Improved gas chromatography procedure for speciated hydrocarbon measurements of vehicle emissions

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ABSTRACT

A dual-column gas chromatography (GC) procedure was developed for speciated analysis of hydrocarbons in automobile exhaust emissions. Light hydrocarbons (C_1–C_3) are analyzed using a 30 m × 0.53 mm GS-Q column; heavier hydrocarbons (C_3–C_{12}) are analyzed using a 60 m × 0.32 mm DB-1 column. The two columns are operated simultaneously within a single GC oven. Variable temperature adsorption traps (VTATs) are used to concentrate samples prior to GC analysis. The detection limits for individual hydrocarbon species are approximately 5–10 ppb (v/v) C. The GC procedure was used to analyze exhaust emissions from both gasoline- and methanol-fueled vehicles. Sample instability was shown to be a problem for diene species in exhaust mixtures —including 1,3-butadiene.

INTRODUCTION

In recent years, increasingly sophisticated analytical techniques have been employed to measure hydrocarbon emissions from motor vehicles. In part, this has been driven by regulations which consider the propensity of hydrocarbons to contribute to the formation of tropospheric ozone [1,2]. Since hydrocarbon compounds vary in their ozone-formation reactivity, highly detailed, speciated analyses are necessary to assess the overall impact of an emissions mixture.

We recently reported the use of a relatively simple, single-column GC procedure for speciating hydrocarbon compounds from C_1 to C_{12} [3]. Similar procedures have been reported by others [4–6]. While advantageous in terms of simplicity and speed, such single-column techniques lack the degree of resolution which is necessary to adequately characterize all hydrocarbon species of interest.

This report describes the development and application of a dual-column GC procedure for hydrocarbon speciation. Multiple-column procedures have also been used by others [7–14], but none incorporates all three advantages offered by our approach: (1) use of "built-in" sample concentration devices, (2) simultaneous analysis on two columns contained within a single GC instrument, and (3) automation of the sampling and analysis procedures.

EXPERIMENTAL

GC equipment

All chromatographic analyses were performed using a Varian Model 3600 GC (Varian, Sunnyvale, CA, USA). The instrument was equipped with an automatic gas sampling valve, two heated sample loops, two variable temperature adsorption traps (VTATs), two analytical columns, and two flame ionization detection (FID) systems. A simple schematic drawing showing all these components is given in Fig. 1. Control of instrument parameters was accomplished by an on-board microprocessor. Data collection and
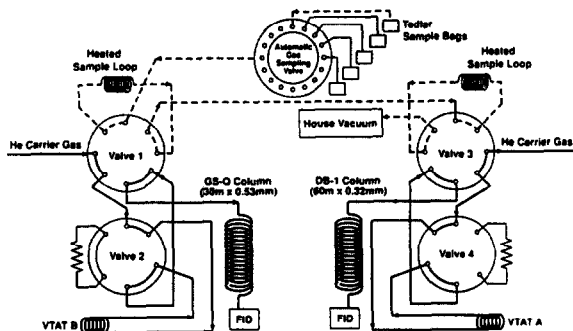
Fig. 1. Plumbing diagram of Varian Model 3600 GC used for speciated hydrocarbon measurements. Configuration shown is for start of run (filling sample loops).

manipulation were done with a Varian Model DS651 data station.

One analytical column was a 60 m × 0.32 mm DB-1 fused-silica capillary column, having a film thickness of 1.0 μm (J & W Scientific, Folsom, CA, USA). This column was used to measure most of the hydrocarbon species in emissions samples (C_3–C_{12}). The other column was a 30 m × 0.53 mm GS-Q Megabore column (J & W Scientific). This was used to measure only a few light hydrocarbons (C_1–C_3).

Vehicle exhaust samples

Vehicle exhaust samples were obtained during standard emissions testing —generally using the 1975 Federal Test Procedure (FTP) [15]. Diluted vehicle exhaust was collected during each of three phases: cold start, stabilized, and hot start (bag 1, bag 2, and bag 3, respectively). A sampling system was used whereby 3-l Tedlar bags for speciated GC analysis were filled simultaneously with the 100-l bags which are generally used for criteria pollutant measurements. This represents an improvement over our previous sampling techniques in which the GC Tedlar bags were filled by transferring samples from the larger bags [3].

Background air samples were routinely obtained during each phase of the FTP emissions test, but only the bag 2 background sample was analyzed by GC. The background composition determined from this sample was assumed to apply for all three FTP bag samples. The pre-

dominant hydrocarbon constituent in background air is methane, which is generally observed at concentrations of 2–3 ppm (v/v). In our testing facility, trace levels (0.01–0.10 ppm C) of major gasoline constituents are also seen. These include *n*-butane, 2-methylbutane, methylpentanes, toluene and xylenes.

House vacuum was used to draw diluted exhaust from the Tedlar bags through two 5.0-ml sample loops that were heated at 125°C (see sampling conditions listed in Table I). Larger sample loops could be used to further improve sensitivity, but 5.0 ml is the largest size that could conveniently fit in the temperature-controlled zones of the GC instrument.

VTAT operation

VTATs were used to concentrate diluted emissions samples prior to injection onto the GC columns. They consisted of 3 ft. × 1/16 in. (1 ft. = 30.48 cm; 1 in. = 2.54 cm) stainless-steel tubing in which the middle 2-ft. section was packed with a polymeric adsorbent material, Hayesep D (60–80 mesh). This adsorbent is preferred over Chromosorb 106 which was used previously [3], since it could be subjected to a higher desorption temperature without releasing objectionable amounts of contaminants.

Operating conditions for the VTATs are summarized in Table II. Although the two VTATs were loaded simultaneously, they were desorbed and injected onto the two analytical columns at different times —injection onto the DB-1 column occurred at 7.0 min; injection onto the GS-Q column occurred at 32.0 min. This was done to coordinate injection timing with optimum temperature conditions for each column.

Chromatographic conditions

The chromatographic conditions used for speciation of emissions samples are summarized in Table I. The initial column temperature of −40°C provided optimal separation of propane and propene on the DB-1 column. The multiple-gradient column temperature conditions were empirically selected as a compromise between maximum peak resolution and minimum analysis time. The entire analysis time —including sampling, VTAT operation, chromatographic sepa-

TABLE I

CONDITIONS FOR SPECIATED ANALYSIS OF HYDROCARBON EMISSIONS

Sampling conditions
Sample draw:	house vacuum
Sampling rate:	40–50 ml/min
Sampling time:	4–6 min
Sample loops:	5.0 ml; heated at 125°C
Sampling valve:	Valco Model A16 automatic gas sampling valve

GC conditions	Side A	Side B
Column type	DB-1	GS-Q
Column dimensions	60 m × 0.32 mm	30 m × 0.53 mm
Film thickness	1.0 μm	–
Carrier gas type	Helium	Helium
Carrier gas flow-rate[a]	4 ml/min	8 ml/min
Makeup gas type	Nitrogen	Nitrogen
Makeup gas flow-rate	26 ml/min	22 ml/min
Detector type	FID	FID
Detector temperature	275°C	275°C
Switching valve temperature	125°C	125°C

Column oven temperature program
Initial temperature of −40°C (hold 12 min)
Increase 3°C/min to 125°C (no hold)
Increase 6°C/min to 185°C (no hold)
Increase 20°C/min to 220°C (hold 2 min)

[a] Flow controllers were used to maintain a constant flow-rate throughout chromatographic runs.

TABLE II

OPERATION OF VARIABLE TEMPERATURE ADSORPTION TRAPS (VTATs)

Time (min)	Function	VTAT A (DB-1 column)		VTAT B (GS-Q column)	
		Temp. (°C)	Direction of flow through VTAT	Temp. (°C)	Direction of flow through VTAT
0.0–0.2	Equilibrate pressure in sample loops	−60	Normal	−99	Normal
0.2–4.0	Load VTATs	−60	Normal	−99	Normal
4.0–5.0	Desorb VTAT A	−60 → 180	No flow	−99	No flow
5.0–7.0	Equilibrate VTAT A	180	No flow	−99	No flow
7.0–28.0	Inject VTAT A	180	Reverse	−99	No flow
28.0–30.0	Desorb VTAT B	180	Reverse	−99 → 180	No flow
30.0–32.0	Equilibrate VTAT B	180	Reverse	180	No flow
32.0–81.0	Inject VTAT B	180	Reverse	180	Reverse

ration, and cool down period —was about 90 min.

Compound identification

Hydrocarbon identifications were assigned by comparing retention times of chromatographic peaks from emissions samples with those from known standard mixtures. A peak library, consisting of 164 compounds, is shown in Table III. The peak numbers given in this table are based upon an in-house nomenclature system which was developed to characterize gasolines. Gaso-

TABLE III

GC PEAK LIBRARY FOR SPECIATED HYDROCARBON ANALYSES

GC conditions are given in Table I.

Peak ID	Compound name	CAS No.	Retention time (min)[a]	Retention index[b]
1	Methane	00074-82-8	32.91	100.0
300	Ethylene	00074-85-1	34.16	163.5
550	Ethyne	00074-86-2	34.80	195.0
2	Ethane	00074-84-0	34.90	200.0
301	Propylene	00115-07-1	11.68	290.0
3	Propane	00074-98-6	11.89	300.0
500	Propadiene	00463-49-0	13.36	326.0
551	Propyne	00074-99-7	13.50	328.3
5	2-Methylpropane	00075-28-5	15.73	362.3
305	2-Methylpropene	00115-11-7	17.85	390.6
302	1-Butene	00106-98-9	17.93	391.6
502	1,3-Butadiene	00106-99-0	18.22	395.1
4	n-Butane	00106-97-8	18.62	400.0
1000	Methanol	00067-56-1	18.80	402.5
304	trans-2-Butene	00624-64-6	19.63	413.6
552	1-Butyne	00107-00-6	20.43	423.9
303	cis-2-Butene	00590-18-1	20.88	429.5
310	3-Methyl-1-butene	00563-45-1	23.65	461.5
1003	Ethanol	00064-17-5	25.05	476.4
7	2-Methylbutane	00078-78-4	25.14	477.3
554	2-Butyne	00503-17-3	26.37	489.5
306	1-Pentene	00109-67-1	26.52	491.0
309	2-Methyl-1-butene	00563-46-2	27.15	497.1
6	n-Pentane	00109-66-0	27.46	500.0
509	2-Methyl-1,3-butadiene	00078-79-5	27.78	504.5
308	trans-2-Pentene	00646-04-8	28.22	510.5
327	3,3-Dimethyl-1-butene	00558-37-2	28.55	514.9
307	cis-2-Pentene	00627-20-3	28.82	518.6
311	2-Methyl-2-butene	00513-35-9	29.19	523.4
505	trans-1,3-Pentadiene	02004-70-8	29.35	525.6
530	Cyclopentadiene	00542-92-7	29.95	533.3
12	2,2-Dimethylbutane	00075-83-2	30.25	537.2
450	Cyclopentene	00142-29-0	31.50	552.6
319	4-Methyl-1-pentene	00691-37-2	32.10	559.9
800	Cyclopentane	00287-92-3	32.33	562.6
13	2,3-Dimethylbutane	00079-29-8	32.69	566.9
1412	2-Methoxy-2-methylpropane (MTBE)	01634-04-4	32.80	568.2
326	2,3-Dimethyl-1-butene	00563-78-0	32.88	569.1
10	2-Methylpentane	00107-83-5	33.17	572.4
324	4-Methyl-trans-2-pentene	00674-76-0	33.36	574.6

TABLE III *(continued)*

Peak ID	Compound name	CAS No.	Retention time (min)[a]	Retention index[b]
11	3-Methylpentane	00096-14-0	34.22	584.4
317	2-Methyl-1-pentene	00763-29-1	34.69	589.6
312	1-Hexene	00592-41-6	34.77	590.5
9	*n*-Hexane	00110-54-3	35.64	600.0
315	*cis*-3-Hexene/*trans*-3-Hexene	07642-09-3	35.88	603.6
314	*trans*-2-Hexene	04050-45-7	36.05	606.1
320	2-Methyl-2-pentene	00625-27-4	36.22	608.7
321	3-Methyl-*cis*-2-pentene	00922-62-3	36.37	610.8
313	*cis*-2-Hexene	07688-21-3	36.70	615.6
322	3-Methyl-*trans*-2-pentene	00616-12-6	37.17	622.4
1450	2-Ethoxy-2-methylpropane (ETBE)	00637-92-3	37.27	623.9
801	Methylcyclopentane	00096-37-7	37.38	625.4
18	2,2-Dimethylpentane	00590-35-2	37.55	627.7
20	2,4-Dimethylpentane	00108-08-7	37.91	632.8
600	Benzene	00071-43-2	39.09	649.3
451	1-Methylcyclopentene	00693-89-0	39.09	649.3
2006	2,3-Dimethyl-2-pentene	10574-37-5	39.38	653.2
2004	2,4-Dimethyl-1-pentene	02213-32-3	39.59	656.0
825	Cyclohexane	00110-82-7	39.73	657.9
2033	2-Methyl-*trans*-3-hexene	00692-24-0	40.21	664.3
2031	5-Methyl-*trans*-2-hexene	07385-82-2	40.55	668.7
15	2-Methylhexane	00591-76-4	40.69	670.6
19	2,3-Dimethylpentane	00565-59-3	40.71	671.0
460	Cyclohexene	00110-83-8	40.90	673.4
1413	2-Methoxy-2-methylbutane (TAME)	00994-05-8	40.92	673.6
16	3-Methylhexane	00589-34-4	41.27	678.1
806	*cis*-1,3-Dimethylcyclopentane	02532-58-3	41.59	682.2
807	*trans*-1,3-Dimethylcyclopentane	01759-58-6	41.78	684.6
805	*trans*-1,2-Dimethylcyclopentane	00822-50-4	41.97	687.1
37	2,2,4-Trimethylpentane	00540-84-1	42.13	689.2
2038	1-Heptene	00592-76-7	42.61	695.2
2042	*trans*-3-Heptene	14686-14-7	42.90	698.7
14	*n*-Heptane	00142-82-5	43.00	700.0
2034	3-Methyl-*cis*-3-hexene	04914-89-0	43.34	705.4
2040	*trans*-2-Heptene	14686-13-6	43.57	709.1
2008	2,3-Dimethyl-2-pentene	10574-37-5	43.88	714.0
826	Methylcyclohexane	00108-87-2	44.18	718.8
811	1,1,3-Trimethylcyclopentane	04516-69-2	44.45	723.0
802	Ethylcyclopentane	01640-89-7	45.02	731.9
31	2,5-Dimethylhexane	00592-13-2	45.20	734.6
30	2,4-Dimethylhexane	00589-43-5	45.31	736.4
817	1,2,4-Trimethylcyclopentane	02815-58-9	45.63	741.3
814	1,2,3-Trimethylcyclopentane	15890-40-1	46.12	748.7
39	2,3,4-Trimethylpentane	00565-75-3	46.32	751.6
38	2,3,3-Trimethylpentane	00560-21-4	46.52	754.6
601	Toluene	00108-88-3	46.52	754.6
815	1,2,4-Trimethylcyclopentane	02815-58-9	46.88	759.9
1414	2-Methoxy-2-methylpentane (THEME)	38772-53-1	47.06	762.7
29	2,3-Dimethylhexane	00584-94-1	47.13	763.7
24	2-Methylheptane	00592-27-8	47.47	768.8
26	4-Methylheptane	00589-53-7	47.57	770.2
25	3-Methylheptane	00589-81-1	47.96	775.9

TABLE III *(continued)*

Peak ID	Compound name	CAS No.	Retention time (min)[a]	Retention index[b]
831	*cis*-1,3-Dimethylcyclohexane	00638-04-0	48.14	778.4
828	1,1-Dimethylcyclohexane	00590-66-9	48.49	783.4
42	2,2,5-Trimethylhexane	03522-94-9	48.66	786.0
861	1-Ethyl-1-methylcyclopentane	16747-50-5	48.90	789.4
2193	1-Octene	00590-66-9	48.95	790.0
830	*trans*-1,2-Dimethylcyclohexane	06876-23-9	49.26	794.5
832	*trans*-1,3-Dimethylcyclohexane	02207-03-6	49.48	797.5
23	*n*-Octane	00111-65-9	49.66	800.0
2198	*cis*-4-Octene	07642-15-1	50.02	806.3
2194	*cis*-2-Octene	07642-04-8	50.39	812.6
43	2,3,5-Trimethylhexane	01069-53-0	50.69	817.8
829	*cis*-1,2-Dimethylcyclohexane	02207-01-4	50.82	820.0
52	2,4-Dimethylheptane	02213-23-2	51.17	825.8
827	Ethylcyclohexane	01678-91-7	51.53	831.9
53	2,3-Dimethylheptane	01072-05-5	51.74	835.4
55	3,5-Dimethylheptane	00926-82-9	51.96	839.0
602	Ethylbenzene	00100-41-4	52.60	849.6
956	1,3,5-Trimethylcyclohexane	01839-63-0	52.80	852.8
604	*m*-Xylene	00108-38-3	53.13	858.2
605	*p*-Xylene	00106-42-3	53.19	859.3
62	4-Methyloctane	02216-34-4	53.72	867.7
60	2-Methyloctane	03221-61-2	53.73	867.9
61	3-Methyloctane	02216-33-3	54.13	874.3
712	Styrene	00100-42-5	54.20	875.4
603	*o*-Xylene	00095-47-6	54.49	880.0
405	1-Nonene	00124-11-8	54.62	882.1
4651	2,2,4-Trimethylheptane	14720-74-2	55.03	888.6
41	*n*-Nonane	00111-84-2	55.77	900.0
607	Isopropylbenzene	00098-82-8	56.45	912.5
151	2,2-Dimethyloctane	15869-87-1	56.80	919.0
835	*n*-Propylcyclohexane	01678-92-8	57.31	928.2
161	4,4-Dimethyloctane	15869-95-1	57.42	930.2
155	2,6-Dimethyloctane	02051-30-1	57.82	937.4
644	*n*-Propylbenzene	00103-65-1	58.16	943.4
609	1-Ethyl-3-methylbenzene	00620-14-4	58.58	951.0
610	1-Ethyl-4-methylbenzene	00622-96-8	58.70	953.1
613	1,3,5-Trimethylbenzene	00108-67-8	59.02	958.7
86	4-Methylnonane	17301-94-9	59.47	966.6
608	1-Ethyl-2-methylbenzene	00611-14-3	59.57	968.4
84	2-Methylnonane	00871-83-0	59.87	973.5
85	3-Methylnonane	05911-04-6	60.16	978.6
612	1,2,4-Trimethylbenzene	00095-63-6	60.42	982.9
960	1-Methyl-2-propylcyclohexane	04291-79-6	60.78	989.2
615	Isobutylbenzene	00538-93-2	60.93	991.6
616	*sec*-Butylbenzene	00135-98-8	61.15	995.4
100	*n*-Decane	00124-18-5	61.42	1000.0
611	1,2,3-Trimethylbenzene	00576-73-8	61.93	1010.0
650	Indan	00496-11-7	62.55	1022.2
658	Indene	00095-13-6	62.95	1029.9
646	1,3-Diethylbenzene	00141-93-5	63.42	1038.9
647	1-Methyl-3-propylbenzene	01074-43-7	63.57	1041.8
648	1-Methyl-4-propylbenzene	01074-55-1	63.79	1045.8
651	1,2-Diethylbenzene	00135-01-3	63.92	1048.4

TABLE III *(continued)*

Peak ID	Compound name	CAS No.	Retention time (min)[a]	Retention index[b]
653	1-Methyl-2-propylbenzene	01074-17-5	64.39	1057.4
654	1,4-Dimethyl-2-ethylbenzene	01758-88-9	64.92	1067.2
655	1,3-Dimethyl-4-ethylbenzene	00874-41-9	65.03	1069.2
163	2-Methyldecane	06975-98-0	65.23	1073.0
656	1,2-Dimethyl-4-ethylbenzene	00934-80-5	65.34	1075.0
657	1,3-Dimethyl-2-ethylbenzene	02870-04-4	65.71	1082.0
659	1,2-Dimethyl-3-ethylbenzene	00933-98-2	66.38	1094.3
101	*n*-Undecane	01120-21-4	66.69	1100.0
635	1,2,4,5-Tetramethylbenzene	00095-93-2	67.01	1107.5
634	1,2,3,5-Tetramethylbenzene	00527-53-7	67.19	1111.7
7800	Methylindan A	27133-93-3	68.03	1131.4
7801	Methylindan B	27133-93-3	68.50	1142.4
633	1,2,3,4-Tetramethylbenzene	00488-23-3	68.70	1146.8
755	1-Methyl-3-butylbenzene	01595-04-6	68.11	1133.2
714	Naphthalene	00091-20-3	69.81	1172.1
102	*n*-Dodecane	00112-40-3	71.05	1200.0
796	2-Methylnaphthalene	00091-57-6	73.89	1285.4
795	1-Methylnaphthalene	00090-12-0	74.39	1299.5
103	*n*-Tridecane	00629-50-5	74.40	1300.0

[a] The first four compounds listed were measured from GS-Q column; all other compounds were measured from DB-1 column.
[b] Retention index (I) is defined as follows:

$$I = 100 \cdot \frac{\log X_i - \log X_{nz}}{\log X_{nz+1} - \log X_{nz}} \cdot 100z$$

where:

z = Number of carbon atoms in *n*-alkane which immediately precedes peak *i*.
X_i = Retention time of peak *i*.
X_{nz} = Retention time of *n*-alkane (having z carbon atoms) which precedes peak *i*.
X_{nz+1} = Retention time of *n*-alkane (having $z + 1$ carbon atoms) which follows peak *i*.

line analysis —using conventional GC as well as GC–MS— was also used to confirm the identities of compounds detected in emissions samples. A DB-1 chromatogram of a reference gasoline sample is shown in Fig. 2.

Another material used for compound identification was a gas standard from the Auto/Oil Air Quality Improvement Research Program [6]. This standard (CLM 3218) contained 21 hydrocarbon species, most at concentrations near 5 ppm C (Scott Specialty Gases, Troy, MI, USA). Chromatograms of this material are shown in Fig. 2 (DB-1 column) and Fig. 3 (GS-Q column). The GS-Q column provided good resolution of C_1–C_3 hydrocarbons, but was not able to resolve completely the C_4 and higher compounds.

Compound quantification

Both GC detectors were calibrated daily using a propane standard with an approximate concentration of 5 ppm C. This standard is traceable to one prepared by the National Institute for Standards and Technology (NIST) and has an accuracy within 2% of the stated concentration. All hydrocarbons (other than oxygenated compounds) were assumed to give a detector response equivalent to that of propane (on a per-carbon basis). This assumption is typically used for speciated emissions measurements, and is implicitly used in the routine measurement of total hydrocarbon emissions.

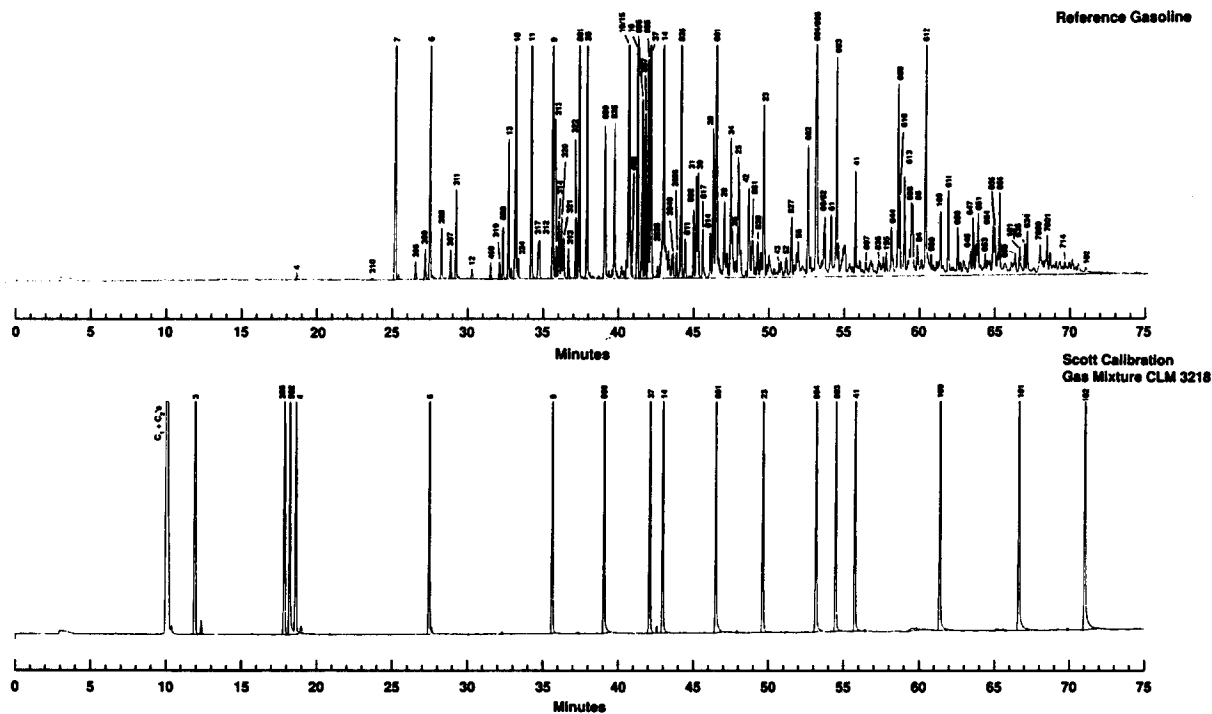Oxygenated compounds give lower detector response than hydrocarbons. Based upon analy-

Fig. 2. Capillary column analyses of reference gasoline and calibration gas mixture. GC conditions are given in Table I. Peak identifications are given in Table III.

sis of known liquid samples (gasoline blends) detector responses were determined for several oxygenated compounds. Relative to a propane response of 1.00, a response of 0.87 was measured for methyl *tert.*-butyl ether (MTBE), 0.89 for *tert.*-amyl methyl ether (TAME), and 0.91 for *tert.*-hexyl methyl ethers (THEME). These

lower response factors were used when quantifying the corresponding oxygenates in emissions samples.

Detector response variability was determined by repetitive analysis of the 21-component gas standard. Fig. 4 shows representative control charts generated from 29 analyses of this stan-
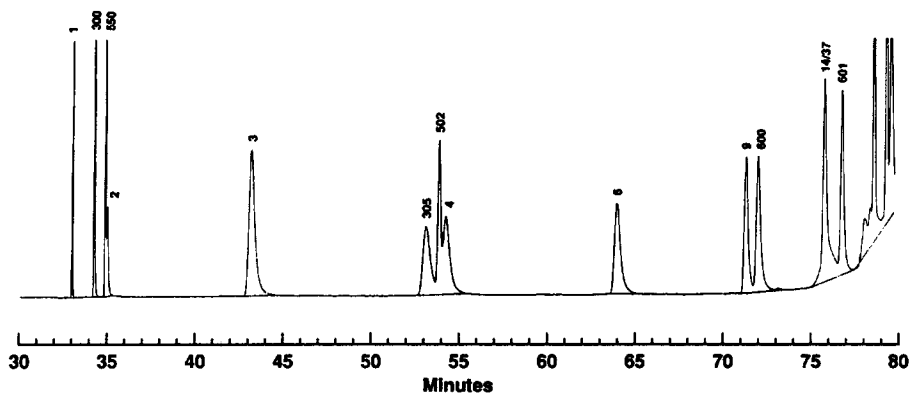

Fig. 3. GS-Q megabore column analysis of Scott calibration gas mixture CLM 3218. GC conditions are given in Table I. Peak identifications are given in Table III.
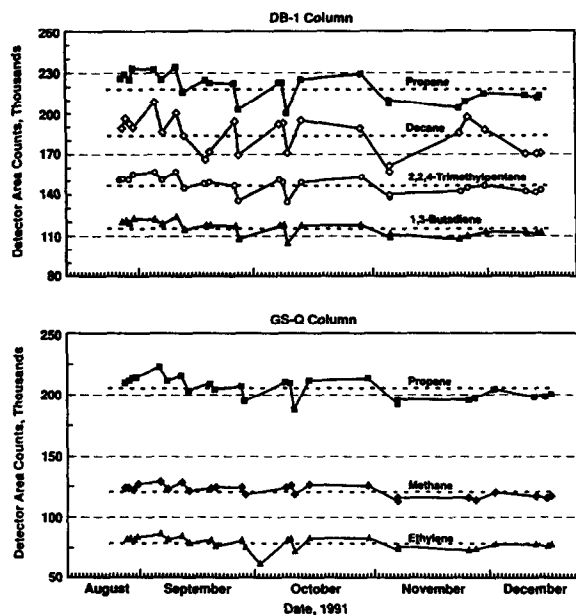
Fig. 4. Detector response control charts for analysis of Scott calibration gas mixture CLM 3218. Dashed lines represent average values.

dard over a 4-month period. These data illustrate that the detector response variability was largely systematic —that is, similar profiles were observed for all compounds. (Slight exceptions are apparent in the control charts for decane and ethylene.) This is attributed in large part to variability in preparing and sampling the Tedlar bags each day, rather than to actual changes in response of the detectors. When analyzing vehicle emissions samples, the effect of these variations was minimized by using a running weighted average response factor, comprising 3/4 of the historical response factor and 1/4 of the current day's factor.

Variability results for all 21 components are summarized in Table IV. For most compounds, the relative standard deviation (R.S.D.) was less than 5% on an absolute basis, and 1–3% when normalized to the propane response. The higher variability measured for ethane was due to the close retention times for acetylene and ethane, and the atypical composition of this standard gas mixture. (In emissions samples from modern vehicles, ethane is generally present at comparable or higher concentrations than acetylene,

while in this standard mixture, ethane's concentration is only about 25% of acetylene's.) The higher variability for the heaviest alkanes ($\geq C_{10}$) is not surprising due to difficulties in sampling and analysis of such materials at low concentration.

Given uncertainties in the composition of this standard mixture, these results also confirm that most compounds give equivalent detector responses. The significantly higher responses measured for the heaviest alkanes ($\geq C_{10}$) are surprising, and remain unexplained. However, this finding is of little consequence since emissions samples generally contain only trace amounts of hydrocarbons in this range.

Detection limit

The GC detection limit was estimated from the same set of replicate analyses described above. Although this gas standard contained only 21 intentionally added hydrocarbons, trace levels of several other compounds were also present. Three of these impurities [cis-2-butene (peak 303; retention time of 20.9 min), 2-methyl-2-butene (peak 311; retention time of 29.2 min), and methylcyclopentane (peak 801; retention time of 37.4 min)] were used to calculate the Method Detection Limit (MDL) as defined by the US EPA [16]. The MDLs for these three compounds varied from 0.004 to 0.007 ppm C. Using the upper value of 0.007 ppm C and our normal emissions testing conditions, this translates to an emission rate detection limit of approximately 0.10 mg/mile for FTP bags 1 and 3, and 0.17 mg/mile for FTP bag 2.

Co-eluting compounds

Co-elution of some compounds is unavoidable with samples as complex as vehicle emissions. As was demonstrated by GC–MS analyses, many of the heavier hydrocarbons ($\geq C_6$) co-elute from the DB-1 column with others. The compounds listed in Table III represent our best estimate of the predominant constituents in most emissions samples.

For several important cases, calculational procedures are used to resolve co-eluting pairs. As described previously [3] the basis for these resolutions is a separate, completely resolved analy-

TABLE IV

GC RESPONSE FACTORS FOR HYDROCARBON COMPOUNDS

29 Replicate analyses of Scott Mixture CLM 3218. GC conditions shown in Table I.

Peak ID No.	Name	Conc. (ppm C)	GC column	Raw results Avg. area counts	Area counts per ppm C	R.S.D. (%)	Propane-normalized results Avg. response	R.S.D. (%)
1	Methane	4.20	GS-Q	120 731	28 745	4.37	1.058	2.01
300	Ethylene	2.79	GS-Q	78 047	27 974	5.22	1.029	1.55
550	Acetylene	4.09	GS-Q	115 031	28 125	5.88	1.035	3.32
2	Ethane	0.89	GS-Q	27 477	30 873	9.78	1.136	5.23
3	Propane	7.56	GS-Q	205 415	27 171	4.45	1.000	–
3	Propane	7.56	DB-1	219 593	29 047	4.49	1.000	–
305	2-Methylpropene	4.93	DB-1	135 623	27 510	4.32	0.947	0.63
502	1 2-Butadiene	3.99	DB-1	115 149	28 859	4.33	0.994	0.69
4	n-Butane	4.46	DB-1	122 909	27 558	3.91	0.949	0.97
6	n-Pentane	4.71	DB-1	143 280	30 420	4.21	1.047	1.08
9	n-Hexane	4.78	DB-1	139 486	29 181	4.01	1.005	1.02
600	Benzene	4.98	DB-1	148 289	29 777	4.47	1.025	0.69
37	2,2,4-Trimethylpentane	4.88	DB-1	147 140	30 152	4.23	1.038	1.29
14	n-Heptane	4.68	DB-1	145 182	30 956	4.12	1.066	1.19
601	Toluene	5.29	DB-1	143 122	27 055	4.87	0.931	1.46
23	n-Octane	5.11	DB-1	149 829	29 321	4.10	1.010	1.42
604	p-Xylene	5.06	DB-1	148 659	29 403	5.35	1.012	2.11
603	o-Xylene	4.95	DB-1	146 401	29 576	5.44	1.018	2.39
41	n-Nonane	5.16	DB-1	161 580	31 314	4.48	1.078	2.67
100	n-Decane	4.99	DB-1	184 056	36 885	7.28	1.270	5.86
101	n-Undecane	5.14	DB-1	234 560	45 634	10.65	1.570	7.56
102	n-Dodecane	5.89	DB-1	234 300	39 779	10.88	1.372	9.48

sis of the fuels used to generate the emissions samples. In three cases where the co-eluting pairs are chemically similar, the ratio of the two in the fuel is applied directly to the emissions: (1) 2-methylhexane/2,3-dimethylpentane (peaks 15/19; retention time of 40.7 min), (2) *m*-xylene/ *p*-xylene (peaks 604/605; retention time of 53.1 min), and (3) 4-methyloctane/2-methyloctane (peaks 62/60; retention time of 53.7 min).

In two other cases, the co-eluting pairs are not chemically similar: benzene/1-methylcyclopentene (peaks 600/451; retention time of 39.1 min) and toluene/2,3,3-trimethylpentane (peaks 601/ 38; retention time of 46.5 min). In these cases, the measurement of a third compound is used to apportion the co-eluting peak into two parts. For instance, the ratio of 2,3,4-trimethylpentane/ 2,3,3-trimethylpentane measured in the fuel is assumed to be the same in emissions. Thus, from analysis of 2,3,4-trimethylpentane in emissions

samples, the amount of 2,3,3-trimethylpentane is calculated, and toluene is computed by difference.

APPLICATIONS

Gasoline vehicle emissions

Representative chromatograms from analysis of a bag 1 exhaust emissions sample from a 1989 gasoline vehicle are shown in Fig. 5. As is typical of emissions from catalyst-equipped vehicles, the bag 1 sample contained a much higher concentration of total hydrocarbons (70 ppm C) than did the bag 2 or bag 3 samples (11 and 17 ppm C, respectively).

The GS-Q chromatogram (bottom of Fig. 5) shows excellent resolution of all C_1–C_3 hydrocarbons. In addition, a small peak attributed to CO_2 is seen at 33.4 min. The DB-1 capillary chromatogram (top of Fig. 5) shows all major
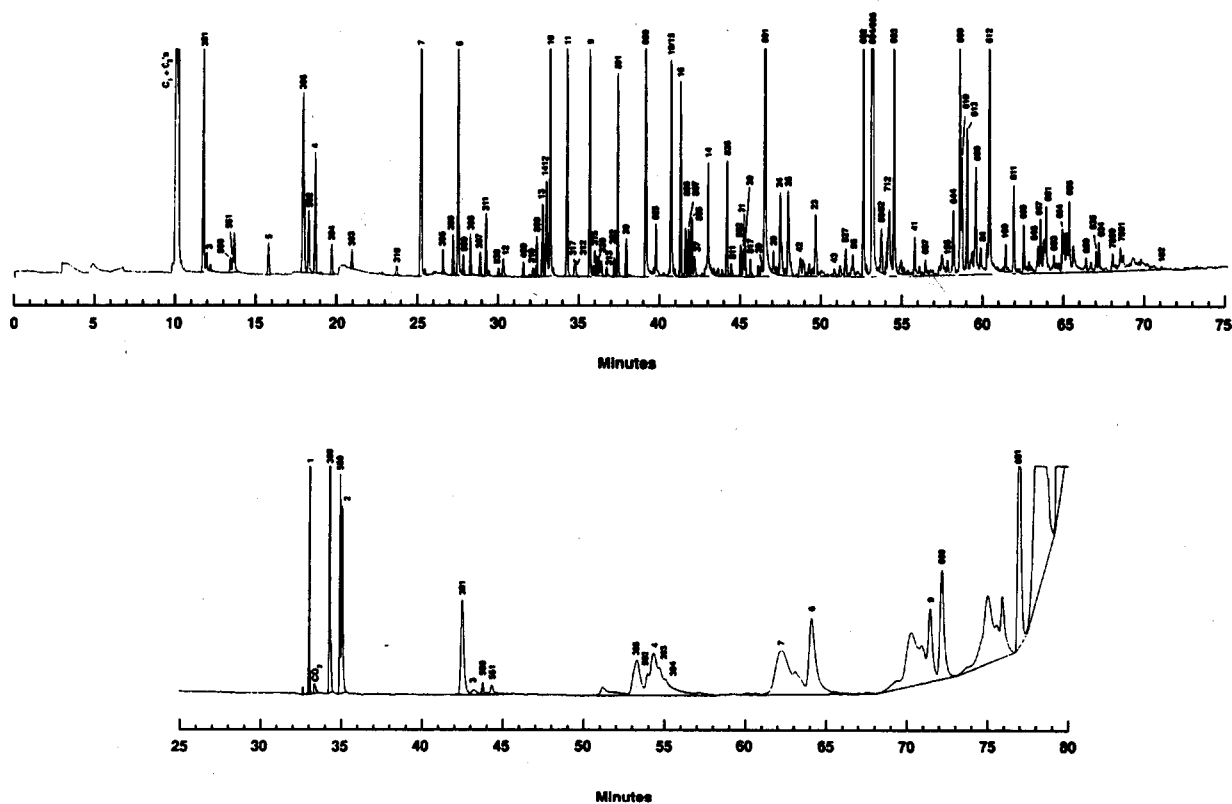

Fig. 5. GC analysis of bag 1 exhaust emissions sample from a gasoline vehicle. Total hydrocarbon concentration of 71.2 ppm C. Top: DB-1 capillary column. Bottom: GS-Q Megabore column. Peak identifications are given in Table III.

TABLE V

STABILITY OF SELECTED SPECIES IN BAG 1 EXHAUST EMISSIONS SAMPLE FROM NONCATALYST VEHICLE

Results are expressed as concentration relative to propylene.

Peak No.	Compound name	Injection No.												
		1	2	3	4	5	6	7	8	9	10	11	12	13
		Aging time (h)												
		0.0	1.6	3.3	4.9	6.6	8.2	9.9	11.6	13.2	14.9	16.5	18.2	19.8
1	Methane	0.500	0.511	0.507	0.506	0.523	0.518	0.524	0.525	0.530	0.539	0.541	0.546	0.550
300	Ethylene	1.143	1.163	1.162	1.152	1.175	1.167	1.174	1.172	1.175	1.173	1.171	1.173	1.163
550	Acetylene	0.457	0.466	0.468	0.469	0.475	0.470	0.477	0.468	0.484	0.468	0.487	0.471	0.470
301-GSQ	Propylene	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
301-DB1	Propylene	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
500	Propadiene	0.062	0.060	0.061	0.061	0.061	0.060	0.061	0.061	0.061	0.062	0.062	0.062	0.061
551	Propyne	0.092	0.081	0.093	0.084	0.081	0.097	0.080	0.080	0.079	0.080	0.080	0.079	0.080
502	1,3-Butadiene	0.188	0.142	0.102	0.083	0.073	0.058	0.053	0.046	0.042	0.040	0.037	0.034	0.032
4	n-Butane	0.412	0.414	0.414	0.418	0.411	0.411	0.413	0.417	0.416	0.418	0.417	0.421	0.420
309	2-Methyl-1-butene	0.097	0.096	0.091	0.094	0.093	0.093	0.091	0.092	0.093	0.093	0.093	0.093	0.092
6	n-Pentane	0.216	0.218	0.213	0.219	0.218	0.217	0.220	0.221	0.219	0.222	0.221	0.222	0.222
509	2-Methyl-1,3-butadiene	0.095	0.034	0.014	0.010	0.009	0.009	0.007	0.011	0.009	0.009	0.008	0.009	0.010
505	trans-1,3-Pentadiene	0.016	0.009	0.005	0.003	0.003	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000
530	Cyclopentadiene	0.038	0.004	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
9	n-Hexane	0.144	0.142	0.144	0.145	0.144	0.145	0.145	0.144	0.151	0.148	0.151	0.150	0.151
600	Benzene	0.846	0.841	0.841	0.847	0.829	0.843	0.835	0.840	0.842	0.845	0.844	0.849	0.847
37	2,2,4-Trimethylpentane	0.723	0.716	0.718	0.732	0.713	0.726	0.719	0.726	0.729	0.732	0.738	0.739	0.741
601	Toluene	2.891	2.884	2.870	2.916	2.833	2.836	2.856	2.876	2.872	2.887	2.882	2.892	2.892
604/605	m/p-Xylene	1.177	1.178	1.163	1.162	1.159	1.143	1.149	1.151	1.151	1.155	1.151	1.149	1.151
712	Styrene	0.135	0.109	0.090	0.076	0.067	0.065	0.048	0.042	0.039	0.035	0.030	0.026	0.026
611	1,2,3-Trimethylbenzene	0.129	0.135	0.125	0.127	0.127	0.123	0.125	0.122	0.125	0.125	0.124	0.121	0.122

fuel constituents as well as a number of combustion-produced hydrocarbons. Of particular note is 1,3-butadiene (peak 502; retention time of 18.2 min) which previously was difficult to resolve [3], but is now baseline-separated.

Resolution of 2-methylpropene and 1-butene (peaks 305 and 302; retention time of 17.9 min) from the DB-1 capillary column is problematic. The graphical capabilities of the chromatography data station are used to magnify this region, thereby permitting the two peaks to be distinguished. In cases where significant levels of MTBE are present in the fuel (as in Fig. 5), 2-methylpropene generally predominates over 1-butene. Use of MTBE in fuels is known to increase emissions of 2-methylpropene [3,17,18].

MTBE itself is seen in the DB-1 chromatogram of Fig. 5 (peak 1412; retention time of 32.8 min). Although the fuel contained approximately 10% MTBE, the relative concentration in the emissions sample was much lower. This preferential removal of MTBE has also been documented before [3,19].

Methanol vehicle emissions

Fig. 6 presents typical chromatograms of a bag 1 exhaust emissions sample produced from a 1989 flexible-fueled vehicle operating on M-85 [methanol–gasoline (85:15, v/v)]. In addition to the major species found in gasoline vehicle exhaust, these chromatograms each show a dominant peak due to methanol. On both the DB-1 and GS-Q columns, methanol elutes very near to *n*-butane, thereby making the quantification of *n*-butane difficult. This is normally a problem only with bag 1 samples, where the methanol concentrations are high. Significantly, methanol does not interfere with measurement of 1,3-butadiene.

The DB-1 chromatogram in Fig. 6 shows a peak with retention time of 24.5 minutes that is attributed to acetonitrile. This is not an emis-
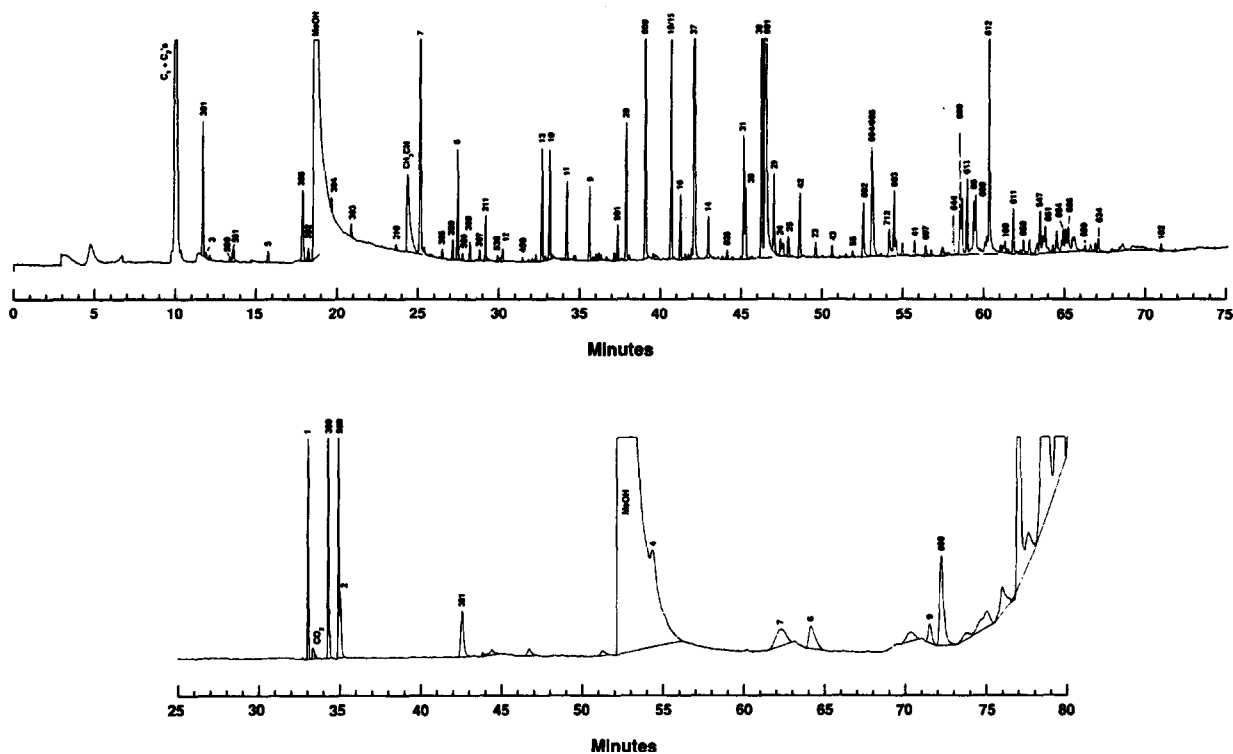

Fig. 6. GC analysis of bag 1 exhaust emissions sample from M-85 vehicle. Total hydrocarbon concentration of 140 ppm C. Top: DB-1 capillary column. Bottom: GS-Q Megabore column. Peak identifications are given in Table III.

sions species, but is a contaminant that arises from impinger techniques that are used to collect aldehydes during vehicle emissions testing.

Stability of emissions species

In recent years, there has been concern about the stability of certain exhaust emissions species when stored in Tedlar bags —particularly 1,3-butadiene. Lipari [4] reported a 25% loss of 1,3-butadiene in a bag 1 emissions sample after storing 24 h, and 70% loss after 48 h. Dempster and Shore [20] reported that "1,3-butadiene deteriorates rapidly when stored in dilute exhaust". Kaiser *et al.* [21] have recently observed degradation of 1,3-butadiene in exhaust samples from a single-cylinder engine [21].

This issue was investigated by generating and repeatedly analyzing a bag 1 exhaust emissions sample. To provide high initial concentrations of the unstable species, the vehicle that was used (1987 Chevrolet Celebrity; 2.8-l engine, 6-cylinder, port fuel injection) had its catalyst removed. This high concentration sample (270 ppm C) enabled accurate monitoring of degradation of several dienes (including 1,3-butadiene) which are normally present at only trace levels.

The exhaust emissions sample was attached to the automatic gas sampling valve on the GC instrument and was analyzed at approximately 90-min intervals until the Tedlar bag was empty. The concentrations of 20 selected compounds were measured at each analysis time. These compounds included all five dienes which are routinely measured in vehicle emissions, as well as representative *n*-alkanes, isoalkanes, alkenes, and aromatics in the range of C_1–C_9.

The results summarized in Table V are expressed as concentrations relative to the concentration of propylene. Propylene is a convenient choice for internal normalization since it can be measured reliably from both GC columns. This normalization eliminates sampling variability and compensates for sample dilution which was unavoidable using our automatic sampling technique. It has been reported that propylene itself is stable in such emissions samples for up to 1 day [4,21]. We independently established propylene's stability in samples aged for 3 days [22].

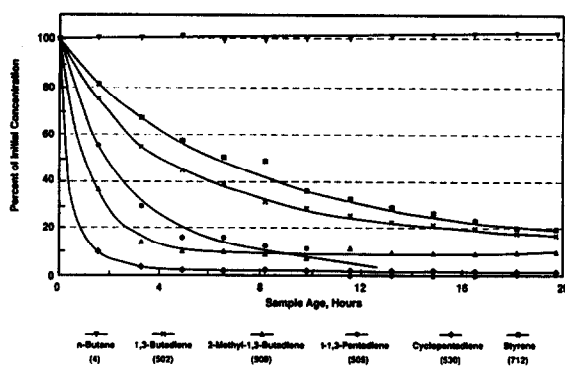Clear differences in stability among the emis-

Fig. 7. Degradation of species in bag 1 exhaust emissions sample from non-catalyst gasoline vehicle.

sions species were seen. The 20 compounds can be broadly categorized as stable (*n*-alkanes, isoalkanes, propylene, acetylene, aromatics and most alkenes), moderately unstable (styrene and 1,3-butadiene), and highly unstable (C_{5+} dienes). Degradation of the unstable species is further illustrated in Fig. 7, with *n*-butane included as a point of reference.

In theory, such degradation curves could be used to adjust the measured concentrations of these unstable compounds in aged samples. However, similar analyses of other emissions samples showed the rates of degradation to be quite variable —although the relative ranking of stability was always similar to that shown in Fig. 7. In particular, lower degradation rates were observed in emissions from catalyst-equipped vehicles. It is not known whether this is due to lower levels of total hydrocarbons, lower NO_x, or other factors. Varying degradation rates for 1,3-butadiene and cyclopentadiene have been reported by others as well [21].

SUMMARY AND CONCLUSIONS

An improved GC methodology has been developed for speciated analysis of C_1–C_{12} hydrocarbons in vehicle exhaust emissions. The simultaneous use of two columns allows for complete analysis of emissions samples using a single GC instrument. Detection limits for individual hydrocarbons are ≤10 ppb C, which corresponds to an emission rate of approximately 0.1 mg/mile for a typical FTP bag sample. While this is

adequate to provide thorough characterization of exhaust emissions from current vehicles, additional sensitivity may be necessary for future, low-emitting vehicles.

This improved GC procedure has been satisfactorily used to analyze exhaust emissions from both gasoline- and methanol-fueled vehicles. The presence of methanol in emissions samples does not seriously hinder measurement of hydrocarbons. Sample instability was found to be a general problem for diene compounds in exhaust mixtures. The rates of degradation are sample dependent, and may be influenced by the amount of other components in emissions. To minimize concerns about sample integrity, exhaust emissions should be analyzed promptly after collection.

ACKNOWLEDGEMENTS

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