Emission of Methane from Stainless Steel Surface Investigated by Using Tritium as a Radioactive Tracer

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Gas-phase methane contamination caused from stainless steel (SS) surface by metal–metal friction was investigated by introducing tritium as a tracer of hydrogen atom in the metal surface. The emissions of HT, CH_3T, and CH_4 were measured by radio-gas-chromatography, and the SS canister containing many small SS balls inside was shaken to reproduce the metal–metal friction. The results indicate that the oxide layer on SS surface is controlling the emission of methane.

Atmospheric methane is one of the greenhouse gases and is believed to cause the global warming.[1] Its present atmospheric concentration is about 1.75 ppmv[2] (ppmv = 10^{-6} v/v) with increasing rate of roughly 0.5–1% per year during the past quarter century by analyzing atmospheric samples collected in flasks using FID gas chromatography.[1–4] This increase of atmospheric methane has been brought by the increasing human activity.[1] In order to investigate the natural background concentration of atmospheric trace gases during the preindustrial era, antarctic ice core samples have been analyzed by extracting the enclosed ancient air. For extracting the air for measurement of the ancient carbon dioxide (CO_2) concentration, a milling cutter or crushing method of ice samples in a evacuated stainless steel (SS) system has been used without melting the ice because of the solubility of CO_2 in water.[5] Although the same dry extraction method of the enclosed ancient air was applied to the measurement of dinitrogen oxide (N_2O) and methane,[6,7] these frozen crushing methods were not able to be applied to the methane measurement owing to unknown and unavoidable large amount methane generation and contamination from the SS parts.[7,8] The methane contamination was also observed from a SS metal bellows pump.[9] Therefore, the determination of the ancient methane concentration at all the institutes in the world is conducted by melting the ice core samples (separately from the CO_2 and N_2O measurements), though the process of methane emission from the SS with metal–metal or metal–ice friction has not been elucidated.

While the distribution and behavior of the hydrogen or hydrogen isotopes in the metal surface have been studied, those spectroscopic methods are not able to be applied to the trace amount methane analysis at the metal surface. Therefore, we have tried to apply radioisotope H-3 (tritium; T) to investigate the generation and emission of methane from SS surface. In order to simulate and accelerate the emission of methane from SS, we prepared SS canisters containing many small SS balls inside to increase the metal surface area and to apply metal–metal friction by shaking the canisters.

All-metal canisters made of Type 316 stainless steel (SS316) (Swagelok SS-4CS-TW-50; 22-mm inner diameter, 1.7-mm wall thickness, 140-mm length, 50-cm^3 inner volume, 103-cm^2 inner surface area) were typically used in the experiment. About 1800 small balls made of SS316 (3-mm diameter, total 200-g weight, 25-cm^3 volume, 500-cm^2 surface area) were placed in each SS canister. The canister with SS balls was evacuated for 24 h at 383 K as conditioning the sample canisters used for background air sampling.

For the injection of tritium into the SS surface, T_2 gas diluted with D_2 ($T_2/D_2 = 0.24\%$; 5.2 TBq/mol) was introduced into the canister up to 150 Pa (T: 7.5 MBq). The whole canister was wrapped with thick aluminum foil, a tape heater, and again thick aluminum foil for uniform heating. It was heated at 500 K for 46 h. The remaining gas in the canister after cooling was analyzed by radio-gas-chromatography (Radio-GC), and 5.4 MBq tritium (72% of introduced) was shown to be adsorbed into the surface of the SS canister and balls.

After evacuation of the remaining gases to high vacuum with a turbo-molecular pump at room temperature, 15 kPa helium (>99.99995%) was introduced into the canister and left for 12 h without shaking. Then, the helium inside was analyzed to confirm that HT, CH_3T, and CH_4 were not found in the canister. After its evacuation, 15 kPa helium was introduced into the canister and heated for 30 min with the tape heater. It was shaken with being heated for 15 min with 240 strokes per minute (3600 strokes in total) using a shaker of main use for separating funnels. The trace gases emitted into the helium in the canister were analyzed with the radio-GC system.

The system consists of a SS vacuum line for sample aliquot introduction, two stage cryogenic purification and/or preconcentration columns at low temperatures, a GC separation column, and an internal-gas-flow type proportional counter for tritiated gas detection, or an FID for CH_4 amount determination.

The analytical conditions are as follows. The sample gas containing desorbed HT and emitted methane (CH_3T and CH_4) was passed through the first trap column (packed with glass beads, SS 1/8-inch o.d., 1-m long) at 201 K to remove water component, then enriched with the second trap column (packed with molecular sieves 13X, 1/8-inch o.d., 1-m long) at liquid nitrogen temperature (77 K). After switching the valves, the second trap column was heated at 363 K and the trapped components were injected into the GC separation column (packed with molecular sieves 13X, 1/8-inch o.d., 2-m long) at 333 K. The separated methane (CH_4) was determined with the FID (Shimadzu FID-14) while HT and CH_3T were determined with the proportional counter (Aloka GC-2003BU).

After evacuation of the remaining gas in the canister to high vacuum, the canister was filled again with pure helium and the experiment was repeated under different temperature conditions. The heating temperature was 298, 343, 393, and 473 K (from the 1st day to the 14th day, three runs every day).

Figure 1 shows the amount of CH_4 emitted from SS. Emission of 3×10^{-6} mmol (in 15 min) corresponds to the contamination of CH_4 in the helium with mixing ratio of 19 ppmv which

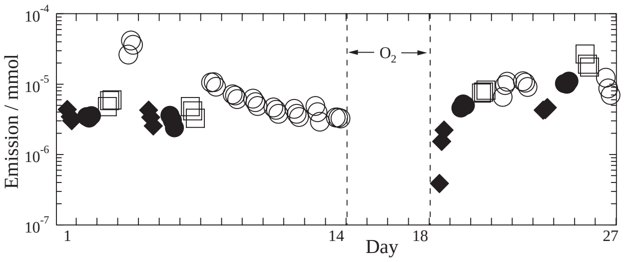

Figure 1. Emission of CH_4 from SS316 canister observed by FID-GC after the 15 min shaking. ◆: 298 K, ●: 343 K, □: 393 K, ○: 473 K.

is much higher than the CH_4 concentration in the atmosphere. Although the emission of CH_4 with shaking increased at 473 K, it was not affected much with temperature at lower temperatures suggesting that the similar methane emission may have occurred at the frozen ice core analysis. The emission of CH_4 gradually decreased with repeated extraction at higher temperature owing to larger emission of CH_4.

Figure 2 shows the emissions of desorbed tritiated hydrogen gas (mainly HT) and newly generated tritiated methane (mainly CH_3T) from SS which were found in the same fractions shown in Figure 1. While the emission of HT showed larger temperature dependence, the emission of CH_3T showed very similar behavior to that of CH_4. The specific radioactivity of methane (CH_3T/CH_4) was almost constant in the first 14 days being independent of the temperature, which also indicates no effect of β-ray radiation from tritium.

Reversal symbols with asterisk in Figure 2 show the result without shaking the canister (i.e., only the temperature change). Only HT was found in the helium with large temperature dependence; no emission at 298 K and sharply increased at from 343 to 473 K. However, CH_3T and CH_4 were not observed at all at any temperature without shaking the canister.

The excellent corrosion resistance of SS is originated in the surface oxide layer which is generated immediately with oxygen in air. Therefore, the surface of SS canister and balls is always covered with the oxide layer. Since only HT was observed when the canister was heated (343 to 473 K) without shaking, hydrogen atoms which exist inside SS passed through the oxide layer, though CH_3T and CH_4 were not observed even at 473 K. This behavior strongly suggests that the carbon-containing species which generate CH_4 and CH_3T are not able to pass through the oxide layer. On the other hand, since CH_4 and CH_3T were observed regardless of temperature when the canister was shaken, a part of the oxide layer may have been destroyed with metal–metal friction or collision by the shaking, and CH_4 and CH_3T (or their precursors) were emitted from the part where the oxide layer was lost temporarily. Moreover, hydrogen atoms (H and T) passed not only through the oxide layer but also through the part where oxide layer had been lost because the emission of HT was also accelerated at lower temperatures by shaking.

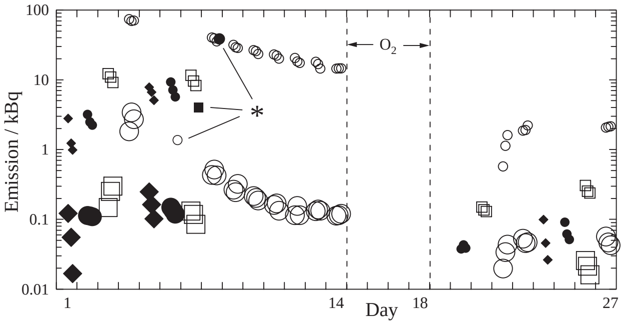

Figure 2. Desorption of HT (above, smaller symbols) and emission of CH_3T (below) both observed by radio-GC after the 15 min shaking. The temperatures for the symbols are the same as those in Figure 1. Symbols with $*$ at between the 6th and 8th day are results without shaking; ○: 343 K, ■: 393 K, ●: 473 K.

In order to confirm that the oxide layer is controlling the emission of CH_3T and CH_4, the gas introduced into the canister was changed from He to O_2, and the same experiment was repeated from the 15th day to the 18th day in the Figures 1 and 2. The emissions of HT, CH_3T, and CH_4 were not observed at any temperature. While the present instrument is not able to measure water, the hydrogen atoms passed through the oxide layer reacted with O_2 (producing HTO and H_2O), and HT was not observed. This result also suggests that the O_2 quickly recovers the part of oxide layer destroyed by metal–metal friction during the shaking. When the introduced gas in the canister was returned from O_2 to He and the experiment was repeated (from the 19th day to the 27th day), HT, CH_3T, and CH_4 were again generated gradually as before. The remaining tritium in the SS started again to be released as HT and CH_3T.

As a conclusion, carbon-containing species in the SS near the surface are suggested to pick up hydrogen atoms (including tritium atoms) and to be emitted from the SS surface as methane (CH_4 and CH_3T) only when the oxide layer is destroyed temporarily by metal–metal friction.

Our experimental results well reproduced and explained the methane contamination from SS during the mechanical extraction of ancient air in the frozen ice core samples under the evacuation and similar methane contamination by SS metal–metal friction.

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References

1 *IPCC, Climate Change 2001: Synthesis Report*, ed. by R. T. Watson, Core Writing Team, Switzerland, **2001**.
2 E. J. Dlugokencky, S. Houweling, L. Bruhwiler, K. A. Masarie, P. M. Lang, J. B. Miller, P. P. Tans, *Geophys. Res. Lett.* **2003**, *30*, 1992, DOI: 10.1029/2003GL018126.
3 D. R. Blake, E. W. Mayer, S. C. Tyler, Y. Makide, D. C. Montague, F. S. Rowland, *Geophys. Res. Lett.* **1982**, *9*, 477.
4 M. A. K. Khalil, R. A. Rasmussen, *Atmos. Environ.* **1987**, *21*, 2445.
5 E. Moor, B. Stauffer, *J. Glaciol.* **1984**, *30*, 358.
6 M. Leuenberger, U. Siegenthaler, *Nature* **1992**, *360*, 449.
7 B. Stauffer, G. Fischer, A. Neftel, H. Oeschger, *Science* **1985**, *229*, 1386.
8 G. I. Pearman, D. Etheridge, F. de Silva, P. J. Fraser, *Nature* **1986**, *320*, 248.
9 Y. Tohjima, T. Tominaga, Y. Makide, Y. Fujii, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3457.