Evaluation of a Variety of GC Stationary Phases for the Analysis of Volatile Organics by US EPA Method 8260.

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Abstract

Many GC stationary phases have been used for the analysis of volatile organic compounds by US EPA Method 8260. With an ever-expanding target list, and the availability of many stationary phases, choosing the correct column can be difficult. Every stationary phase has limitations, whether related to temperature range, stability, or selectivity. Selectivity limitations can be a function of sample-specific compounds that share common ions for quantification.

This paper will examine the performance of various stationary phases, with varied sample concentrations, in volatiles analysis, and will include example chromatograms for situations for which each column is best suited. Compound identifications, purge and trap conditions, interfering ions, and other factors specific to the GC/MS analysis will be presented.

Introduction

Qualitative identification of a target compound by GC/MS is based on retention time and on the comparison of the sample mass spectrum to a reference mass spectrum. Identification of compounds uses three ions of the greatest intensity. The quantitation ion is usually the highest m/z fragment and is used for determining concentrations of a particular analyte. It is important that there be no coelution between compounds shaing ions used for quantitation. As long as unique quantitation ions can be selected for compounds that share retention time, chromatographic coelution is acceptable. When using any column for GC/MS, attention must be given to coeluting compounds to determine if acceptable quantitation ions can be found. This paper will examine optimized conditions on four different stationary phases for suitability by EPA Method 8260.

Purge and trap used for this work was the O.I. 4560 & 4660 Eclipse.

Instrument Courtesy of O.I.Analytical.

Coelutions by Phase:

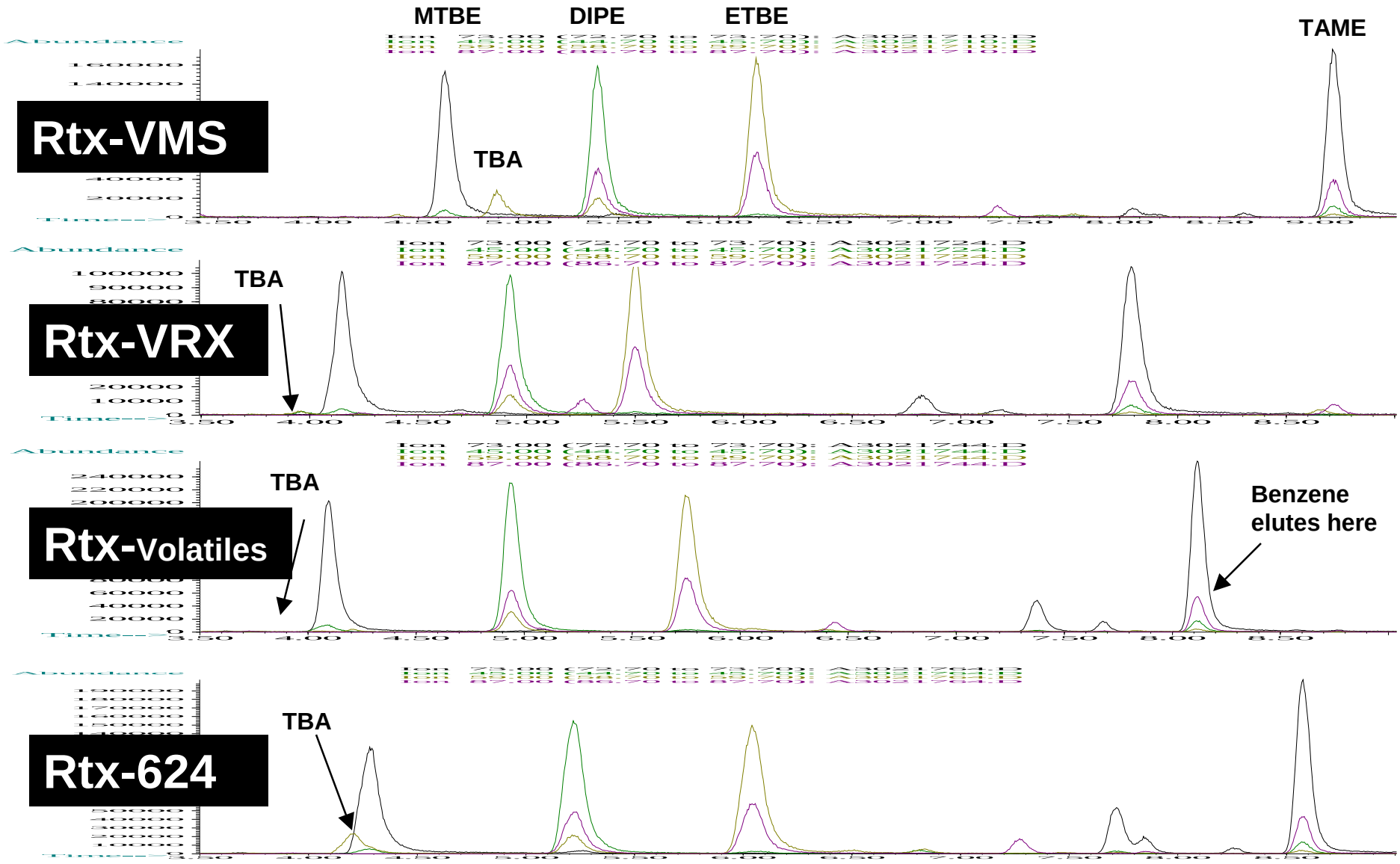
Calibration curves for the four columns evaluated passed EPA 8260 criteria (SPCC & CCC) for response factors and relative standard deviations. Two compounds in the test set showed poor response, acetone and TBA. The Rtx-VMS, Rtx-VRX, Rtx-Volatiles and Rtx-624 were tested in the 30m x 0.25mm x 1.4df column dimensions. The compounds are listed by quantification ion and retention time (see Table 1).

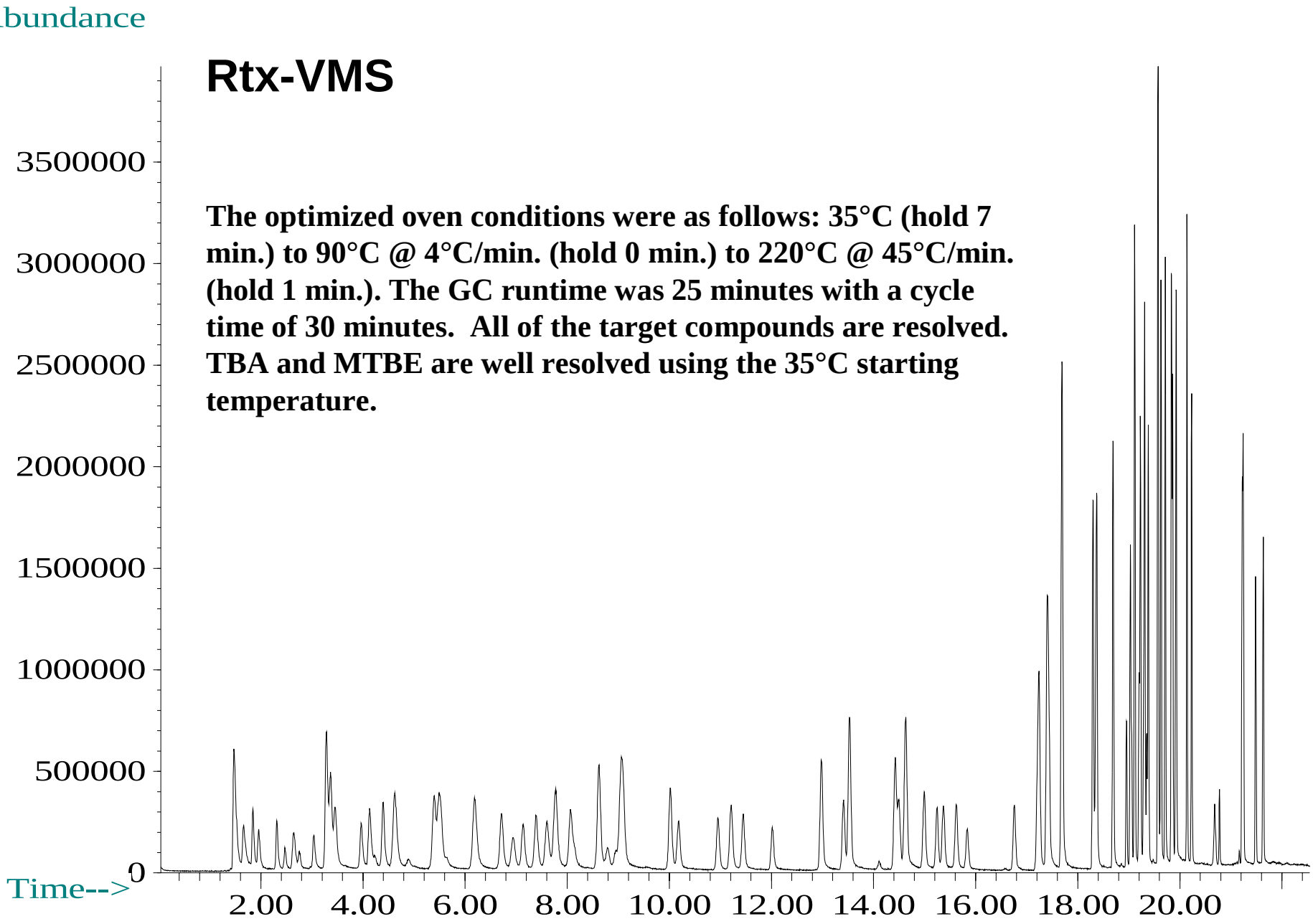
Compound	SigMS	Char. Ion	Rtx-VMS	Rtx-VRX	Rtx-VOLATILES	Rtx-624
dichlorodifluoromethane	85	85 87	1.65	1.74	1.69	1.52
chloromethane	50	50 52	1.84	1.80	1.84	1.69
vinyl chloride	62	62 64	1.95	1.94	1.95	1.81
bromomethane	94	94 96	2.30	2.20	2.27	2.16
chloroethane	64	64 66	2.46	2.31	2.34	2.27
trichlorofluoromethane	101	151 101 153	2.63	2.72	2.63	2.51
diethylether	59	74 45	3.03	2.92	2.89	2.86
1,1-dichloroethene	96	96 61 63	3.26	3.17	3.20	3.14
carbon disulfide	76	78 76	3.28	3.47	3.73	3.37
Freon 113	101	151 101 85	3.35	3.38	3.11	3.14
iodomethane	142	127 141	3.44	3.17	3.49	3.37
allyl chloride	76	41 39 78	3.95	2.66	3.62	3.69
methylene chloride	84	49	4.12	3.30	3.73	3.93
acetone	43	43 58	4.23	2.81	3.04	3.38
trans-1,2-dichloroethene	96	96 61 98	4.38	3.95	4.21	4.29
methyl-d3-tert-butyl-ether	76		4.59	4.07	4.08	4.18
methyl-tert-butyl-ether	73	73 57	4.62	4.15	4.08	4.45
tert-butyl alcohol	59	59 84	4.87	3.21	3.31	4.14
acetonitrile	41	40 39	5.00	3.33	3.61	3.60
diisopropyl ether	45	43 87	5.38	4.88	4.94	5.22
chloroprene	64	(53) 88 90 51	5.50	4.70	5.08	5.23
1,1-dichloroethane	63	63 65 83	5.52	4.24	4.87	5.23
acrylonitrile	53	52 51	5.63	4.70	3.82	4.29
ethyl-tert-butyl ether	59	57 87	6.17	5.49	5.75	6.04
cis-1,2-dichloroethene	96	96 61 98	6.70	4.93	6.06	6.51
2,2-dichloropropane	77	77 97	6.93	5.38	11.96	6.51
bromochloromethane	128	128 49 130	7.13	5.17	6.68	7.05
chloroform	83	83 85	7.28	5.26	6.44	7.27
carbon tetrachloride	117	117 119	7.59	7.11	7.84	7.73
tetrahydrofuran	42	72 71 41	7.72	5.80	5.60	7.60
methyl actrylate	55	85	7.76	5.40	6.44	6.82
1,1,1-trichloroethane	97	97 99 61	7.76	6.46	7.34	7.48
dibromofluoromethane	111	111 192	7.78	5.41	6.86	7.64
1,1-dichloropropene	75	75 77 39	8.06	6.84	7.68	7.86
2-butanone	72	43 57 (use 43)	8.13	4.80	5.68	6.67
benzene	78	78	8.62	7.17	8.10	8.26
propionitrile	54	54 52 55 40	8.74	ND	ND	6.96
methacrylonitrile	41	41 67 39 52 66	8.79	4.95	6.22	7.27
1,2-dichloroethane-d4	65		8.95	6.14	8.10	8.26
pentrafluorobenzene	168	99 137 117	9.02	6.27	7.00	7.88
tert-amyl-methyl ether	73	87 55	9.06	7.79	8.12	8.57
1,2-dichloroethane	62	62 98	9.10	6.27	8.10	8.57
trichloroethene	95	95 97 139 132	10.02	8.67	9.31	9.64
1,4-difluorobenzene	114	88 63	10.17	7.81	8.77	9.27
dibromomehtne	93	93 95 174	10.95	8.38	9.93	10.39
1,2-dichloropropane	63	63 112	11.21	8.52	9.57	10.17
bromodichloromethane	83	83 85 127	11.45	8.67	9.91	10.75
methyl methacrylate	69	41 100 39	12.01	9.53	9.85	10.52
cis-1,3-dichloropropene	75	75 77 39	12.98	10.59	10.93	11.63
2-chloroethyl-vinyl-ehter	63	63 65 106	12.99	10.16	10.62	11.45
toluene-d8	98		13.42	12.75	11.34	12.00
toluene	92	92 91	13.54	12.97	11.47	12.11
2-nitropropane	43	41 39 27	14.12	14.26	10.07	11.37
tetrachloroethene	166	(164) 129 131	14.43	15.61	12.53	13.05
2-bromo-1-chloropropane	77	77 107 41 158	14.50	12.75	11.96	12.57
4-methyl2-pentanone	43	(100) 58 85	14.62	11.19	10.72	11.99
trans-1,3-dichloropropene	75	75 110 77	14.65	12.01	11.76	12.75
1,1,2-trichloroethane	83	83 97 85	15.00	12.37	11.96	13.05
ethyl methacrylate	69	41 99 86 114	15.25	14.03	11.96	12.91
dibromochloromethane	129	129 127	15.38	13.84	12.68	13.73
1,3-dichloropropane	76	76 78	15.63	13.23	12.37	13.37
1,2-dibromoethane	107	107 109 188	15.85	14.67	12.99	13.93
2-hexanone	43	58 57 100	16.77	14.26	12.14	13.60
chlorobenzene-D5	117	82 54	17.22	18.25	13.65	14.83
chlorobenzene	112	112 77 114	17.26	18.38	13.72	14.88
ethylbenzene	91	91 106	17.41	19.38	13.89	15.07
1,1,1,2-tetrachloroethane	131	131 133 119	17.45	18.16	13.81	15.07
m-xylene	106	106 91	17.70	19.96	14.02	15.07
p-xylene	106	106 91	17.70	19.96	14.02	15.07
o-xylene	106	106 91	18.31	20.70	16.65	15.92
bromoform	173	173 175 254	18.36	19.78	15.02	16.24
styrene	104	104 78	18.38	20.57	14.68	15.97
isopropylbenzene	105	105 120	18.70	21.34	15.24	16.47
4-bromo-1-fluorobenzene	95	95 174 176	18.97	21.30	15.52	16.73
bromobenzene	156	156 77 158	19.04	21.52	15.75	16.88
cis-1,4 dichloro-2-butene	53	(75) 53 77 124	19.07	20.49	15.19	16.73
1,4-dichlorobutane	55	55 90 75	19.12	20.64	15.29	16.73
n-propylbenzene	91	91 120	19.13	21.96	15.84	17.04
1,1,2,2-tetrachloroethane	83	83 131 85	19.21	16.18	15.40	17.04
2-chlorotoluene	91	91 126	19.24	21.99	16.02	17.16
1,2,3-trichloropropane	75	75 77 97 110	19.30	20.92	15.60	17.04
1,3,5-trimethylbenzene	105	105 120	19.32	22.37	16.65	17.27
trans-1,4-dichloro-2-butene	53	88 75	19.36	21.10	15.75	17.15
4-chlorotoluene	91	91 126	19.40	22.10	16.10	17.15
tert-butylbenzene	119	119 91 134	19.58	22.62	16.61	17.68
pentachloroethane	167	130 132 165	19.59	22.28	16.61	17.76
1,2,4-trimethylbenzene	105	105 120	19.64	22.77	16.61	17.30
sec-butylbenzene	105	105 134	19.73	22.86	16.93	17.95
p-isopropyltoluene	119	119 134 91	19.85	23.09	17.13	18.14
1,3-dichlorobenzene	146	146 111 148	19.87	22.86	17.13	18.05
1,4-dichlorobenzene-d4	152	150	19.93	22.94	17.24	18.22
1,4-dichlorobenzene	146	146 111 148	19.94	22.94	17.28	18.22
n-butylbenzene	91	91 92 134	20.15	23.47	17.66	18.62
1,2-dichlorobenzene	146	146 111 148	20.24	23.28	17.72	18.65
1,2-dibromo-3-chloropropan	75	75 155 157	20.79	23.70	18.60	19.55
nitrobenzene	123	51 77	21.19	23.92	18.69	19.80
hexachlorobutadiene	225	225 223 227	21.24	25.10	19.77	20.51
1,2,4-trichlorobenzene	180	180 182 145	21.27	24.84	19.57	20.38
naphthalene	128	128	21.52	25.01	19.77	20.64
1,2,3-trichlorobenzene	180	180 182 145	21.66	25.18	20.04	20.38

Oxygenate Extracted Ions by EPA Method 8260.

Adding compounds such as the oxygenates to the 8260 compound list can result in critical coelutions. Several examples are given. The Rtx-624 30 meter x 0.25mm x 1.4df column does not resolve the TBA from MTBE. These compounds share 59 ion. The Rtx-Volatiles phase has a coelution of TAME/Benzene m/z 73.

Oxygenate Extracted Ions by EPA Method 8260.




Abundance
Rtx-VMS
The optimized oven conditions were as follows: 35°C (hold 7 min.) to 90°C @ 4°C/min. (hold 0 min.) to 220°C @ 45°C/min. (hold 1 min.). The GC runtime was 25 minutes with a cycle time of 30 minutes. All of the target compounds are resolved. TBA and MTBE are well resolved using the 35°C starting temperature.
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Time-->
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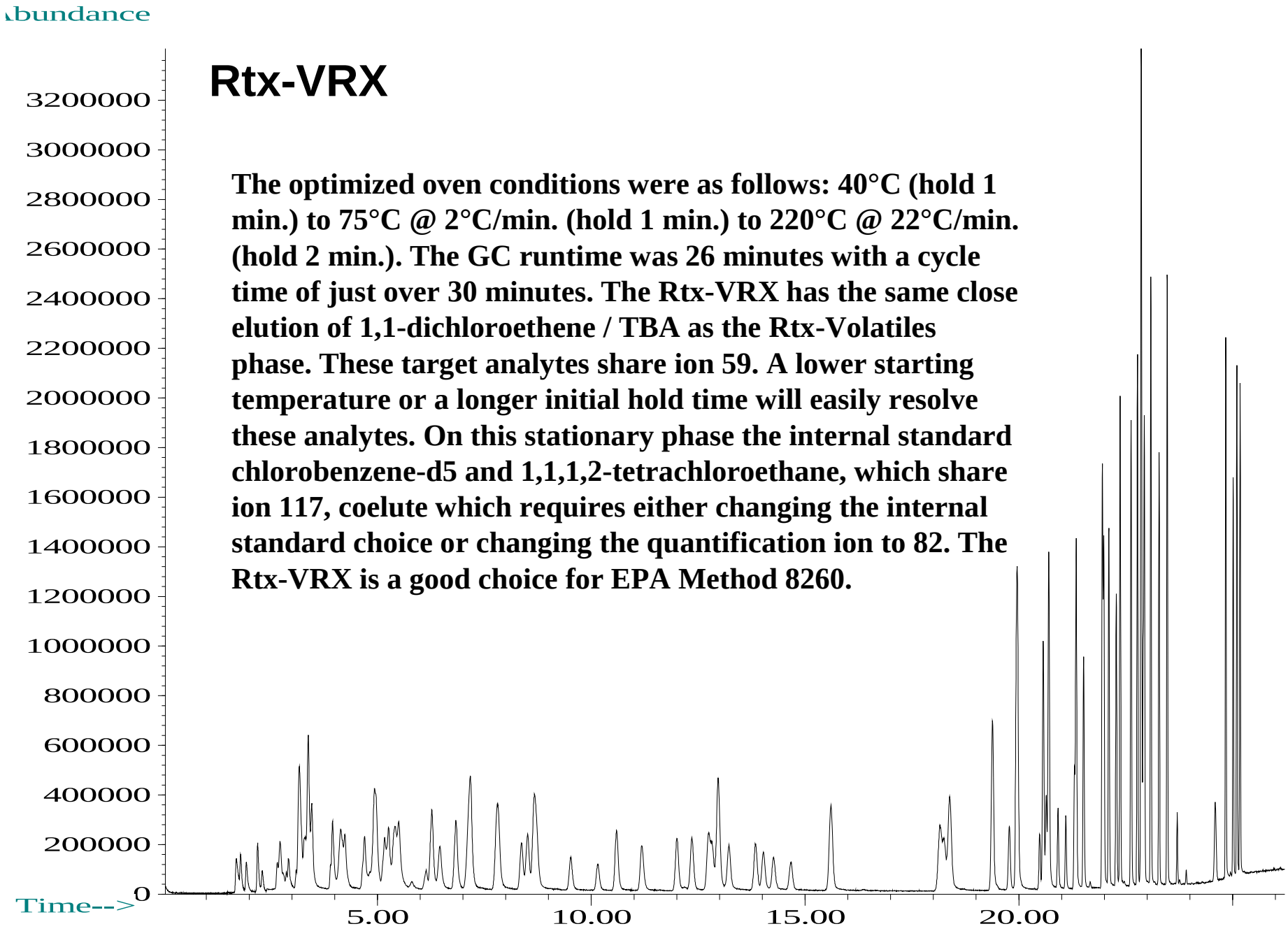
16.00
18.00
20.00


TIC: A3021724.D
Abundance
Rtx-VRX
The optimized oven conditions were as follows: 40°C (hold 1 min.) to 75°C @ 2°C/min. (hold 1 min.) to 220°C @ 22°C/min. (hold 2 min.). The GC runtime was 26 minutes with a cycle time of just over 30 minutes. The Rtx-VRX has the same close elution of 1,1-dichloroethene / TBA as the Rtx-Volatiles phase. These target analytes share ion 59. A lower starting temperature or a longer initial hold time will easily resolve these analytes. On this stationary phase the internal standard chlorobenzene-d5 and 1,1,1,2-tetrachloroethane, which share ion 117, coelute which requires either changing the internal standard choice or changing the quantification ion to 82. The Rtx-VRX is a good choice for EPA Method 8260.
3200000
3000000
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1800000
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600000
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200000
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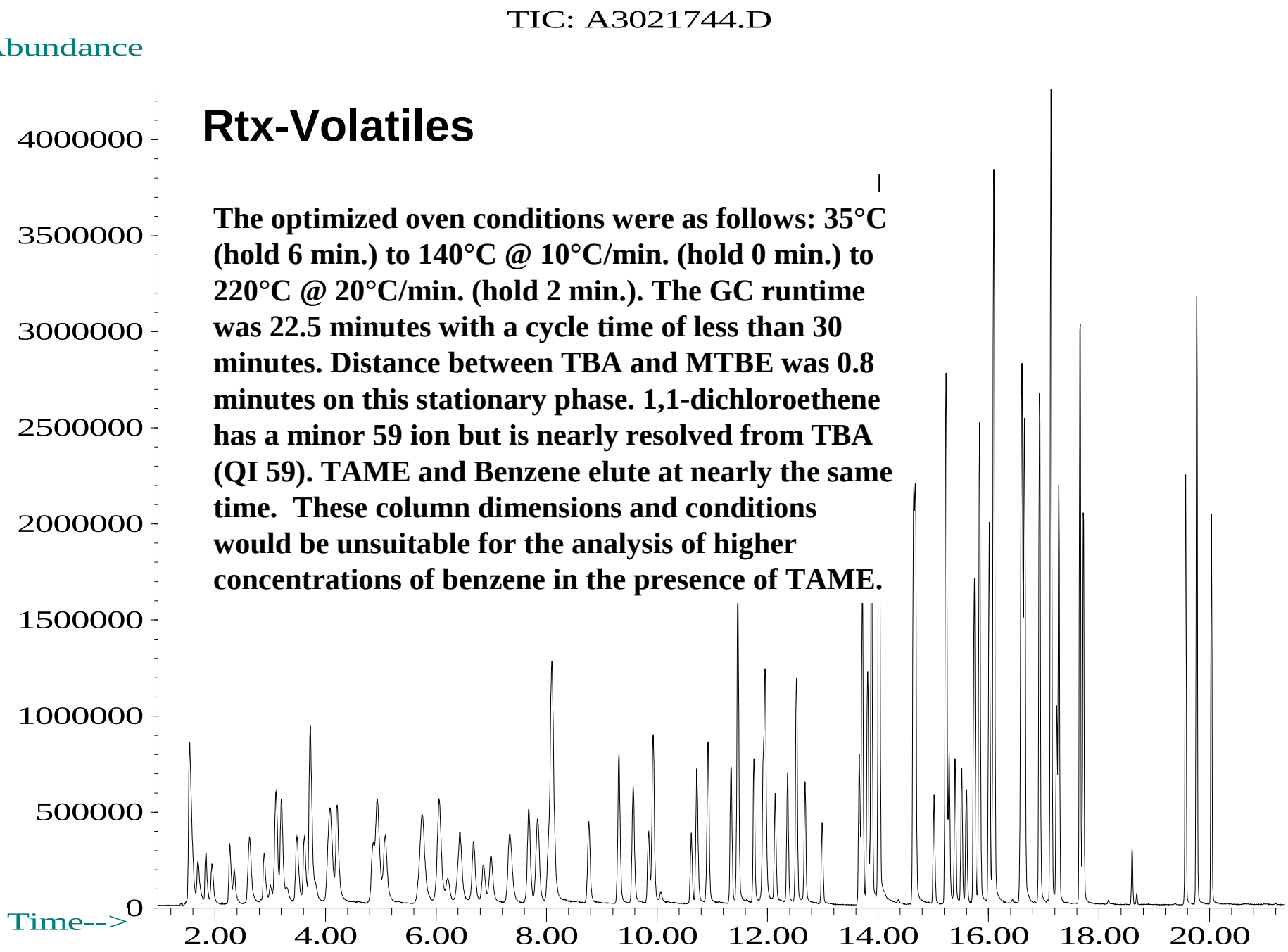
Time-->
5.00
10.00
15.00
20.00


TIC: A3021744.D
Abundance
Rtx-Volatiles
The optimized oven conditions were as follows: 35°C (hold 6 min.) to 140°C @ 10°C/min. (hold 0 min.) to 220°C @ 20°C/min. (hold 2 min.). The GC runtime was 22.5 minutes with a cycle time of less than 30 minutes. Distance between TBA and MTBE was 0.8 minutes on this stationary phase. 1,1-dichloroethene has a minor 59 ion but is nearly resolved from TBA (QI 59). TAME and Benzene elute at nearly the same time. These column dimensions and conditions would be unsuitable for the analysis of higher concentrations of benzene in the presence of TAME.
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
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Time-->
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6.00
8.00
10.00
12.00
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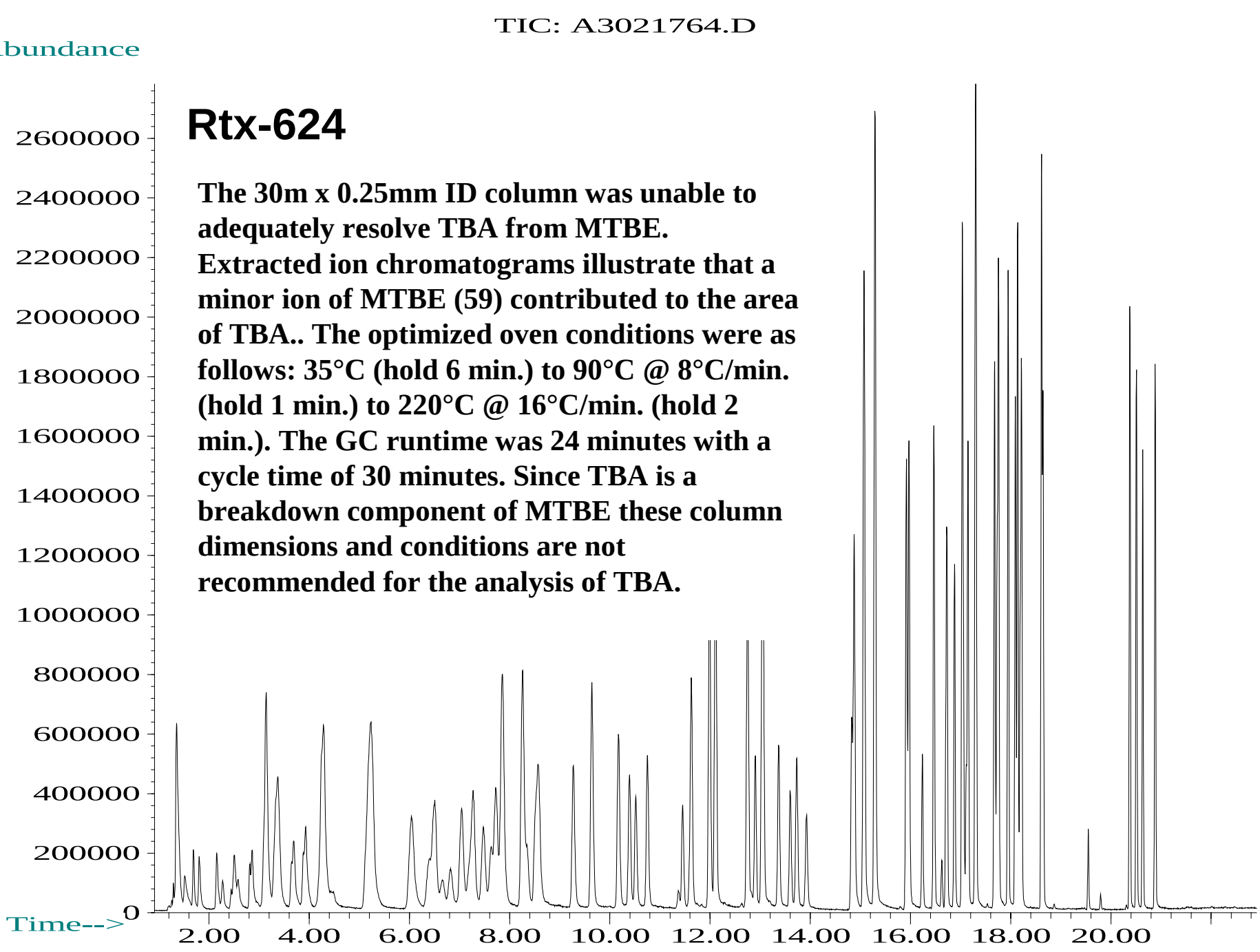
20.00


TIC: A3021764.D
Abundance
Rtx-624
The 30m x 0.25mm ID column was unable to adequately resolve TBA from MTBE. Extracted ion chromatograms illustrate that a minor ion of MTBE (59) contributed to the area of TBA.. The optimized oven conditions were as follows: 35°C (hold 6 min.) to 90°C @ 8°C/min. (hold 1 min.) to 220°C @ 16°C/min. (hold 2 min.). The GC runtime was 24 minutes with a cycle time of 30 minutes. Since TBA is a breakdown component of MTBE these column dimensions and conditions are not recommended for the analysis of TBA.
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
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Time-->
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4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00

Conclusions

The Rtx-VRX and Rtx-VMS had the best performance given the compound list and column dimensions. Incomplete resolution of TAME and benzene make the Rtx-Volatiles a poor choice for an extended list of volatiles. The Rtx-624 also suffers from a coelution of TBA/MTBE, but with a longer column this pair is able to be resolved. With an expanding target list and difficult sample matrixes, care must be taken to assure correct compound identification in the presence of interfering analytes.