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Development of Low-Cost Network of Sensors for Extensive In-Situ and Continuous Atmospheric CO₂ Monitoring

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1. Introduction

Extensive and dedicated measurements of carbon dioxide concentrations in the atmosphere are increasingly recognized as a necessary step in verifying anthropogenic carbon dioxide emissions and as necessary methods to support international climate agreements (Marquis & Tans, 2008; NRC, 2010; Tollefson, 2010). The successful launch of the Greenhouse Gas Observing Satellite (GOSAT) on 23 Jan 2009 by Japan's Aerospace Exploration Agency (Heimann, 2009), followed by a not successful launch of Orbiting Carbon Observatory (OCO) on 24 Feb 2009 (Brumfiel, 2009; Kintisch, 2009) all vindicate the importance of extensive and accurate carbon dioxide measurements as a necessary step in global carbon emission verification (Haag, 2007; Normile, 2009; Tollefson & Brumfiel, 2009). We note that a replacement to the OCO is now actively in plan in NASA (Hand, 2009). Other satellite instruments such as Aqua AIRS (Chahine et al., 2006), and SCIAMARCHY (Barkley et al., 2006) have also provided retrieved CO₂ concentration in the vertical column.

In Europe, an ongoing new research infrastructure called Integrated Carbon Observing System (ICOS) is dedicated to establish and harmonize a network of atmospheric greenhouse sites (<http://www.icos-infrastructure.eu>). A list of present-day carbon dioxide monitoring sites whose standard gases have traceability to the World Meteorological Organization (WMO) standard is reported in WDCGG (2007).

In addition to these satellite remote sensing measurements and land-based in-situ measurements, carbon dioxides also been measured from in-service commercial aircrafts such as CONTRAIL (Matsueda & Inoue, 1996; Machida et al., 2008) and the planned flights of IAGOS (Volz-Thomas et al., 2007), research aircraft such as the HIPPO (<http://www.ucar.edu/news/releases/2009/hippovisuals.shtml>), and in-service container cargo ships (Watson et al., 2009;).

Given the important status of carbon dioxide in affecting earth's climate, however, detailed measurements of carbon dioxide close to areas with heavy industrial emissions and intense anthropogenic activities are relatively rare (Tollefson, 2010). This is in a sharp comparison with other intensively observed air pollutants such as ozone, carbon monoxide, nitrogen

oxides, sulfur dioxide, and suspended particles. Since detailed measurements of carbon dioxides close to anthropogenic areas where carbon dioxide is being relentlessly emitted into the atmosphere are required to estimate its annual emission inventories (NRC, 2010), more portable and flexible measurements but in the meantime accurate and traceable to WMO standards are needed to significantly increase carbon dioxide measurements where carbon dioxide been emitted. Burns et al. (2009) described a portable trace-gas measuring system to measure carbon dioxide. In this work we develop a GFC-based measurement system for extensive carbon dioxide measurements that are traceable to the WMO NOAA CO₂ standards.

2. Method

In this work we use a fast-response high-precision CO₂ analyzer as the core for our CO₂ measurements. The analyzer, EC9820T, was made by ECOTECH, Australia (ECOTECH, 2007). The EC9820T was built based on the principle of gas filter correlation (GFC) and the nondispersive infrared (IR) absorption of CO₂ near 4.5 microns which is used to determine the presence of the CO₂.

Analyzer

Fig. 1. A top view of the EC9820 CO₂ analyzer.

Fig. 1 shows a photo of the top view of the CO₂ analyzer used in this work. The analyzer comprises three basic components: the sample flow components (valve manifold, particulate filter, pump, Teflon tubes, dryer, etc), the optical measurement components (motor, IR sources, measurement cell, IR detector), and computer control component (microprocessor boards located at the lower half of the unit, power supply, and fan).

Fig. 2. A schematic diagram showing the major component of the EC9820 CO₂ analyzer (ECOTECH, 2007).

The exact locations of these components are shown in more details in Fig. 2. The FRONT presents a mini-terminal like operational interface where the operations and calibrations of the analyzer can be done from this region. The REAR indicates area where sample flow tubes (including ZERO CO₂ airs, span gases, exhaust, and purged air which provide zero CO₂ air to the chamber that houses gas correlation wheel) are connected with the analyzer. The optical components are the locations where the GFC principle is in action and measuring the atmospheric CO₂ concentrations. The measured results are stored in the onboard computer storages. The measurement cycles, and the control of manifold valves where different airs (zero CO₂ air, span CO₂ airs, and sample air) are entirely controlled by the onboard microprocessor unit. The analyzer analyzes CO₂ concentrations, using the GFC principle, and stores the analyzed (measured) results in the onboard computer storage area. This distinctive capability makes the analyzer a self contained unit which is characteristically suitable to conduct portable and accurate CO₂ measurements that are traceable to WMO NOAA standards. The independent of the analyzer from the need of an additional data logger makes the entire operation understandable and sustainable.

Fig. 3 is a flow chart showing a typical loop for sample air measurement. The sample air is sucked in from the SAMPLE IN (on the left) by the the PUMP which connected to SAMPLE EXHAUST (on the right). The pump maintains the sample flow rates at 1 liter per minute. The sample air first passes filter paper where filters our suspended particles in the sample before entering the measurement cell. On the top, the MOTOR drives the rotation of gas filter wheel, which is illuminated with the broadband IR sources (more details of the operational principle of IR sources and gas filter wheel will be discussed later). The DETECTOR detects the concentrations of CO₂ in the sample air, and the electrical signals are sent to preprocessor and micro processor boards to determine and store the measured results.

Fig. 3. A flow-chart diagram for the EC9820 CO2 analyzer (ECOTECH, 2007).

Fig. 4. A pneumatic diagram for EC9820 CO2 analyzer (ECOTECH, 2007).

Fig. 4 shows a pneumatic diagram of the CO₂ analyzer. The externally given zero CO₂ air, span gases, and sample airs are input to the analyzer through the electronic valve manifold. The span gases normally comprise of two working standards which are calibrated against WMO NOAA CO₂ standards provided by NOAA ESRL CCL. All inlet airs pass through a particulate filter to remove suspended particle in the air. The inlet air then enters the measurement cell where GFC principle used to measure CO₂ levels. Additional zero CO₂ air is provided through auxiliary (AUX) inlet at a flow rate of 0.5 liter per minute. The purpose of this purge air is to fill the chamber that houses gas correlation wheel and the IR source with zero CO₂ air therefore the interference of CO₂ between IR source and gas correlation wheel can be removed.

Fig. 5. A schematic diagram showing the optical component of the analyzer (ECOTECH, 2007)

More detailed structure of GFC principle used in measuring CO₂ levels is shown in Fig. 5. From the left-most part is the motor, which rotates the gas filter correlation wheel. Between the motor and the wheel is a broadband IR sources that constantly emit IR sources to the two small chambers that enclose pure CO₂ and N₂ airs, respectively (Fig. 6). When the IR sources pass CO₂ chamber, the IR centered at 4.5 microns will be absorbed and removed while the rest IR spectrums pass CO₂ chamber and enter the measurement cell. On the other hand, when the IR sources pass N₂ chambers, nothing will be absorbed by the N₂ chamber and all IR sources enter the measurement cell where the absorption at 4.5 microns will be occurred due to the CO₂ in the measurement cell. The IR sources then pass a narrow band pass filter that allow near 4.5 microns the leave the measurement cell and to be detected by the IR detector on the right-most part.

GFC-based technology has been extensively used for providing CO measurements in the atmosphere (Dickerson & Delany, 1988; Doddridge et al., 1994; Doddridge et al., 1998; Gerbig et al., 1999; Novelli, 1999; Chen and Xu, 2004; Wong et al, 2007; Zellweger et al., 2009).

Fig. 6. A schematic diagram showing the top and side views of the gas correlation wheel used in the optical component of the analyzer (ECOTECH, 2007).

3. Results

3.1 Constant SPAN test

Fig. 8. A constant span test for a CO₂ analyzer in the laboratory.

A total of eleven EC9820 CO₂ analyzers have been installed since June 2009 for atmospheric CO₂ measuring. Each CO₂ analyzer was tested in the laboratory before start taking measurements. Fig. 8 shows a constant span test that run continuously for 48 hours using a given working standard. This test was run with 2-hour background frequency (the white gas seen in the data). The output frequency is 2 seconds. The results show that the instrument is very stable from this continuous span test. The constant span tests, and later added constant zero CO₂ tests, are good ways to rigorously test if an analyzer is stable and fit for making measurements.

3.2 Inter comparisons between analyzers

Fig. 9. Inter comparisons of CO₂ sample measurements (raw data, in the units of ppm) between three analyzers for the period from 28 October to 4 November 2009.

Fig. 10. Intercomparisons of CO₂ sample measurements (raw data, in the units of ppm) between two analyzers for the period from 28 October to 4 November 2009.

In addition to the constant span tests and zero tests, analyzers were continuously tested against each other in the laboratory. Fig. 9 shows a time-series plot of a test run between three CO₂ analyzers from 28 October 4 November 2009. The results shown here are raw data (un-calibrated data), which shows great consistency in these analyzers. Fig. 10 shows another test results from inter comparisons of two analyzers in a second laboratory. The occasional short bursts of high CO₂ concentrations close to 500 ppm were resulted from the researchers making routine maintenance and download of data from the analyzers. Fig. 10 very nicely show that measurements are consistent with each other; and the effect of human presence can be quickly response in the measured data.

3.3 Inter comparisons between GFC and CRDS analyzers

Fig. 11. Inter comparisons of CO₂ measurements between GFC and CRDS-based analyzers for the period from 25 November to 8 December 2009

During the period of late 2009 and early 2010, we have had a chance to have an analyzer based on cavity ring down spectroscopy (CRDS) principle running in our laboratory. This analyzer was built by Los Gatos Research Inc., USA (van der Lann et al., 2009). Fig. 11 shows a comparison of time-series plot for the period from 25 November to 8 December 2009. These results indicate a good consistency between the measurements (correlation coefficient= 0.99).

3.4 CO₂ measurements in campus

Fig. 12 shows a time-series plot of CO₂ measurements at two sites in the campus of National Central University (NCU) for the period from 13 to 21 February 2010. These two sites are separated by 400 m. One analyzer has its sample inlet located at 15 meter height (blue

curve), while the other analyzer has its sample inlet located at 35 meter height (red curve). Both measurements were conducted with two working standards that are traceable to WMO NOAA standards. Fig. 12 shows that the measurements are very consistent with each other. The period from 24 to 19 February 2010 is the Chinese New Year in Taiwan, and the measured CO2 concentrations are basically very close to 400 ppm and with little variations. However, after the long holiday was over, the return of working people clearly impacted CO2 levels as shown in the days on 20 and 21 February 2010. After 22 February 2010, Fig. 13 shows variations of CO2 during the normal human activity. The CO2 concentrations vary between 400 and above 470 ppm. The sharp contrast between the long holiday period (Fig. 12) and normal working days (Fig. 13) clearly shows the impact of anthropogenic activity on the atmospheric CO2 concentrations.

Fig. 12. A time-series plot shown CO2 measurements at two site in the campus of National Central University (NCU) for the period from 13 to 21 February 2010.

Fig. 13. CO2 measurements at a site in the campus for the period from 22 February to 2 March 2010.

Fig. 14. Time-series plots of CO2 measurements (in the units of ppm) at two sites (blue curve indicates results from 15-m height sample inlet, red curves indicates results from 35-m height sample inlet) in the NCU campus for the period from 12 to 17 May 2010.

Fig. 14 shows another comparison of continuous CO2 measurements at two sites in the NCU campus. Again, we observe the great consistency of CO2 measurements. These results vindicate that our methodology can be consistently applied for a long period, and the use of the GFC-based analyzer with the working standards traceable to WMO NOAA standards ensure that our measurements meet WMO requirements (WDCGC, 2007).

3.5 Indoor CO2 measurements

Fig. 15. Indoor CO2 measurements taken in a classroom with 30 students inside on 8 Mar 2010.

In addition to outdoor CO2 measurements shown before, we have also conducted indoor CO2 measurements to understand the variations of CO2 inside a room. Fig. 15 shows a time-series plot of CO2 measurements in a classroom with 30 students at NCU campus on 8 Mar 2010. The build up of the CO2 from 14:30 to 15:20 local time was due to the close of both doors of the classroom. The reduction from about 15:20 to 17:00 was due to the open of a door for ventilation (the air was too stuffy). The effect of ventilation in removing indoor accumulation of CO2 is clearly seen in these results. The measurements also nicely contrast indoor CO2 concentrations with those coming for ambient air, which was taken after 17:00 local time.

Fig. 16. Indoor CO2 measurements taken in a 100-people working office for the period from 9 Mar to 16 Mar 2010.

Fig. 16 shows another indoor CO2 measurement taken in a 100-people working office for the period from 9 to 16 Mar 2010. Here we see clearly the daily accumulation of CO2 inside the office from about 08:00 local time to peak at about 13:00-15:00 in the early afternoon. The reductions after 15:00 are due to the gradual leaving of people from the office and the accumulated effect of ventilation to counter the CO2 accumulation inside the office. The smooth CO2 concentrations inside the office during the weekend (13-14 March) are clearly seen.

3.6 CO2 measurements onboard a in-service container ship

One of the main motivations to develop GFC-based CO2 measurements is to conduct global CO2 measurements over the Pacific regions. We have vigorously tested this idea since June 2009. Fig. 17 shows a service route from a container ship called EVER DECENT during its service for the period from 22 January to 26 Mar 2010. The detailed operations and installation of the GFC analyzer and CO2 working standards will be reported in a separate work. Fig. 18 shows results from this cruise. The measurements show that CO2 levels are close to 400 ppm when the measurements were taken over the marine atmospheric boundary layer. However, the CO2 levels increase sharply as soon as the ship approached a port. This plot very nicely shows that anthropogenic activity as the key sources for atmospheric CO2 levels. More results on the ship-based measurements will be presented in separate publications this year.

Fig. 17. A service route for EVER DECENT for the period from 22 January to 26 Mar 2010.

Fig. 18. A time-series plot of a ship-based measurement made by EVER DECENT

4. Summary

In this work we demonstrate the development of a GFC-based technology for making continuous in-situ atmospheric CO₂ measurements for climate policy decision makers. All GFC-based analyzers were rigorously tested in the laboratory before went to the field for measurements. All CO₂ measurements were made with two CO₂ working standards that are traceable to the WMO NOAA CO₂ standards. All CO₂ working standards were routinely calibrated again six bottles of WMO NOAA CO₂ standards.

Great effort has been taken to ensure that the atmospheric CO₂ measurements follow the WMO standards (WDCGC, 2007). We have developed a series of tests to verify the measurements, including constant span test, constant zero tests, inter comparisons between GFC analyzers, and inter comparisons between GFC and a CRDS analyzer. We show some results from the land-based measurements taken in the NCU campus, indoor measurements, and a ship-based measurement. These results indicate encouraging results that can significantly increase our understanding of atmospheric CO₂ distribution.

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The book addresses the subjects related to the selected aspects of pollutants emission, monitoring and their effects. The most of recent publications concentrated on the review of the pollutants emissions from industry, especially power sector. In this one emissions from opencast mining and transport are addressed as well. Beside of SO_x and NO_x emissions, small particles and other pollutants (e.g. VOC, ammonia) have adverse effect on environment and human being. The natural emissions (e.g. from volcanoes) has contribution to the pollutants concentration and atmospheric chemistry governs speciation of pollutants, as in the case of secondary acidification. The methods of ambient air pollution monitoring based on modern instrumentation allow the verification of dispersion models and balancing of mass emissions. The comfort of everyday human's activity is influenced by indoor and public transport vehicles interior air contamination, which is effected even by the professional appliances operation. The outdoor pollution leads to cultural heritage objects deterioration, the mechanism are studied and the methods of rehabilitation developed. However to prevent emissions the new technologies are being developed, the new class of these technologies are plasma processes, which are briefly reviewed at the final part of the book.

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