

## Synthesis and evaluation of near real air CO<sub>2</sub> reference gas

Keiichi Katsumata<sup>1</sup>, Toshinobu Machida<sup>1</sup>, Hitoshi Mukai<sup>1</sup>, Jun Sonobe<sup>2</sup>, Megumi Isaji<sup>2</sup>, Tracey Jacksier<sup>3</sup>, and Adelino Fernandes<sup>4</sup>

<sup>1</sup> National Institute for Environmental Studies, Japan; katsumata.keiichi@nies.go.jp

<sup>2</sup> Air Liquide Laboratories, Japan

<sup>3</sup> Delaware Research & Technology Center, Air Liquide, USA

<sup>4</sup> Air Liquide Portugal, Portugal

Laser-based instruments are the widely-used analyzers for measuring atmospheric CO<sub>2</sub> and trace gas mole fractions because of its high precision as well as easiness of operation. However, these measurements are affected by both the isotopic composition of CO<sub>2</sub> (Lee et al., 2006, Tohjima et al., 2009) and by the O<sub>2</sub>/N<sub>2</sub>/Ar composition of Air (Chen et al., 2010, Nara et al., 2012). Several kinds of “near real air” gas mixtures were synthesized, measured and evaluated using several analyzers.

Gas mixtures of pure CO<sub>2</sub> with adjusted isotope ratios in balance air were used as “near real air” samples: compressed dry natural air gas was used as the “real air” sample. The isotope ratio of pure CO<sub>2</sub> gas was adjusted to  $\delta^{13}\text{C} = -8.0\text{‰}$  (VPDB) and  $\delta^{18}\text{O} = +11.9\text{‰}$  (VPDB) by mixing CO<sub>2</sub> gases which had different isotope ratios by Air Liquide. Gas mixtures of containing the pure isotopically adjusted CO<sub>2</sub> and purified natural air (Grade 1, Japan Fine Products) were filled in 10L Luxfer aluminum cylinders at NIES. Gas mixtures of the adjusted isotopically pure CO<sub>2</sub> and CO<sub>2</sub>-free natural air (Alphagaz Natural Air, Air Liquide) were also filled in 10L Luxfer aluminum cylinders at NIES. Dry natural air gases were filled in aluminum cylinders by NIES at Tsukuba, Japan (CO<sub>2</sub> ~ 410 ppm, H<sub>2</sub>O < 3 ppm) and by Air Liquide in Spain (Alphagaz Natural Air, Air Liquide). In these experiments, gas mixtures of CO<sub>2</sub> with fossil fuel combustion origin and purified natural air were used as reference gases. Both the sample gases and reference gases were calibrated using NDIR (LI-6252, Li-COR) against NIES 09 CO<sub>2</sub> scale. Mole fractions of sample gases were corrected for biases due to different CO<sub>2</sub> isotopes ratios between the sample gases and the secondary reference gases because the secondary reference gases were mixtures of fossil fuel combustion CO<sub>2</sub> ( $\delta^{13}\text{C} = -32.5$  to  $-25.3\text{‰}$  (VPDB),  $\delta^{18}\text{O} = -29.4$  to  $-22.7\text{‰}$  (VPDB)) and purified natural air (Tohjima et al., 2009). To evaluate these samples, they were measured with CRDS (G2401, Picarro and G2101i, Picarro) based on the reference gases.

### References

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