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Application Note
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2017 EPA Method Update Rule and EPA Method 624.1

PETROCHEMICAL SERIES

Introduction

Method 624 is for the determination of volatile organic compounds in industrial discharges and other liquid environmental samples by gas chromatography combined with mass spectrometry (GC/MS). The method was developed and validated through inter-laboratory studies more than 29 years ago. The purge and trap parameters were restricted to purging the sample at ambient temperature at 40ml/minute for 11 minutes and desorbing for 4 minutes. The method also has a relatively limited analyte list. Method 624.1 is a performance-based method. New technology such as capillary columns, better purge and traps, optimized instrument parameters, and more sensitive GC/MS instruments will enable laboratories to achieve better precision and % Relative Standard Deviation (%RSD) for calibrations than the prescribed 35% in Method 624 and 624.1. Allowing such high RSD values on most compounds is often an indicator that the analytical system is out of control and associated data may be suspect. The analyte list for 624.1 has been expanded and includes many compounds that can also be run by 8260.

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Internal Standards and Surrogate Standards can now be varied by compound and concentration to match 8260. Also since laboratories are permitted to use more stringent acceptance criteria than the method prescribes, it may be possible to analyze samples for Method 624.1 and 8260 at the same time. Method 624.1 requires running a matrix spike and matrix spike duplicate on 5% of samples from every site or each discharge type sample, which can be a hardship on the lab. It also provides improvement in the procedure for Method Detection Limit (MDL) studies using 40 CFR Part 136 which many labs are already implementing for Method 8260.

The purpose of this paper is to use Method criteria from 624.1 and 8260 in a way that will most effectively and efficiently allow labs to run 624 and 8260 in the same batch.

Experimental

The instrumentation used for sample concentration was an OI Analytical 4760 Purge and Trap with a #10 trap which contains Tenax, silica gel and carbonized molecular sieve along with a 4100 Sample Processor. An Agilent 7890A/5975C GC/MS was used for chromatographic separation and detection. Please see Table 1 for instrument parameters.

50 ng of Bromofluorobenzene(BFB) was injected on all days that the instrument was run for this study. An eight-point calibration was analyzed, which included all compounds listed as Priority Pollutants in Method 624.1 Table 1, additional purgeables from Method 624.1 Table2, and many compounds from the Method 8260 scope of work. The list chosen was based on compounds which are representative of volatiles analysis by 8260, availability of standards, and appropriateness of the method. Purge and trap may be a difficult or inappropriate technique for several compounds listed in both methods. The calibration range for most compounds was 2ppb to 200ppb with higher concentrations run for the poor performers such as ketones, alcohols, nitriles, and 1,4-Dioxane. Internal Standards and Surrogates were chosen based upon what is readily available in commercial mixes for 8260. An initial demonstration of capability (IDOC) was run at 50ppb for most compounds with the aforementioned compounds at higher concentrations. A method detection limit study was performed over a three day period at varying concentrations.

Figure 1. 4100, 4760, and GC/MS

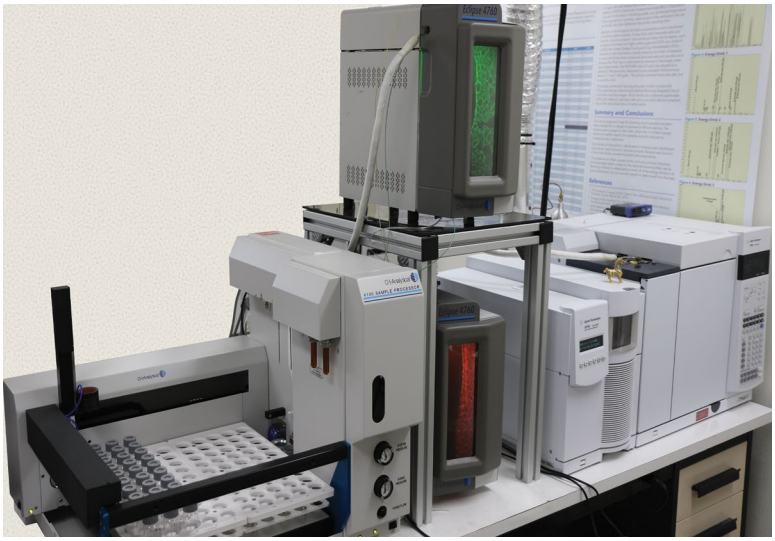


Table 1. Instrument Parameters

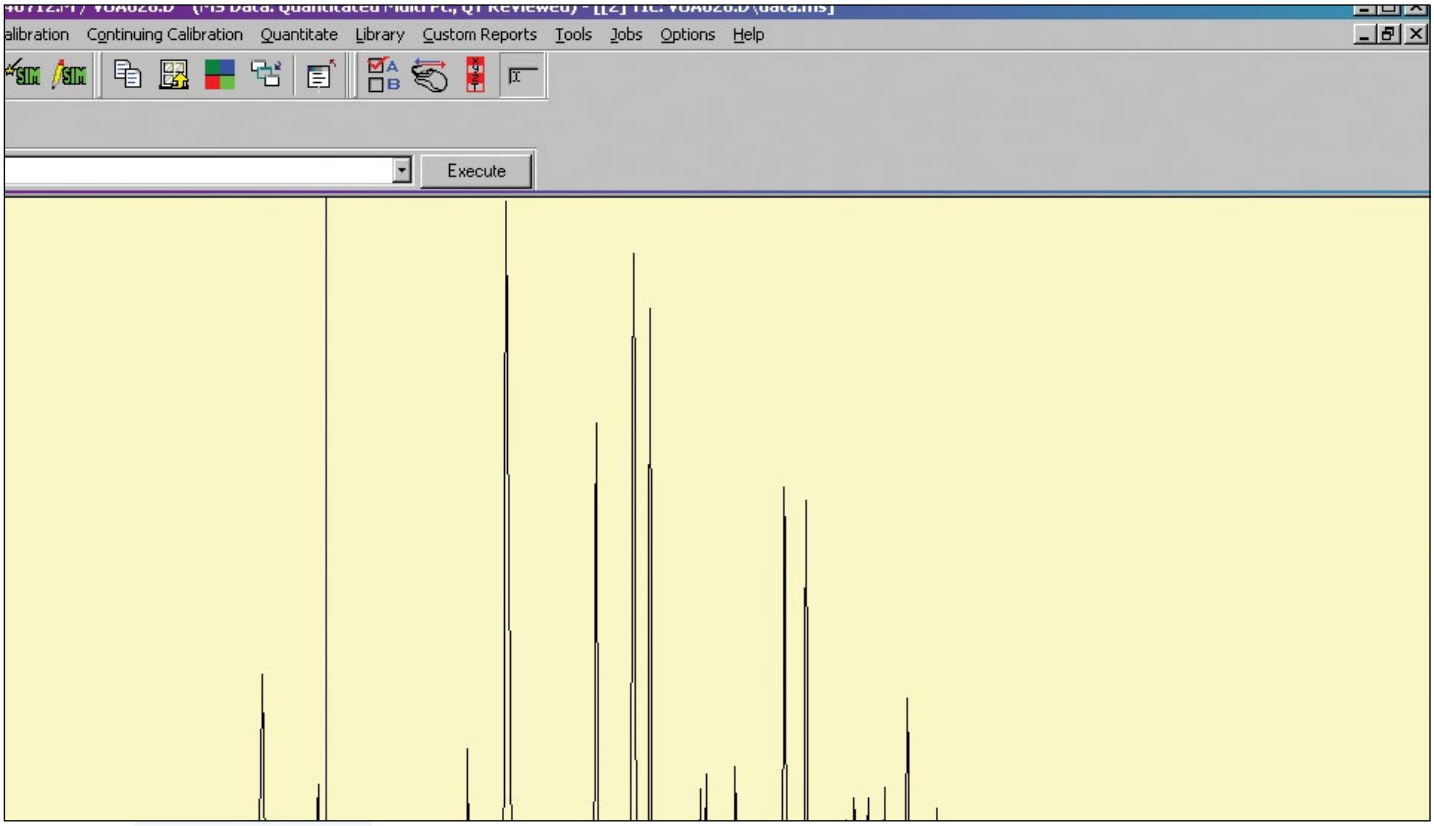
Purge-and-Trap	Eclipse 4760 P&T Sample Concentrator
Trap	#10 trap; Tenax® / Silica gel / CMS
Purge Gas	Zero grade Helium at 40 mL/min
Purge Time	11 min
Sparge Mount Temperature	45 °C
Sample Temperature (purge)	45 °C
Sample Temperature (bake)	55 °C
Desorb Time	0.5 min
Bake Time	3 min
OI #10 Trap Temperature	Ambient during purge 180 °C during desorb pre-heat 190 °C during desorb 210 °C during bake
Water Management	120 °C during purge Ambient during desorb 240 °C during bake
Transfer Line Temperature	140 °C
Six-port Valve Temperature	140 °C
Gas Chromatograph	**Agilent 7890A**
Column	Restek Rtx – VMS 30 meter, 0.25 mm ID, 1.4 µm
Carrier Gas	Zero grade helium
Inlet Temperature	240 °C
Inlet Liner	Agilent Ultra Inert, 1 mm straight taper
Column Flow Rate	0.8 mL/min
Split Ratio	125:1
Oven Program	Hold at 40 °C for 2 min 16 °C/minute to 180 °C 40 °C/minute to 220 °C Hold at 220 °C for 2.5 min Total GC Run is 14.25 min
Mass Spectrometer	**Agilent 5975C**
Mode	Scan 35-300 amu
Scans/Second	5.19
Solvent Delay	1.60 min
Transfer Line Temperature	250 °C
Source Temperature	300 °C
Quadrupole Temperature	200 °C
Draw Out Plate	6 mm

Results

BFB criteria listed in Table 4 of Method 624.1, Table 4 of 8260B, and Table 3 of 8260C were met each day the instrument was run. The calibration easily met the 624.1 RSD criteria of 35%. The calibration met the 15% RSD criteria for Method 8260B, and the System Performance Check Compound (SPCC) criteria and Calibration Check Compound (CCC) criteria. Method 8260C requires a 20% RSD, so if Method 8260B criteria are met, all three methods could be used to report data. Laboratories will need to check with reporting authorities for this allowance.

Each calibration point was re-quantitated using the average response factor and also linear regression weighted with the inverse of concentration (1/C). This provided readback for each calibration level, ensuring that all levels had a good calculated recovery. The results for this re-quantitation were evaluated using % Relative Standard Deviation (%RSD) as well as % Relative Standard Error (%RSE). The RSE indicates if any point has a high deviation from the curve. The %RSD and %RSE were very similar for quantitation using average response and linear. Since the %RSD criteria was met for both Method 624.1 and 8260B/C, the IDOCs and MDLs were processed using average response. The DOC recovery and RPD limits for compounds listed in Table 6 of Method 624.1 were met. Interim criteria of 60-140% recovery and 30% RPD were easily met for the remainder of the compounds. The MDL's met 40 CFR Part 136 rules for acceptance. The MDL spike level was greater than the calculated MDL, and the ratio of the spiked amount to calculated MDL was less than 10. Please see table 2 for results.

Figure 2. 50ppb Calibration Standard



Compound	Quant Ion	RL (ppb)	Avg RF	% RSD	% RSE (Avg RF Calc.)	%RSE (Linear 1/C Calc.)	MDL (ppb)	IDOC Precision (% RPD)	IDOC Accuracy (% REC)
Pentafluorobenzene (IS)	168	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Dichlorodifluoromethane	85	2	0.18	4.08	4.07	5.59	0.28	4.97	96.1
*Chloromethane(S)	50	2	0.54	7.01	7.01	11.0	0.17	1.29	101
*Vinyl chloride(C)	62	2	0.42	7.48	7.48	10.7	0.17	1.08	99.9
*Bromomethane	94	2	0.23	6.06	6.06	8.01	0.35	8.22	103
*Chloroethane	64	2	0.23	3.63	3.63	2.95	0.28	1.29	99.6
Trichlorofluoromethane	101	2	0.54	4.82	4.81	7.91	0.30	1.62	101
Ethyl ether	74	2	0.21	4.14	4.19	4.44	0.37	1.41	106
Ethanol	45	100	0.01	6.75	10.3	3.17	26.3	19.8	90.0
*1,1-Dichloroethene(C)	96	2	0.34	5.63	5.66	5.27	0.22	1.18	99.1
Carbon disulfide	76	2	0.94	5.35	5.34	5.90	0.36	1.32	102
1,1,2-Trichloro-1,2,2-trifluoroethane	101	2	0.36	3.56	3.55	4.96	0.22	1.86	101
Methyl iodide	142	2	0.64	3.30	3.32	4.00	0.13	0.84	101
*Acrolein	56	4	0.10	5.10	5.11	3.57	0.75	4.95	107
Allyl chloride	76	2	0.21	1.90	1.94	1.24	0.27	1.94	102
Isopropanol	45	20	0.07	9.21	9.20	10.1	7.15	19.8	99.0
*Methylene chloride	84	2	0.37	3.98	4.01	6.09	0.16	1.06	103
Acetone	58	10	0.08	5.34	5.33	7.90	2.10	8.85	105
*trans-1,2-Dicholroethene	96	2	0.48	9.05	9.12	2.38	0.43	1.26	97.3
Methyl tert-butyl ether	73	2	1.99	4.66	4.60	1.45	0.08	1.27	105
2-Methyl-2-propanol	59	10	0.11	5.59	5.59	5.54	3.98	13.8	106
Acetonitrile	41	20	0.07	4.27	4.26	3.02	1.27	13.9	106
Chloroprene	53	2	1.14	3.50	3.54	2.28	0.11	1.43	104
Diisopropyl ether	45	2	2.07	5.00	4.95	3.81	0.06	1.15	103
*1,1-Dichloroethane(S)	63	2	1.07	1.97	1.98	1.92	0.14	1.34	103
*Acrylonitrile	53	2	0.33	5.72	5.69	5.25	0.26	7.00	112
Vinyl acetate	43	2	1.96	5.73	5.66	1.93	0.24	1.68	106
Ethyl-tert-butyl ether	59	2	1.72	2.76	2.77	2.70	0.12	1.04	103
cis-1,2-Dichloroethene	96	2	0.51	2.19	2.21	2.56	0.20	1.23	102
2,2-Dichloropropane	77	2	0.40	9.19	9.17	12.9	0.34	1.49	102
Bromochloromethane	128	2	0.28	3.53	3.46	3.56	0.15	0.94	104
*Chloroform(C)	83	2	0.84	1.86	1.89	2.65	0.16	1.29	104
Methyl acrylate	55	2	1.02	5.90	5.90	5.13	0.13	2.05	107
*Carbon tetrachloride	117	2	0.71	3.64	3.66	5.45	0.14	2.43	102
Tetrahydrofuran	42	2	0.35	4.15	4.38	2.86	0.35	3.67	108
Dibromofluoromethane (SS)	113	N/A	0.46	1.08	1.09	1.17	N/A	1.58	101
*1,1,1-Trichloroethane	97	2	0.69	3.41	3.41	5.59	0.13	0.48	102
2-Butanone	72	10	0.08	6.01	6.01	5.52	1.99	3.98	106
1,1-Dichloropropene	75	2	0.62	1.98	1.97	2.36	0.20	1.36	104
1,4-Difluorobenzene (IS)	114	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
*Benzene	78	2	1.24	2.09	2.10	3.46	0.08	1.33	103
Propionitrile	54	2	0.22	6.89	6.88	3.59	1.28	9.00	99.5
Methacrylonitrile	41	2	0.58	6.08	6.14	3.60	0.41	1.85	106
tert-Amyl methyl ether	73	2	0.69	4.29	4.23	5.26	0.22	1.65	101
1,2-Dichloroethane-d4 (SS)	102	N/A	0.05	1.67	1.67	1.81	N/A	2.11	103
Isobutanol	43	20	0.04	4.39	5.06	4.36	3.10	7.25	99.8
*1,2-Dichloroethane	62	2	0.61	2.46	2.47	4.28	0.14	1.43	104
*Trichloroethene	130	2	0.40	3.05	3.09	4.30	0.16	1.00	102
tert-Amyl ethyl ether	59	2	0.96	2.91	2.89	1.37	0.09	0.67	101
Dibromomethane	93	2	0.27	2.77	2.78	4.88	0.12	2.13	105
*1,2-Dichloropropane(C)	63	2	0.49	2.47	2.46	3.40	0.19	0.66	102
*Bromodichloromethane	83	2	0.48	3.23	3.22	5.41	0.07	0.99	104
Methyl methacrylate	69	2	0.30	4.97	4.97	4.37	0.12	5.17	108
1,4-Dioxane	88	50	0.003	9.28	4.42	4.03	10.7	21.1	96.0
*2-Chloroethyl-vinyl-ether	63	2	0.35	5.83	5.85	3.23	0.18	0.91	105
*cis-1,3-Dichloropropene	75	2	0.54	1.83	1.80	2.60	0.10	0.90	104
Chlorobenzene-d5 (IS)	117	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Compound	Quant Ion	RL (ppb)	Avg RF	% RSD	% RSE (Avg RF Calc.)	%RSE (Linear 1/C Calc.)	MDL (ppb)	IDOC Precision (% RPD)	IDOC Accuracy (% REC)
Toluene-d8(SS)	98	N/A	1.27	0.77	0.76	0.83	N/A	0.66	99.9
*Toluene(C)	92	2	0.96	1.87	1.89	2.04	0.12	1.02	102
2-Nitropropane	43	2	0.29	1.97	1.97	2.16	0.28	2.65	102
4-Methyl-2-pentanone	100	10	0.06	5.93	5.92	2.08	0.87	1.37	104
*Tetrachloroethene	164	2	0.38	2.58	2.59	4.60	0.13	0.89	102
*trans-1,3-Dichloropropene	75	2	0.60	3.00	3.01	2.78	0.10	1.17	104
Ethyl methacrylate	69	2	0.49	7.38	7.33	5.15	0.16	1.47	106
*1,1,2-Trichloroethane	83	2	0.36	2.19	2.16	2.83	0.19	0.96	102
*Chlorodibromomethane	129	2	0.56	1.91	1.91	2.73	0.07	1.45	103
1,3-Dichloropropane	76	2	0.56	2.05	2.08	2.38	0.08	0.87	103
1,2-Dibromoethane	107	2	0.48	3.00	3.00	4.26	0.09	1.28	102
2-Hexanone	43	10	0.72	8.40	8.40	5.88	0.30	1.63	107
*Chlorobenzene(S)	112	2	1.18	2.31	2.31	4.04	0.08	0.94	103
*Ethylbenzene(C)	91	2	1.82	1.77	1.77	2.55	0.12	0.80	103
1,1,1,2-Tetrachloroethane	131	2	0.39	2.43	2.44	4.09	0.17	1.32	102
m,p-Xylenes	106	4	0.69	2.98	2.98	2.03	0.13	0.58	105
o-Xylene	106	2	0.63	1.90	1.89	2.04	0.11	0.31	103
Styrene	104	2	1.10	4.01	3.98	1.63	0.17	0.85	105
*Bromoform(S)	173	2	0.43	2.14	2.13	3.14	0.19	1.19	103
Isopropylbenzene	105	2	1.62	2.80	2.78	3.00	0.08	0.89	104
cis-1,4-Dichloro-2-butene	75	2	0.21	4.99	4.98	4.67	0.20	1.75	104
1,4-Dichlorobenzene-d4 (IS)	152	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
4-Bromofluorobenzene (SS)	95	N/A	0.94	1.35	1.36	1.46	N/A	1.05	99.7
n-Propylbenzene	91	2	4.43	3.79	3.84	3.19	0.06	1.45	104
Bromobenzene	156	2	1.14	3.21	3.23	3.92	0.12	1.34	102
*1,1,2,2-Tetrachloroethane(S)	83	2	1.28	3.34	3.33	4.61	0.16	1.39	101
2-Chlorotoluene	91	2	2.85	2.41	2.41	3.10	0.06	0.91	103
1,3,5-Trimethylbenzene	105	2	2.96	3.75	3.73	2.88	0.09	0.86	103
1,2,3-Trichloropropane	75	2	1.51	2.65	2.80	2.68	0.27	1.72	103
trans-1,4-Dichloro-2-butene	53	2	0.68	2.62	2.62	2.87	0.21	1.07	103
4-Chlorotoluene	91	2	2.65	2.69	2.67	2.87	0.12	1.08	103
tert-Butylbenzene	119	2	2.42	3.00	2.95	3.03	0.10	0.97	101
1,2,4-Trimethylbenzene	105	2	2.98	3.88	3.88	2.83	0.08	1.37	104
sec-Butylbenzene	105	2	3.71	2.94	3.00	3.40	0.09	1.48	102
p-Isopropytoluene	119	2	3.04	3.92	3.87	2.25	0.10	1.27	103
*1,3-Dichlorobenzene	146	2	1.92	2.89	2.90	4.54	0.14	1.08	100
*1,4-Dichlorobenzene	146	2	1.92	2.21	2.20	3.58	0.12	0.77	101
n-Butylbenzene	91	2	2.91	3.10	3.14	2.20	0.06	1.12	102
*1,2-Dichlorobenzene	146	2	1.77	2.00	2.00	3.42	0.11	1.29	99.6
1,2-Dibromo-3-chloropropane	75	2	0.26	4.72	4.75	4.84	0.56	4.26	97.7
Hexachlorobutadiene	225	2	0.55	3.61	3.60	3.51	0.17	1.50	97.6
1,2,4-Trichlorobenzene	180	2	1.04	3.56	3.57	3.82	0.13	1.23	98.7
Naphthalene	128	2	3.26	5.18	5.14	4.24	0.16	2.40	99.7
1,2,3-Trichlorobenzene	180	2	1.00	4.07	4.08	5.49	0.14	1.75	99.0

*Priority Pollutant (40 CFR 423, Appendix A)

IS - Internal Standard

SS – Surrogate Standard

S – 8260B System Performance Check Compound (SPCC)

C – 8260B Calibration Check Compound (CCC)

Conclusions

Method performance is significantly improved with the allowance of better purge and trap parameters, such as the 0.5 minute desorb and heating sample during purge, as well as significant instrument improvements which have been made over the past 29 years. For these reasons method performance is better than Method 624.1 requires which may allow the laboratory to combine QC criteria with Method 8260 thus increasing sample capacity and productivity in the lab.

References

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