

## Measurement and Estimation of VOC Composition from Gasoline Evaporation

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### Abstract

Source profiles were developed for a total of 45 volatile organic compounds (VOC) that can be emitted from gasoline evaporation. The gasoline samples of five major brands (for each season) were blended on the basis of the market share in Seoul area and analyzed by a GC-MS/FID system. In addition, we calculated gasoline evaporative compositions using the Raoult's law from the liquid gasoline compositions. The measured and estimated gasoline vapor compositions agree well each other. As a group, alkanes are the most abundant in the gasoline vapor profiles (77.4% on average), followed by alkenes (19.1%), and aromatics (1.7%). As a specie in gasoline vapor, *i*-pentane is the most abundant, followed by *n*-butane, *n*-pentane, *i*-butane, *trans*- and *cis*-2-butenes, 2-methyl-2-butene, and *trans*- and *cis*-2-pentenes. It was also seen that aromatic content was much lower in the vapor phase compositions. From the comparison between experimental and calculated compositions, we identified the fact that once the gasoline vapor composition is reliably constructed entirely from the measured gasoline composition and the Raoult's law calculations, the need for doing separate chemical analyses of the gasoline vapor can be reduced.

**Key words :** Volatile organic compounds (VOCs), Gasoline evaporative emissions, Raoult's law

### 1. INTRODUCTION

The importance of volatile organic compounds (VOC) produced by human activities is now recognized with respect to photochemical formation of secondary air pollutants such as ozone (O<sub>3</sub>) or peroxyacetyl nitrate (CH<sub>3</sub>C(O)OONO<sub>2</sub>) and to their impact upon human health. In urban areas, it is known that vehicle exhaust, gasoline evaporation, and solvent uses are the main

emission sources of VOC. Based on the Korean Ministry of Environment, gasoline evaporation is responsible for 6% of the VOC emissions in Korea (MOE, 2001). The variations of the strength of the sources along with meteorological conditions can cause a diurnal, seasonal, and annual variation of the VOC concentrations (Na and Kim, 2001; Na *et al.*, 2001).

The composition pattern of VOC species emitted from a source category is called source profile and expressed as the mass fractions of the species mass emission rate to the sum of the species mass emission rates. The source profiles of VOC have been developed for

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several urban areas of US, Canada, Japan, and Australia. It is known that accurate speciation of source profiles that reliably reflect source composition of a given area is crucial in developing control strategies. In Korea, preliminary source profiles were obtained by National Institute of Environment Research (NIER) for five emission sources in 1998 (Kim, 1998). Also, tunnel measurement of VOC composition has been carried out (Na and Kim, 2000).

Gasoline is a complex mixture of  $C_4$ – $C_{13}$  hydrocarbons and oxygen-containing compounds such as Methyl Tertiary-Butyl Ether ( $C_5H_{12}O$ , MTBE). The mass fraction of gasoline is illustrated in Fig. 1 according to carbon number.  $C_7$  hydrocarbons have the highest fraction in gasoline, followed by  $C_6$ ,  $C_5$ ,  $C_8$ , and  $C_9$ . The remainder accounts for about 8.5% of gasoline (Korea Petroleum Quality Inspection Institute, KPQII, personal communication).

The most important factor affecting the degree of evaporative emissions is vapor pressure. Recently, to reduce VOC emissions by gasoline evaporation, seasonal vapor pressure limits for gasoline have been mandated. Gasoline can enter the atmosphere by complete evaporation (as in spillage or vehicle “hot-soak” emission) in which case the composition will be that of the gasoline, or by partial evaporation (as in storage tank

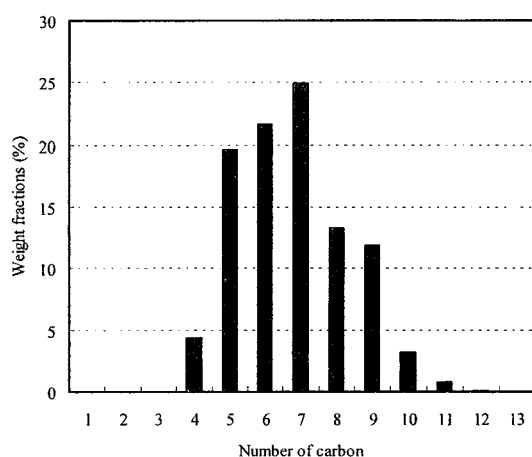


Fig. 1. Gasoline compositions according to carbon number.

evaporation or vehicle diurnal evaporation) in which case the composition will be that of the vapor in equilibrium with the gasoline at the relevant temperature. Evaporative emissions are divided into five types: (1) Diurnal evaporation, which is the emissions when the vehicle is at rest which occur due to ambient temperature changes over a typical 24-h period (the portion of emissions at rest driven by the impact of temperature on the vapor pressure above the fuel). (2) Hot soak, which is driven by residual engine heat once a warmed-up vehicle is parked and the engine is shut off. (3) Running loss, which occurs when the vehicle is being driven. (4) Resting loss (the constant at rest evaporative emissions). (5) Refueling loss (displaced vapors and drippage resulting from refueling)

In this paper, emission profiles from gasoline evaporation is measured and estimated.

## 2. EXPERIMENT

To obtain the gasoline evaporative profiles, a 250 mL flask containing gasoline was immersed in constant temperature bath maintained at  $0^{\circ}C$  for the winter data. This temperature was selected to reflect the feature of the gasoline evaporation during wintertime. To obtain a pure gasoline vapor composition in the flask, air in head space of flask were completely replaced with pure nitrogen (99.999%).

After a 20-min equilibrium period, air sample 500- $\mu$ L of the headspace was taken from the flask and injected into evacuated ( $<0.1$  torr) 6 L SUMMA-polished canisters with filling the canister with pure nitrogen (99.999%) to 15 psig. All tubes connected with the canister were sufficiently purged with the pure nitrogen before the injection of the headspace sample.

Analysis of the vapor samples were carried out at Advanced Analysis Center at Korea Institute of Science and Technology. The canisters were analyzed by a GC/FID and GC/MS system. The GC/FID was used to quantify  $C_2$ – $C_3$  hydrocarbons and the GC/MS was used to identify  $C_2$ – $C_9$  hydrocarbons and quantify  $C_4$

~C<sub>9</sub> hydrocarbons. For the analysis of C<sub>2</sub> and C<sub>3</sub> hydrocarbons, a GC/FID (STAR 3600CX, Varian, USA) was used. Separation was achieved by a 60 m long, 0.32 mm I.D., 3.0 μm film thickness RTX-1 column. Initial oven temperature was -60°C for 7 min and raised to 70°C at the rate of 10°C min<sup>-1</sup> and then oven was heated to the final temperature, 220°C, at the rate of 7°C min<sup>-1</sup> and was kept at 220°C for 15 min. Flow rate of the carrier gas, N<sub>2</sub> (99.9999%) was 3 ml min<sup>-1</sup> and that of the detector make up gas (N<sub>2</sub>) was 30 ml min<sup>-1</sup>. Flow rates of H<sub>2</sub> and air were 19 and 250 ml min<sup>-1</sup>, respectively. Detector was heated to 250°C. Sample was concentrated for 5 min at the flow rate of 40 ml min<sup>-1</sup>. Liquid nitrogen was used as the coolant for the cryogenic trap and temperature of which was -150°C for 5 min. Then samples were desorbed at 200°C for 2.5 min.

C<sub>4</sub>~C<sub>9</sub> hydrocarbons were identified by means of a combined gas chromatography/mass spectrometry (GC/MS) system (3400CX GC & Saturn 2000 MS, Varian, USA). A sample preconcentration trap for the standards and samples was packed with 60~80 mesh glass bead. To concentrate the hydrocarbons, an aliquot of a canister air was transferred into a trap immersed in liquid nitrogen in the flow rate of 20 ml min<sup>-1</sup> for 5 min. The total volume concentrated was 100 ml. The concentrated sample was revolitized by heating the trap up to 170°C and then held for 11.3 min. Hydrocarbons were separated in a 60 m long, 0.32 mm I.D., 1.0 μm film thickness DB-1 column (J&W Scientific, USA), and subsequently analyzed by the GC/MS. The GC oven program used was: initial temperature 0°C for 7 min, rising at 15°C min<sup>-1</sup> up to 170°C where it remains for 6 min. Calibration standards (Scott, USA) were used to establish the retention times and detector responses of GC/MS.

Precision, as determined from five replicate analyses of the standards and samples, is within 15% for the compounds at the concentrations above 5 ppbC and the lower quantifiable limits were between 0.1 and 0.5 ppbC depending on component for the 100 ml of sample concentrated. The percent difference of the concen-

trations of VOC for the six duplicate samples measured during the period of this study is less than 35%. The accuracy was demonstrated through the comparison analysis between KIST and Atm AA, an environmental consulting laboratory, USA on four of the same samples. The results show that the relative errors calculated on the basis of Atm AA range from 3 to 49%.

The liquid gasoline samples were made of gasoline of five major brands for each season blended on the basis of the market share in Seoul. The analysis on the three gasoline mixtures for each season (winter, spring, and summer) were carried out by KPQII.

### 3. VAPOR PRESSURE ESTIMATION

Gasoline vapor composition can be measured as described in Section 2. It can also be calculated from the liquid gasoline composition and vapor pressure data.

The measured compositions of the liquid gasoline mixtures are presented in Table 1, and were used to calculate gasoline vapor compositions by means of the Raoult's Law. The compositions calculated by the Law accurately reflect the equilibrium vapor composition by measurements of the vapor over individual gasoline samples. The Raoult's law states that the mole fraction of component *i* (*x<sub>i</sub>*) in an ideal solution is equal to the ratio of the partial pressure of *i* above the solution (*P<sub>i</sub><sup>part</sup>*) to the vapor pressure of pure component *i* (*P<sub>i</sub><sup>pure</sup>*), provided vapor behaves as an ideal gas (Smith and Van Ness, 1988):

$$\frac{P_i^{part}}{P_i^{pure}} = x_i \quad (1)$$

If the mole fraction and the vapor pressure of each component *i* in gasoline are known, the preceding equation can be solved for the partial pressure of each component *i* above the gasoline. The partial pressures are proportional to the composition of the vapor above the gasoline.

The vapor pressures of pure components were calculated for a specific temperature by using the Antoine

**Table 1. Gasoline and gasoline vapor source profiles.**

Compounds	This study						(a) Australia	(b) Canada	(c) Japan	(d) US
	Gasoline			Gasoline vapor						
	Winter	Spring	Summer	Winter	Spring	Summer				
Ethane	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.14	
Propane	0.08	0.06	0.04	2.33	1.53	1.40	1.5	1.8	0.97	
n-Butane	2.71	3.14	2.20	17.34	20.70	19.88	18.7	19.92	19.1	21.80
i-Butane	1.32	1.07	0.72	13.03	10.32	9.73	11.1	5.68	15.2	5.13
n-Pentane	5.65	4.75	7.76	8.21	8.27	8.42	10.7	12.30	13.1	7.40
i-Pentane	11.73	10.64	12.39	24.38	25.32	25.32	25.4	25.65	35.8	27.90
2-Methylpentane	6.68	6.04	6.27	3.48	4.20	4.45	3.5	3.83	6.3	3.53
3-Methylpentane	4.45	4.16	4.36	2.05	2.58	2.74	2.2	2.20	3.1	1.93
2,2-Dimbutane	0.80	0.78	0.78	0.69	0.84	0.87	0.6	0.33		0.68
2,3-Dimbutane	1.38	1.26	1.29	0.82	0.98	1.02	1.1	1.22		1.49
n-Hexane	4.50	4.08	4.32	1.56	1.99	2.15	1.9	2.27	3.2	1.20
2-Methylhexane	4.96	5.67	5.37	0.65	1.17	1.31	0.7			0.46
3-Methylhexane	3.97	4.69	4.42	0.48	0.89	1.00	0.5	0.47		0.44
2,4-Dmpentane	0.85	0.86	0.84	0.18	0.27	0.27	0.2			0.52
n-Heptane	2.81	3.51	3.10	0.23	0.49	0.46	0.3	0.21		0.21
2-Methylheptane	1.07	1.23	1.15	0.03	0.07	0.08		0.05		0.06
3-Methylheptane	1.28	1.46	1.39	0.04	0.08	0.09		0.05		0.01
Octane	1.05	1.32	1.25	0.02	0.05	0.06	0.0	0.03		0.03
Nonane	0.27	0.34	0.32	0.00	0.00	0.00	0.0	0.00		0.01
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00	0.0			0.01
Propylene	0.00	0.00	0.00	0.00	0.00	0.00	0.0			0.13
1-Butene	0.26	0.15	0.13	2.05	1.19	0.92	1.6			0.98
t-2-Butene	0.96	0.53	0.79	5.80	3.06	4.12	3.7			1.54
c-2-Butene	0.83	0.44	0.35	4.49	2.78	2.99	2.9			1.38
1-Pentene	0.73	0.63	0.64	1.37	1.39	1.32	0.7			1.19
Isoprene	0.00	0.00	0.00	0.00	0.00	0.00				0.07
t-2-Pentene	1.95	1.65	1.67	2.76	2.83	2.73	1.5			2.29
c-2-Pentene	1.04	0.90	0.90	1.44	1.51	1.46	0.9			1.25
2-M-2-butene	2.81	2.60	2.62	3.61	4.08	3.94	2.6			2.88
Acetylene	0.00	0.00	0.00	0.00	0.00	0.00	0.0			0.01
Cyclopentane	0.74	0.37	0.41	0.62	0.39	0.42	0.6	0.72		1.49
Mycyclopentane	2.72	2.13	2.13	0.85	0.94	0.95	0.9			0.81
Cyclohexane	0.48	0.26	0.28	0.10	0.08	0.09	0.3			0.12
Mycyclohexane	1.13	1.05	1.03	0.10	0.15	0.15	0.2	0.13		0.12
Benzene	2.92	1.99	1.67	0.57	0.59	0.51	0.9	0.93	0.9	0.86
Toluene	12.86	11.40	10.18	0.62	0.96	0.93	1.0	1.27	1.0	1.26
Ethylbenzene	1.53	1.54	1.30	0.02	0.04	0.04	0.1	0.07	0.1	0.11
m-/p-Xylene	5.20	5.68	4.50	0.06	0.13	0.12	0.2	0.27	0.3	0.32
o-Xylene	2.20	2.68	2.17	0.02	0.05	0.05	0.1	0.08	0.1	0.12
Styrene	0.00	0.00	0.00	0.00	0.00	0.00	0.0			0.01
1,2,4-TMbenzene	4.75	8.68	8.83	0.01	0.05	0.06	0.0			0.11
1,3,5-TMbenzene	1.33	2.25	2.44	0.00	0.01	0.02	0.0			0.04
Alkanes	55.57	55.06	57.95	75.50	79.76	80.18				
Alkenes	8.57	6.90	7.11	21.52	16.84	16.47				
Alkynes	0.00	0.00	0.00	0.00	0.00	0.00				
Napthenes	5.07	3.81	3.86	1.67	1.56	1.61				
Aromatics	30.79	34.23	31.09	1.31	1.83	1.73				
Total	100.00	100.00	100.00	100.00	100.00	100.00				

(a): Nelson *et al.*, 1983; (b): McLaren *et al.*, 1996; (c): Wadden *et al.*, 1986; (d): Conner *et al.*, 1995

Blank values mean not reported ones.

Gasoline compositions were measured by KPQII.

equation, which relates vapor pressure ( $P$ , in torr) and temperature ( $T$ , in K) as follows:

$$\log P = A - \frac{B}{T+C} \quad (2)$$

where, A, B, and C are constants characteristic of each species (Reid *et al.*, 1988).

#### 4. RESULTS AND DISCUSSION

Gasoline evaporative compositions calculated from the Raoult's law at 0°C are compared with the measured compositions in Fig. 2 for 45 species. The measured vapor compositions are obtained from analysis of the compositions of headspace vapor of the flask filled with the gasoline mixtures. The profile for the gasoline headspace vapor reflects evaporative emissions due to refueling, diurnal emissions, and running losses. Profile abundance has been normalized for the species partial pressures calculated using the Raoult's law as described above. Agreement between calculated and measured headspace composition is very good ( $R^2=0.95$ ).

Relationship between the calculated and the measur-

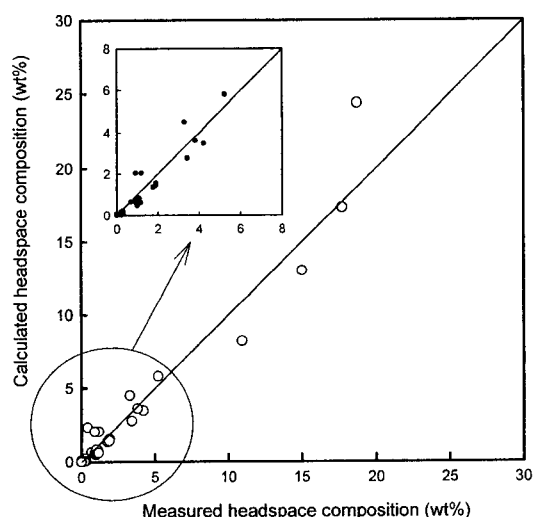


Fig. 2. Gasoline headspace vapor composition calculated from the Raoult's law for 0°C versus measured 0°C headspace composition.

ed results is as follows:

$$\text{Calculation} = 1.04 \times \text{measurement} - 0.08 \quad (3)$$

The difference between the calculated and measured values for each species, as well as the difference between the calculated and regression-derived values, is less than 25% for this sample.

It suggests that if the gasoline vapor composition can be reliably constructed entirely from a measured gasoline composition and the Raoult's law calculations, the need for doing separate chemical analyses of the gasoline vapor could be eliminated. In theory, vapor composition could be calculated at any ambient temperature, within the vapor pressure calculation restrictions. This would represent considerable saving in samples required and in analyses performed.

The calculated compositions of the gasoline vapor are listed in Table 1, together with the analyzed gasoline compositions and the results from other foreign studies. The temperature for the spring and summer were 11 and 24°C, respectively. These temperature values are the 30-year average temperatures of March-May and June-August for spring and summer, respectively. Calculated profiles that reflect the composition of the gasoline vapor above the liquid gasoline are quite different from the gasoline profiles. Alkanes and alkenes contents are higher in headspace vapors than those in gasoline, especially *i*-pentane, *n*-butane, *n*-pentane, *i*-butane, *trans*- and *cis*-2-butenes, 2-methyl-2-butene, and *trans*- and *cis*-2-pentenes. Whereas, aromatic content is much lower in the gasoline vapor profiles.

The abundance of butanes is the lowest in summer, possibly due to changes in vehicle technology and efforts to reduce fuel Reid Vapor Pressure (RVP) that have occurred in recent years. At present, RVP is largely controlled by the contents of butanes in gasoline. The partial pressures of the compounds decrease as molecular weights increase beyond the  $C_6$  compounds (higher boiling point). Thus, components beyond  $C_6$  constitute lesser fractions of the gasoline vapor compared with the gasoline, especially aromatics. Alkanes

is the most abundant in the gasoline vapor profiles (77.4% on average), followed by alkenes (19.1%), and aromatics (1.7%).

For the purpose of chemical mass balance modeling, Nelson *et al.* (1983) and Conner *et al.* (1995) calculated gasoline vapor compositions from their average gasoline compositions by means of the Raoult's law. They applied the calculated gasoline profiles to the apportionment of VOC to their sources.

The calculated profiles would not fully represent the real world of the gasoline evaporative emissions. However, the calculated profiles have advantages of the savings of time and cost. Considering the previous studies and the strong advantages, we used the calculated profiles for receptor modeling.

Gasoline vapor composition in this study is generally in agreement with other studies, especially for aromatic hydrocarbons. Our result shows the best correlation ( $R^2 = 0.99$ ) with Australia, while the worst correlation with US ( $R^2 = 0.94$ ). But the difference is not large. It suggests that there is no big problem in mutual application of these profiles. Canada and US have lower *i*-butane compositions compared to the other countries. Japan shows somewhat different pattern in the compositions of  $C_4 \sim C_6$  alkanes.

## 5. SUMMARY

Accurately speciated source profiles that reliably reflect source composition of a given area are crucial to the success of the developed control strategies. Source profiles were developed for source apportionment modeling applications from the concentrations of 45 VOC in the emissions from gasoline evaporation.

To make gasoline evaporation profiles, the gasoline samples of five major brands for each season were blended on the basis of the market share in Seoul area and analyzed by a GC-MS/FID. Also, we calculated gasoline evaporative compositions using the Raoult's law from the liquid gasoline compositions. The measured and estimated gasoline vapor compositions agree

well to each other.

Alkanes is the most abundant in the gasoline vapor profiles (77.4% on average), followed by alkenes (19.1%), and aromatics (1.7%). In gasoline vapor, *i*-pentane is the most abundant, followed by *n*-butane, *n*-pentane, *i*-butane, *trans*- and *cis*-2-butenes, 2-methyl-2-butene, and *trans*- and *cis*-2-pentenes. Whereas, aromatic content is much lower in the vapor phase compositions. From the comparison between experimental and calculated compositions, we identified the fact that if the gasoline vapor composition can be reliably constructed entirely from the measured gasoline composition and the Raoult's law calculations, the need for doing separate chemical analyses of the gasoline vapor could be eliminated.

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