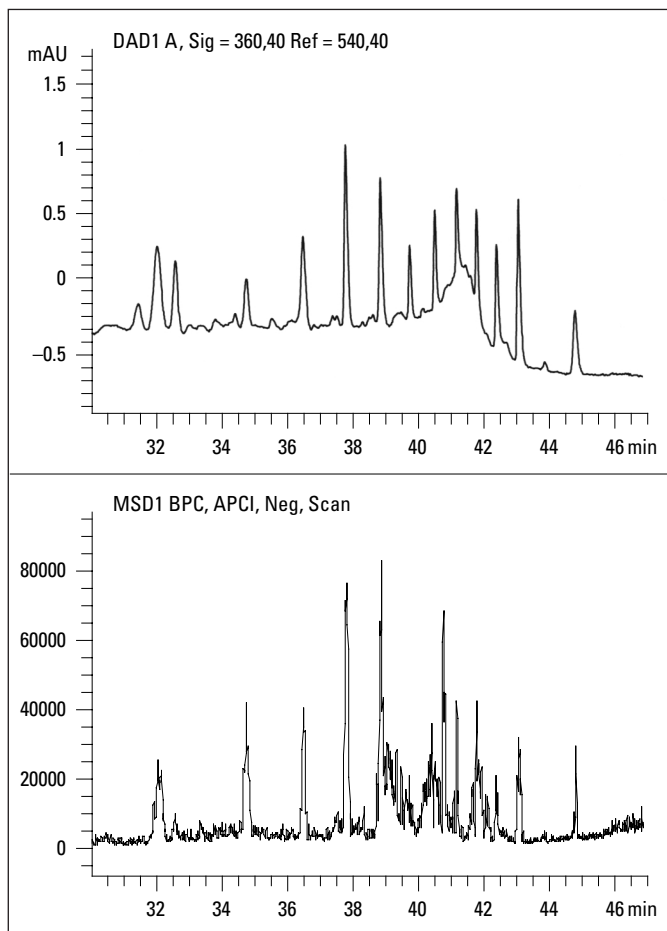


Figure 5b. Expanded region from C6 to C18 alkanals of the analysis in Figure 5b: (top) UV 360 nm chromatogram; (bottom) APCI negative ion base peak chromatogram (BPC).

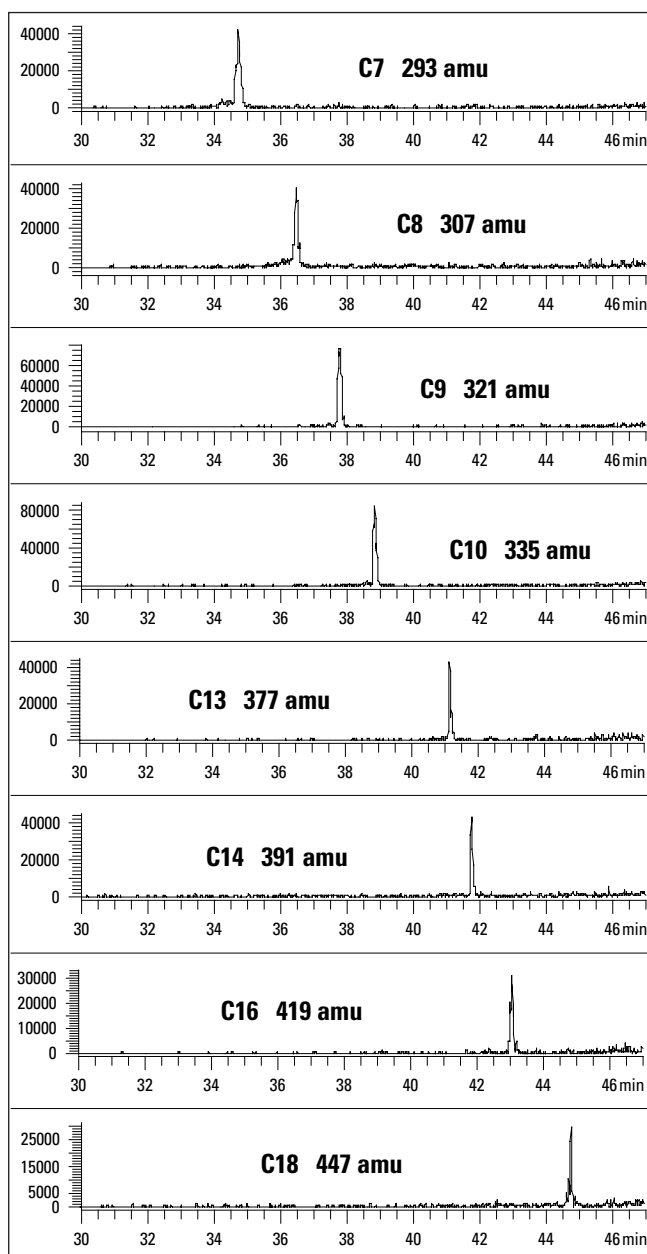


Figure 5c. Extracted ion chromatograms of the  $[M-H]^-$  ion for 1-alkanal DNPH derivatives in Brazil air sample. Each EIC is labeled with the carbon number of the 1-alkanal DNPH derivative and the observed mass of the  $M-H$  ion.

## Summary and Conclusions

This note describes the straightforward addition of API mass spectrometry to a well-established LC method for carbonyl analysis. The resulting APCI-LC/MS method is robust and sensitive, with application not only to simple aldehydes and ketones, but also to hydroxy carbonyls, dicarbonyls, carbonyl esters and keto acids as well. This development has improved a long-standing technique in environmental research, and is applicable to many other fields in which carbonyl-containing compounds are important but difficult to analyze with adequate selectivity, sensitivity, and/or confidence in identification.

## Acknowledgments

The authors would like to thank *Christine Miller* of Agilent Technologies for review and helpful comments.

## References

1. Grosjean, E., Grosjean, D., Green, Peter G., *Anal. Chem.* 1999, 71, 1851–1861.
2. Druzik, C. M., Grosjean, D., Van Neste, A., Parmar, S. S., *Int. J. Environ. Anal. Chem.* 1990, 38, 495–512.
3. Grosjean, E., Grosjean, D., *Int. J. Environ. Anal. Chem.* 1995, 61, 47–64.
4. Grosjean, E., Grosjean, D., *Int. J. Environ. Anal. Chem.* 1995, 61, 343–360.
5. Grosjean, E., Grosjean, D. J., *Atmos. Chem.* 1997, 27, 271–289.
6. Grosjean, E., Grosjean, D., Fraser, M. P., Cass, G. R., *Environ. Sci. Technol.* 1996, 30, 2687–2703.
7. Grosjean, E., Grosjean, D., Gunawardena, R., Rasmussen, R. A., *Environ. Sci. Technol.* 1998, 32, 736–742.

## Authors

*Eric Grosjean* is a research chemist at DGA, Inc., and *Daniel Grosjean* is president of DGA, Inc., Ventura, CA.

*Peter Green* is a senior scientist at the Environmental Analysis Center, Environmental Engineering Science, California Institute of Technology, Pasadena, CA.

*John Hughes* is a senior applications consultant at Agilent Technologies, Pleasanton, CA.

**Table 1. Summary of Data for the DNPH Derivatives of 1-Alkanals.**

Carbonyl	Carbonyl-DNPH			
	RRT <sup>a</sup>	UVmax <sup>b</sup>	MW <sup>c</sup>	BP <sup>de</sup>
formaldehyde	1.00	355	210	209
acetaldehyde	1.40	364	224	223
propanal	2.30	365	238	237
butanal	3.65	366	252	251
pentanal	5.98	367	266	265
hexanal	7.92	366	280	279
heptanal	8.54	366	294	293
octanal	8.96	365	308	307
nonanal	9.28	363	322	321
decanal	9.52	362	336	335
undecanal	9.74	362	350	349
dodecanal	9.92	361	364	363
tridecanal	10.09	361	378	377
tetradecanal	10.24	361	392	391
pentadecanal	10.43	361	406	405
hexadecanal	10.62	361	420	419
heptadecanal	10.85	360	434	433
octadecanal	11.12	360	448	447

<sup>a</sup> RRT = retention time of carbonyl-DNPH relative to that of formaldehyde-DNPH (4.08 ± 0.02 min).

<sup>b</sup> UV max = wavelength of maximum absorption, nm, from 200–600 nm absorption spectrum recorded with diode array detector.

<sup>c</sup> MW = molecular weight of carbonyl-DNPH.

<sup>d</sup> BP = base peak (most abundant ion), *m/z*, in atmospheric pressure negative chemical ionization mass spectrum.

<sup>e</sup> No ions other than BP and <sup>13</sup>C contribution to BP (see text) were present in the spectra of the DNPH derivatives of 1-alkanals.

## LC/DAD/MS Analysis of Carbonyl (2,4-Dinitrophenyl)hydrazones

**Table 2. Summary of Data for the DNPH Derivatives of Other Saturated Aliphatic Carbonyls.<sup>a</sup>**

Carbonyl	Carbonyl-DNPH				
	RRT	UV max	MW	BP	Other Ions <sup>b</sup>
ALDEHYDES					
2-methylpropanal	3.69	363	252	251	none
3-methylbutanal	5.51	363	266	265	none
2-methylbutanal	5.70	363	266	265	263 (1)
2,2-dimethylpropanal	5.66	364	266	265	none
cyclohexylmethanal	8.09	366	292	291	none
KETONES					
acetone	2.01	368	238	237	none
acetone- <i>d</i> <sub>6</sub>	1.98	367	244	243	237–242 <sup>c</sup>
2-butanone	3.44	369	252	251	none
2-pentanone	5.51	371	266	265	none
3-pentanone	5.51	370	266	265	263 (2)
3-methyl-2-butanone	5.52	370	266	265	263 (2)
3,3-dimethyl-2-butanone	7.78	370	280	279	263 (1)
2,4-dimethyl-3-pentanone	8.27	370	294	293	277 (8)
cyclohexanone	5.36	373	278	277	275 (23)
2-methylcyclohexanone	7.94	371	292	291	289 (25)
nopinone <sup>d</sup>	8.30	372	318	317	315 (5)

<sup>a</sup> RRT, UV max, MW, and BP are defined in footnotes *a–d* of Table 1.

<sup>b</sup> *m/z*; Not including <sup>13</sup>C contribution to BP; see text. The percent abundance of the ion relative to that of BP is given in parentheses.

<sup>c</sup> Abundances relative to that of BP = 3% (*m/z* = 237), 4% (238), 6% (239), 13% (240), 24% (241), and 44% (242).

<sup>d</sup> 6,6-Dimethylbicyclo [3.1.1] heptan-2-one.

## LC/DAD/MS Analysis of Carbonyl (2,4-Dinitrophenyl)hydrazones

**Table 3. Summary of Data for the DNPH Derivatives of Unsaturated Aliphatic Carbonyls.<sup>a</sup>**

Carbonyl	Carbonyl-DNPH				
	RRT	UV max	MW	BP	Other Ions <sup>b</sup>
ALDEHYDES					
acrolein	2.01	380	236	235	none
crotonaldehyde <sup>c</sup>	3.08	382	250	249	none
methacrolein	3.44	381	250	249	none
2-ethylacrolein	5.55	379	264	263	none
<i>trans</i> -2-hexenal	7.60	382	278	277	275 (7)
2-methyl-2-pentenal	7.67	384	278	277	275 (3)
<i>cis</i> -4-heptenal	7.78 <sup>d</sup>	365	292	291	289 (7)
	7.95 <sup>e</sup> (2%)	366	292	291	289 (7)
<i>trans</i> -2-decenal	9.41	381	334	333	331 (6)
<i>trans</i> -2-undecenal	9.64	380	348	347	345 (5)
KETONES					
methyl vinyl ketone	2.68 <sup>e</sup> (13%)	368	250	249	none
	2.87 <sup>e</sup> (3%)	372	250	249	none
	3.06 <sup>d</sup>	379	250	249	none
1-penten-3-one	4.76 <sup>d</sup>	378	264	263	247 (8)
	4.99 <sup>e</sup> (12%)	376	264	263	247 (9)
3-penten-2-one	4.43 <sup>e</sup> (3%)	382	264	263	none
	4.83 <sup>d</sup>	384	264	263	none
4-methyl-3-penten-2-one	6.94	386	278	277	263 (3)
4-hexen-3-one <sup>c</sup>	7.12 <sup>e</sup> (4%)	385	278	277	none
	7.38 <sup>e</sup> (35%)	357	278	277	none
	7.72 <sup>d</sup>	357	278	277	none
6-methyl-5-hepten-2-one <sup>f</sup>	8.27	368	306	305	289 (4)
4-acetyl-1-methylcyclohexene	8.64	369	318	317	301 (4)

<sup>a</sup> RRT, UV max, MW, and BP are defined in footnotes *a*–*d* of Table 1.

<sup>b</sup> *m/z*; not including <sup>13</sup>C contribution to base peak; see text. The percent abundance of the ion relative to that of BP is given in parentheses.

<sup>c</sup> Predominantly the *trans* isomer.

<sup>d</sup> Largest peak.

<sup>e</sup> Smaller peak; percent of largest peak (peak height basis at 360 nm) given in parentheses.

<sup>f</sup> Two coeluting peaks.

LC/DAD/MS Analysis of Carbonyl  
(2,4-Dinitrophenyl)hydrazones

Table 4. Summary of Data for the DNPH Derivatives of Aromatic Carbonyls.<sup>a</sup>

Carbonyl	Carbonyl-DNPH				
	RRT	UV max	MW	BP	Other Ions <sup>b</sup>
benzaldehyde	4.75	384	286	285	none
<i>o</i> -tolualdehyde	7.13	386	300	299	none
<i>m</i> -tolualdehyde	7.29	385	300	299	none
<i>p</i> -tolualdehyde	7.35	388	300	299	none
acetophenone	6.77	382	300	299	none
2,5-dimethylbenzaldehyde	8.15	389	314	313	none
2-hydroxybenzaldehyde (salicylaldehyde)	2.97	391	302	301	none
4-methoxybenzaldehyde ( <i>p</i> -anisaldehyde)	4.98	398	316	315	none
3,4-dimethoxybenzaldehyde	3.07	398	346	345	none
4-hydroxy-3-methoxybenzaldehyde (vanillin)	1.75	402	332	331	329 (2), 315 (1)
4-hydroxy-3-methoxyacetophenone (acetovanillone)	2.37	393	346	345	343 (5), 329 (45), 313 (4), 298 (2)
3,5-dimethoxy-4-hydroxybenzaldehyde (syringaldehyde)	1.54	436	362	361	360 (40), 359 (1), 345 (1)
4-hydroxy-3-methoxycinnamaldehyde (coniferyl aldehyde)	2.67	415	358	357	356 (12), 355 (22), 325 (5), 310 (10)

<sup>a</sup> RRT, UV max, MW, and BP are defined in footnotes *a-d* of Table 1.

<sup>b</sup> *m/z*; not including <sup>13</sup>C contribution to BP; see text. The percent abundance of the ion relative to that of BP is given in parentheses.

LC/DAD/MS Analysis of Carbonyl  
(2,4-Dinitrophenyl)hydrazones

Table 5. Summary of Data for the DNPH Derivatives of Dicarbonyls.<sup>a</sup>

Carbonyl	Carbonyl-DNPH					
	RRT	UV max	MW (mono)	MW (di)	BP	Other Ions <sup>b</sup>
glyoxal	6.09	415	238	418	417	237 (14), 238 (16)
methylglyoxal	7.90	432	252	432	431	251 (14), 249 (17)
2-oxobutanal <sup>c</sup>	8.31	410	266	446	445	263 (12)
2,3-butanedione	1.50 <sup>e</sup> (1%)	362	266		265	none
	1.79 <sup>e</sup> (2%)	369	266		265	none
	8.31 <sup>d</sup>	403		446	445	265 (7), 263 (48)
succinic dialdehyde	0.81 <sup>e</sup> (5%)	360	266		265	
	1.55 <sup>d,f</sup>	338 <sup>f</sup>			247 <sup>f</sup>	
	6.42 <sup>e</sup> (12%)	368		446	445	263 (80)
glutaraldehyde	7.34	368	280	460	459	279 (10)
2,3-pentanedione	8.72	402	280	460	459	443 (8), 279 (15)
2,4-pentanedione	1.03	310	280	460	262	302 (14), 232 (6), 360 (7), 279 (0.1), 288 (5)
3,4-hexanedione	8.89	400	294	474	473	293 (5), 291 (12)
pinonaldehyde <sup>g</sup>	3.73 <sup>e</sup> (9%)	368	348		347	none
	9.07 <sup>d</sup>	368		528	527	345 (16)

<sup>a</sup> RRT, UV max, and BP are defined in footnotes a–d of Table 1. MW (mono) and MW (di) are the molecular weights of the mono-DNPH derivative and di-DNPH derivative, respectively.

<sup>b</sup> *m/z*; not including <sup>13</sup>C contribution to BP; see text. The percent abundance of the ion relative to that of BP is given in parentheses.

<sup>c</sup> Prepared by reaction of ozone with 1-penten-3-one, 2-ethylacrolein, and 4-hexen-3-one.

<sup>d</sup> Largest peak.

<sup>e</sup> Smaller peak; percent of largest peak (peak height basis at 360 nm) is given in parentheses.

<sup>f</sup> This compound is not the mono-DNPH derivative; see text.

<sup>g</sup> (2,2-Dimethyl-3-acetylcyclobutyl) ethanal, prepared by reaction of ozone with pinene.

LC/DAD/MS Analysis of Carbonyl  
(2,4-Dinitrophenyl)hydrazonesTable 6. Summary of Data for the DNPH Derivatives of Other Carbonyls.<sup>a</sup>

Carbonyl	Carbonyl-DNPH				
	RRT	UV max	MW	BP	Other Ions <sup>b</sup>
methyl glyoxylate <sup>c</sup>	0.89 <sup>f</sup> (60%)	355	268	267	none
	1.72 <sup>e</sup>	357	268	267	none
ethyl glyoxylate	1.24 <sup>f</sup> (65%)	356	282	281	none
	2.71 <sup>e</sup>	359	282	281	none
2-oxoethyl acetate <sup>d</sup>	1.14 <sup>e</sup>	360	282	281	249 (18)
	1.22 <sup>f</sup> (13%)	356	282	281	249 (16)
methoxyacetone	1.59 <sup>e</sup>	363	268	267	none
	2.25 <sup>f</sup> (30%)	370	268	267	none
2-furaldehyde	2.14 <sup>e</sup>	392	276	275	none
	3.00 <sup>f</sup> (25%)	383	276	275	none

<sup>a</sup> RRT, UV max, MW, and BP are defined in footnotes *a-d* of Table 1.

<sup>b</sup> *m/z*; not including <sup>13</sup>C contribution to base peak; see text. The percent abundance of the ion relative to that of BP is given in parentheses.

<sup>c</sup> Prepared by reaction of ozone with methyl acrylate and with methyl *trans*-3-methoxyacrylate (MTMA).

<sup>d</sup> Prepared by reaction of ozone with MTMA and with *trans*-2-hexenyl acetate.

<sup>e</sup> Largest peak.

<sup>f</sup> Smaller peak; percent of largest peak (peak height basis at 360 nm) is given in parentheses.

Agilent Technologies shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance or use of this material.

Information, descriptions and specifications in this publication are subject to change without notice.

Copyright © 2000  
Agilent Technologies  
All rights reserved.  
Reproduction and adaptation is prohibited.

Printed in the U.S.A. January 2000  
(23) 5968-8850E