FAST ANALYSIS OF ALDEHYDES AND KETONES USING UPLC

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INTRODUCTION

Aldehydes and ketones are products of combustion that permeate the environment. A number of these compounds are known carcinogens and, as a result several USEPA and state methods have been developed for their analysis. These methods, USEPA TO5 (air), 554 (drinking water), 8315A, Options 1 and 2, (waste water,soil and air) along with California Method 1004 (carbonyl compounds as alcohol oxidants in auto exhaust) describe the derivatization of these compounds using Dinitrophenylhydrazine (DNPH) followed by UPLC™ separation and UV detection at 360 nm; target analytes vary slightly by method. Present HPLC methods describe run times of over 40 minutes[1] and multiple column setups[2] to achieve acceptable analyte resolution.

This poster demonstrates that with UPLC ™ analysis time can be reduced by as much as 75%. In addition, excellent resolution is achieved for acetone, acrolein and propanal in Method 8315A, Option 2 and methacrolein and MEK in California method 1004.

METHOD

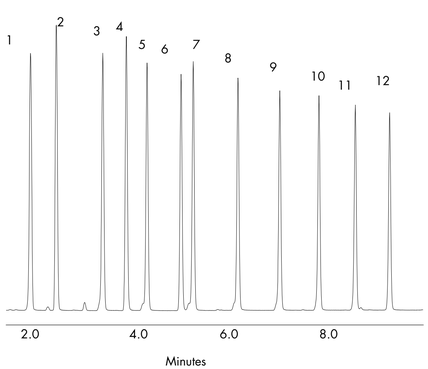
Chromatographic Conditions
System: Waters ACQUITY UPLC™
Column: Waters ACQUITY UPLC™ BEH Phenyl, 2.1X100 mm, 1.7µ
@ 35° C
Eluent: A– 90:10 Water– THF (Stabilized)*
B– Acetonitrile
* Mix 900 ml water and 100 ml stablized tetrahydrofuran (THF), filter and degas
Flow Rate: 0.5 ml / min
Injection Volume: 5 µl
Gradient Elution*
Detection: UV @ 360 nm
Data: Waters Empower™ Chromatography Software
* The chromatographic gradient profiles are unique per the method used due to differences in the selectivity of the target analytes.

RESULTS AND DISCUSSION

EPA Method 554 (drinking water) and 8315 Option 1 (collected by Method 0011) target the same 12 analytes including the strongly retained C_5-C_{10} compounds (Pentanal-Decanal) The gradient profile (Table 1) and the UPLC™ chromatogram (Figure 1) are shown

Step	Time	Flow	%A	%B	Curve
1	Initial	0.5	70.0	30.0	-
2	9.0	0.5	36.0	64.0	6
3	9.5	0.5	70.0	30.0	11

Table 1 Gradient Profile for EPA Methods 554 and 8315 Option 1



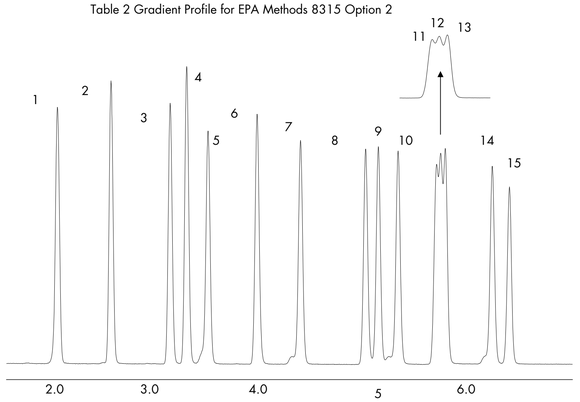
1- Formaldehyde
2- Acetaldehyde
3– Propanal
4– Crotonaldehyde
5– Butanal
6– Cyclohexanone
7– Pentanal
8– hexanal
9– Heptanal
10– Octanal
11– Nonanal
12– Decanal

Figure 1 EPA 554, 8315A Option 1 analytes
20 ppm as DNPH derivatives

EPA Method 8315A Option 2 targets 15 analytes includes the difficult baseline triad of acetone, acrolein and propanal along with the three tolualdehyde isomers (o,p,m). This is an indoor air method using collection protocol 0100.The gradient profile(Table 2) and the UPLC™ chromatogram (Figure 2) are shown

Step	Time	Flow	%A	%B	Curve
1	Initial	0.5	70.0	30.0	-
2	6.5	0.5	53.0	47.0	6
3	9.5	0.5	70.0	30.0	11

Table 2 Gradient Profile for EPA Methods 8315 Option 2



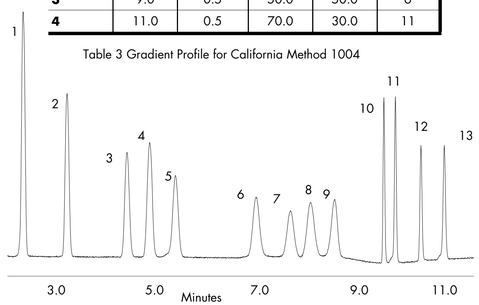
1- Formaldehyde
2- Acetaldehyde
3- Acetone
4- Acrolein
5- Propanal
6- Crotonaldehyde
7- Butanal
8- Benzaldehyde
9- Isovaleraldehyde
10- Pentanal
11- o-Tolualdehyde
12- p-Tolualdehyde
13- mTolualdehyde
14- Hexanal
15– 2-5 Dimethylbenzaldehyde

Figure 2, EPA 8315A Option 2 analytes
20 ppm as DNPH derivatives

California Method 1004 targets 13 analytes, the alcohol oxidation products from auto engine exhausts. Here, the critical pair is Methyl Ethyl Ketone (MEK) and Methacrolein.The gradient profile(Table 3) and the UPLC™ chromatogram (Figure 3) are shown

Step	Time	Flow	%A	%B	Curve
1	Initial	0.5	70.0	30.0	-
2	8.0	0.5	70.0	30.0	6
3	9.0	0.5	50.0	50.0	6
4	11.0	0.5	70.0	30.0	11

Table 3 Gradient Profile for California Method 1004



1- Formaldehyde
2- Acetaldehyde
3- Acetone
4- Acrolein
5- Propanal
6- Crotonaldehyde
7- MEK
8- Methacrolein
9- Butanal
10– Benzaldehyde
11- Pentanal
12- mTolualdehyde
13– Hexanal

Figure 3, California Method 1004 analytes
0.75 ppm as parent compounds

As in any separation, retention time (RT)and area reproducibility are essential. Figure 4 is an overlay of 5 injections of the EPA 554 standard. As demonstrated in Table 4, RT and area reproducibility are less than 0.2 % and 0.5 % for all analytes respectively.

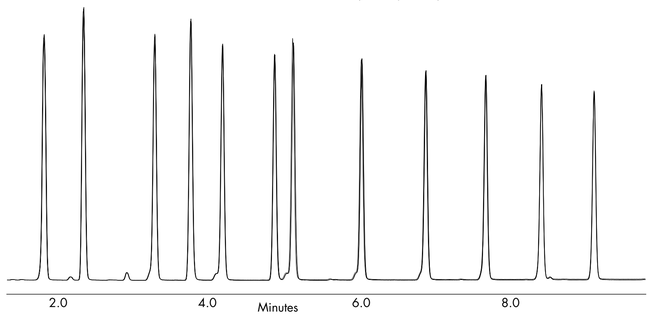


Figure 4 Overlay of 5 injections, EPA 554 analytes

Analyte	% RSD RT	% RSD Area
Formaldehyde	0.163	0.398
Acetaldehyde	0.119	0.408
Propanal	0.078	0.410
Crotonaldehyde	0.071	0.377
Butanal	0.061	0.336
Cyclohexanone	0.053	0.308
Pentanal	0.103	0.471
Hexanal	0.075	0.296
Heptanal	0.049	0.288
Octanal	0.039	0.267
Nonanal	0.026	0.333
Decanal	0.024	0.338

Table 4 Reproducibility Data for 5 injections, EPA 554 Analytes

CONCLUSION

Aldehydes and ketones can be analyzed as DNPH derivatives rapidly and efficiently using ACQUITY UPLC™. Results can be obtained several times faster than conventional HPLC technologies with corresponding cost savings, which allows more samples to be processed in a given day. By a simple variant of gradient conditions, the separation requirements of the major EPA Methods 554, 8315A Options 1 and 2 along with California Method 1004 can be achieved.

REFERENCES

1– Bashe W.J. and Eichelberger J. W. USEPA Method 554, " Determination of Carbonyl Compounds in Drinking Water by Dinitrophenylhydrazine Derivatization and High Performance Liquid Chromatography" Rev. 1.0, August 1992, p. 554-17

2– " Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography " Method No. 1004, Part F of " California Non-Methane Organic Test Procedures " Monitoring and Laboratory Division, Southern Laboratory Branch, Mobile Source Division, 9528 Telstar Avenue, El Monte, CA 91731, Section 4.1.5, p. F-5

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