In Situ, Fast-response, Molecular-selective Methods for Measuring Emission Factors of Volatile Organic Compounds (VOCs) into the Atmosphere

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(Received October 21, 2008; CL-081014; E-mail: jmatsu@tmu.ac.jp)

A sensitive, real-time, and molecular-selective analyzer using a resonance-enhanced multiphoton ionization/time-of-flight mass spectrometer (REMPI-TOFMS) was combined with the chamber method to measure emission factors of VOCs during painting. Temporal variation of VOC emission was successfully captured on site on a second time scale. Exact and detailed assessment of emission is realized with molecular-dependent characteristics considered.

Volatile organic compounds (VOCs) have been a focus as critical precursors of tropospheric ozone, as well as nitrogen oxides (NO_x).[1,2] To effectively control emission of VOCs into the atmosphere and to address the photochemical oxidant problem, detailed information of emission at the source is essential. Under the present regulations in Japan, total hydrocarbon (THC) is measured as an index of VOC emission. THC reflects the total carbon in a sample and is convenient for a comprehensive regulation of organic compounds. However, ozone formation potentials vary for individual species. Even among isomers, the potentials are different. For example, California maximum incremental reactivity (MIR) indexes of ozone formation are 7.4, 10.6, and 4.2 $gO_3/gVOC$ for *o*-, *m*-, and *p*-xylene, respectively.[3] Thus, molecular-selective analysis of VOCs in exhaust is essential. As a source of atmospheric VOCs, vaporization of solvent, like paint, is dominant.[1,4] To obtain detailed emission information of VOCs during painting, fast-response, in situ, real-time measurement is desirable because highly volatile compounds can be rapidly vaporized. The chamber method is adopted industrially and widely used to determine the emission factor *EF*, emitted quantities per unit area and time, of VOCs.[5] However, the conventional method is not useful for temporally varying samples because the method consists of batch sampling and later analysis. Recently, the authors have constructed a sensitive, real-time, molecular-selective analyzer of aromatic hydrocarbons in exhaust gases by a resonance-enhanced multiphoton ionization/time-of-flight mass spectrometer (REMPI-TOFMS).[6,7] In this study, the REMPI analyzer is combined with the conventional chamber method, and in situ, fast-response, molecular-selective monitoring of *EF*s during painting is reported.

As a whole, the system consists of a glass chamber and REMPI analyzer. When uniform mixing in the chamber is assumed, variation of the number of target molecules ΔN within a temporal interval Δt can be described as:

$$\Delta N = VA\Delta C = AC_0F\Delta t - AC(t)F\Delta t + EF(t)S\Delta t \qquad (1)$$

where V is defined as the volume of the chamber, C as target concentration in ppmv (10^{-6} by volume), A as a constant to convert units (2.5×10^{13} molecules cm^{-3} ppmv^{-1} at 298 K), ΔC as a variation of concentration $C(t + \Delta t) - C(t)$, C_0 as the inflow concentration, F as volume flow rate through the chamber, $EF(t)$ as emission factor, and S as the sample surface area. The terms in the right-hand side of eq 1 represent the inflow, outflow and emission of molecules, respectively. When C_0 is negligible, EF can be derived as:

$$EF(t) = (1 + \alpha)AFC(t)/S, \quad \alpha = V\Delta C/\{FC(t)\Delta t\} \qquad (2)$$

The parameter α represents the impact of short-term variation of C. When the emission is stable and balances with inflow/outflow flux, α is negligible and $C(t)$ reaches a steady-state value, $C(\mathrm{SS})$. Then EF can be described as:

$$EF(\mathrm{SS}) = AFC(\mathrm{SS})/S \qquad (3)$$

which corresponds to EF by the conventional method.[5]

First, emission from paint is explored by the steady-state chamber method. Figure 1 shows the observed variation of toluene after a reservoir of 100-cm^3 fresh oil-based paint (for wood and iron by Kanpe Hapio Co., Ltd.) was opened and put into the chamber. This experiment was conducted with the excitation laser tuned to the resonant wavelength of toluene (266.83 nm). In this case, toluene reached SS where $C(\mathrm{SS})$ was 1.1 ppmv. It was thought that 100-cm^3 liquid paint was sufficient for SS to be reached. From eq 3, $EF(\mathrm{SS})$ of toluene was acquired as 1.2×10^{13} molecules $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ for $F_{\mathrm{tot}} = 10\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ and $S = 22\,\mathrm{cm}^2$. To validate the observed variation of toluene, $C(t + \Delta t)$ was calculated sequentially from $C(t)$ by eq 1 with EF set to zero and $EF(\mathrm{SS})$ before and after $t = 0$, respectively. As indicated in Figure 1, observed variation agrees well with theory. The chamber method with REMPI-TOFMS was effective for analysis of the fast VOC emission. It should be noted that fluctuation of observed $C(t)$ was significant. As 1-s data, standard deviation was 0.18 ppmv which corresponds to 17% of $C(\mathrm{SS})$. Then the random error of $EF(\mathrm{SS})$ was estimated by error propagation as 20%. In this case of the first challenge, the limit of detection (LOD) of REMPI-TOFMS was 0.08 ppmv ($S/N = 3$, $\Delta t = 1$ s). Standard deviation during calibration for standard gas (4.3 ppmv) was 0.4 ppmv (9% of C). Fluctuation observed in

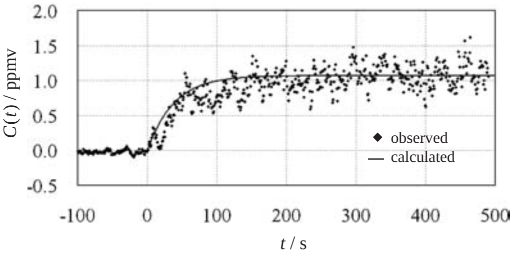

Figure 1. Variations of toluene emitted from 100-cm^3 reservoir of fresh oil-based paint: observation (diamonds) and theoretical prediction with a stable emission factor assumed (solid line).

Table 1. Emission factor *EF*(SS) for oil- and water-based paints

	Benzene	Toluene	Phenol	*o*-Xylene	*m*-Xylene	*p*-Xylene
REMPI-TOFMS settings:[a]						
λ/nm	259.03	266.83	275.03	268.00	270.59	272.24
m/z	78	92	94	106	106	106
EF(SS) of paint (molecules $\mathrm{cm^{-2}\,s^{-1}}$):[b]						
oil-based	2.0 (12)	1.2 (13)	1.0 (11)	9.5 (13)	1.1 (14)	2.2 (13)
water-based	2.7 (11)	9.3 (10)	1.6 (10)	—[c]	—[c]	—[c]

[a] REMPI-TOFMS settings are also listed. [b] A (B) represents $A \times 10^B$. [c] —means no experiment in this study.

Figure 1 was significant and could be resulted from the variation of sample concentration. Settings like F and V are important to control such fluctuations. Experimental dependence of the system on F and V agrees with theory in the range of $F = 8$–$400\,\mathrm{cm^3\,s^{-1}}$ and $V = 300$–$4500\,\mathrm{cm^3}$ (figure not shown).

Table 1 summarizes observed *EF*(SS) together with each setting of REMPI-TOFMS for each compound. For benzene, toluene, and phenol, both oil- and water-based paints (Kanpe Hapio Co., Ltd.) were investigated. It was confirmed that use of water-based paint in place of oil-based is effective for reduction of VOC, especially toluene (by a factor of 130). It should be noted that reduction factors for benzene and phenol were 7 and 6, respectively. Effects of adopting water-based paint were not uniform for compounds.

EF(SS) values of three isomers of xylenes were acquired individually for oil-based paint. It was found that the relative distribution of emission was: *m*-xylene 48%, *o*-xylene 42%, and *p*-xylene 10%. As for concentrations, *m*- and *o*-xylenes were dominant in the paint vapor. Meanwhile, the products of emission and MIR (index of ozone formation) were: *m*-xylene 59%, *o*-xylene 36%, and *p*-xylene 5%. As for ozone formation, *m*-xylene was found to be significant. By conventional gas chromatography, *m*- and *p*-xylenes cannot be separated owing to similarity of their thermal properties. In this study, it was confirmed that *m*-xylene was much more significant than *p*-xylene in the oil-based paint vapor.

Second, varying emission of VOC from paint as eq 2 is examined. Figure 2a shows the observed variation of toluene concentration after an angle plate was partly coated with fresh paint and the plate was put into the chamber at $t = 0$. The weight of coated paint was 0.52 g and other settings were: $F = 8\,\mathrm{cm^3\,s^{-1}}$, $V = 390\,\mathrm{cm^3}$, $S = 72\,\mathrm{cm^2}$, and $\Delta t = 1\,\mathrm{s}$. LOD of REMPI-TOFMS was 0.04 ppmv. Standard deviation during calibration was 4% of C. In this case, the concentration rapidly reached a peak and then gradually decreased. In contrast to the bulk liquid case (Figure 1), emission from the thin film of paint was not constant. From eq 2, decreasing $EF(t)$ was successfully captured every 30 s as shown in Figure 2b. Typically, relative variation $|\Delta C/C|$ was within 0.03 and $|\alpha|$ was within 0.05 for $\Delta t = 30\,\mathrm{s}$. The random error of $EF(t)$ was estimated as 15%. The decreasing time constant τ of $EF(t)$ was acquired as 437 s by regression to an exponential curve. To validate the observed variation, $C(t + \Delta t)$ was calculated sequentially from $C(t)$ by eq 1 with the regressed $EF(t)$. Observed $C(t)$ agrees with the calculated values with differences less than 0.4 ppmv.

Finally, the results of simultaneous monitoring of multiple compounds are presented. When the toluene-resonant setting is adopted (laser wavelength: 266.83 nm), instrumental sensitivities for other compounds are low (typically by an order of 10^3 than resonant settings) but not zero owing to nonresonant MPI. In fact, significant signals were observed at $m/z = 106$ and 120, which were assumed to be xylenes (XYLs) and trimethylbenzenes (TMBs), respectively. Note that ethylbenzene is present in XYLs for MPI. This indicated that XYLs and TMBs were significantly present in the paint vapor. The greatest benefit of the MPI is that the same samples can be analyzed for multiple compounds. For the paint analysis, comparison among compounds can be conducted without influences of the coating manner. Relative variations of nonresonant species were reasonably observed although isomers could not be separated. In the experiment shown in Figure 2 (0.52-g oil-based paint, $\lambda = 266.83\,\mathrm{nm}$, $F = 8\,\mathrm{cm^3\,s^{-1}}$, $V = 390\,\mathrm{cm^3}$, and $S = 72\,\mathrm{cm^2}$), $m/z = 106$ and 120 were simultaneously monitored. The decreasing time constants τ were observed as $1.1 \times 10^3\,\mathrm{s}$ and $2.3 \times 10^3\,\mathrm{s}$ at $m/z = 106$ and 120, respectively. The saturated vapor pressures at 298 K were 0.04, 0.01, and 0.003 bar for toluene, *m*-xylene, and 1,3,5-TMB, respectively.[8] It was confirmed experimentally that highly volatile compounds were rapidly vaporized from paint. To accurately determine detailed emission factors of highly volatile compounds for paint samples, the chamber combined with REMPI-TOFMS is powerful and promising.

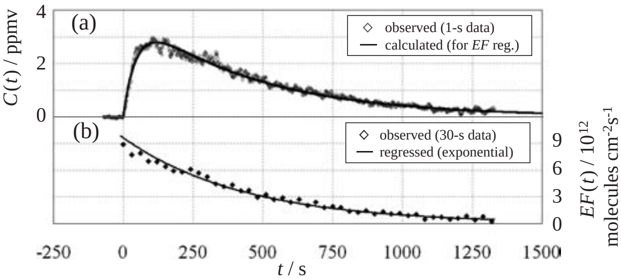

Figure 2. Variations of toluene emitted from a paint-coated plate: (a) observed concentrations (diamonds); (b) emission factors *EF*, observed (diamonds) and exponential regression (solid line). Concentration calculated from *EF* is indicated as solid line in (a).

This work was supported in part by a Grant-in-Aid for Scientific Research, KAKENHI (No. 19710006) and the Special Coordination Funds for Promoting Science and Technology, from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government.

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Published on the web (Advance View) December 13, 2008; doi:10.1246/cl.2009.74