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INSTRUMENTATION FOR TRACE-LEVEL MEASUREMENT OF CARBON MONOXIDE IN PRISTINE ENVIRONMENTS

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ABSTRACT

Trace level measurements of carbon monoxide (CO) in air are important for the understanding of sources and sinks of biogeochemical CO cycles in the atmosphere [Novelli et al. 1992]. Ambient CO mixing ratios of 50 parts per billion or less in pristine environments make sufficiently low detection limits necessary in order to understand the creation and propagation of CO. Some custom modifications to existing, EPA-approved, continuous CO monitors that allow such low-level measurements have been reported in the past [Dickerson and Delaney, 1988]. We report similar modifications that were implemented as standard options in modern CO monitors and which improve selectivity and stability of such instruments and decrease the detection limit significantly compared to standard instruments.

INTRODUCTION

Although gas filter correlation (GFC), non-dispersive, infrared absorption (NDIR) is the US EPA's reference method for continuous measurement of trace levels of carbon monoxide in ambient air, problems occur if the method is applied to measurements of background CO at levels below one part per million (ppm, 10^{-6} moles per mole).

Such problems can be categorized into three groups: (a) interferences by water vapor and CO₂, (b) effects of ambient temperature changes on the measurements and (c) instrument drift about the zero point.

In preparation for INDOEX, a project that involves measuring background CO in the Indian Ocean, we measured ambient CO in a mixed urban and marine environment at the Scripps Institution of Oceanography, La Jolla, California, between June and October, 1997. The mentioned problems and their solutions are characterized for the described instrument and yield a method for reliable, continuous measurements of CO that is suitable for levels below 50 parts per billion (ppb, 10^{-9} moles per mole) ambient mixing ratio.

METHOD

We describe here an Advanced Pollution Instrumentation, Inc. (API) Model 300 Gas Filter Correlation CO Analyzer, which was only slightly modified from its standard configuration. The instrument was equipped with an internal zero and span (IZS) option, which allows for internal creation of zero gas by means of a heated, metallic surface scrubber that effectively removes ambient levels of CO from the

sample gas. In addition to standard instrument options, a semi-permeable membrane dryer (Permapure NAFION dryer, model PD-625-24) was used to remove water vapor.

The detection and measurement of CO in a gas filter correlation analyzer is based on the absorption of infra red (IR) radiation by CO molecules at wavelengths near 4.7 μm . In practice, these devices use a high energy, heated element to generate broad-band IR light. This light is passed through a rotating gas filter wheel which causes the beam to alternately pass through a measurement cell containing nitrogen (N_2) and a reference cell filled with a mixture of high-concentration CO in N_2 . This alternation occurs at a rate of 30 cycles per second and causes the beam to be modulated into reference and measurement pulses. During a reference pulse, CO in the gas filter wheel effectively strips the beam of all IR energy in the absorption band of CO. This results in a beam which is unaffected by CO in the sample cell. During the measurement pulse, IR energy at 4.7 μm is not attenuated by the N_2 in the measurement cell and passes into the sample cell where CO molecules in the air sample can absorb this energy. The wheel also incorporates a chopper mask which superimposes a 360 Hz chopper signal on the IR beam to optimize detector signal-to-noise ratio.

After passing the GFC wheel, the IR beam enters the multi-pass sample cell which uses an optically-folded light path to achieve an effective absorption length of 16 m. When the light exits the sample cell, it passes through an interference-type, narrow, bandpass filter, centered at 4.7 μm and finally reaches the detector surface. The detector itself is a lead salt photo conductor, which is thermo-electrically cooled to minimize detector noise and increase sensitivity. Figure 1 shows a diagram of a gas filter correlation CO analyzer.

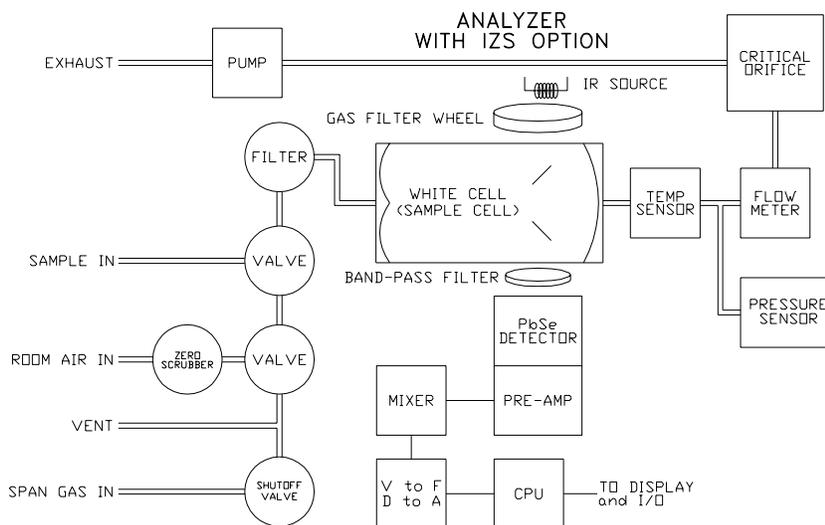


FIG.1: Gas filter correlation CO analyzer (flow diagram)

INTERFERENT GASES

At normal, urban CO levels in the low part per million (ppm, 10^{-6} moles per mole) range, interfering effects of H_2O and CO_2 are minimized by the GFC wheel yielding rejection ratios of these species on the order of $5 \times 10^{-6}:1$ and $2 \times 10^{-5}:1$ [Dickerson and Delaney, 1988]. However, the measurement is ultimately based on the Beer-Lambert Law, where the concentration is a logarithmic function of light intensity, hence, the effects of interferences increase as the CO level drops and become quite significant in the sub-ppm regime.

Fortunately, the concentration of CO₂ in ambient air is fairly stable in the short term (over several days) and, thus, is automatically corrected for using the instrument's internal zero calibration option, which produces CO-free air, which contains ambient level CO₂. If CO₂-free nitrogen were used to carry out the zero adjustment, this interference (about +7.6 ppb CO equivalent) would have to be accounted for at low CO mixing ratios.

Water vapor was reduced to about 600 ppb (-25°C dew point), resulting in an interference of no more than -3 ppb CO equivalent (the interference is negative). Interferences from other gases are small and can be neglected for practical applications owing to the very low concentrations of such gases in ambient air.

TEMPERATURE COEFFICIENTS

Temperature gradients acting on the optical components of the gas filter correlation CO analyzer can cause significant changes in the output of the device. The standard, unmodified analyzer uses a number of temperature controlled components to negate such effects. These include stabilization of the gas filter wheel (68 ± 0.05 °C) and measurement cell (48 ± 0.01 °C) which, together, account for most of the temperature related drift. Further gains could be achieved by temperature controlling the sample stream itself. However, it was found that temperature-induced fluctuations in the non-modified instrument, although non-zero, were within acceptable limits and showed significant influence only on the zero drift (see next section).

Figure 2 shows internal instrument temperatures as a function of time during one week in July, 1997. Notable on this figure is the diurnal fluctuation of the instrument's surrounding (box) temperature, which reflects the laboratory temperature, and the insensitivity of the instrument's optical components to these room temperature changes.

One design modification in the analyzer that has considerably improved the suppression of temperature coefficients is the introduction of replicated mirrors in the folded cell. In the past, glass mirrors were glued to an aluminum substrate. This glue would expand and contract under the influence of temperature gradients, practically changing the optical geometry of the cell. After 32 passes in the 0.5 meter cell, these changes could affect the angle of incidence on the detector causing measurable drift. Replicated mirrors consist of a reflective front surface molded onto an aluminum substrate, eliminating the need for gluing ground mirrors onto the substrate.

Another criterion for effective suppression of temperature effects is gas law correction. The density of the sample changes with temperature, ultimately affecting the measurement, which detects the number of CO molecules in the sample path. The analyzer is a microprocessor based instrument and uses the sample temperature and pressure as measured by a precision thermistor and differential pressure transducer to perform an ideal gas law correction to the measurement, which significantly improves measurement precision. In addition, the instrument maintains a fairly constant sample flow rate and, hence, sample pressure to minimize this correction.

One remaining, temperature related problem is illustrated in Figure 3, which shows the uncompensated zero drift values for a week of operation in September, 1997. The detector drift seems to be well correlated with even small changes in laboratory temperature (measured inside the instrument box) and the change in temperature appears to be much more influential than the absolute temperature. Thus, this problem can easily be overcome by maintaining a constant environmental temperature around the analyzer. The shown temperature changes were caused by a diurnal cycle in laboratory temperature due to insufficient or non-existing air conditioning during the shown period.

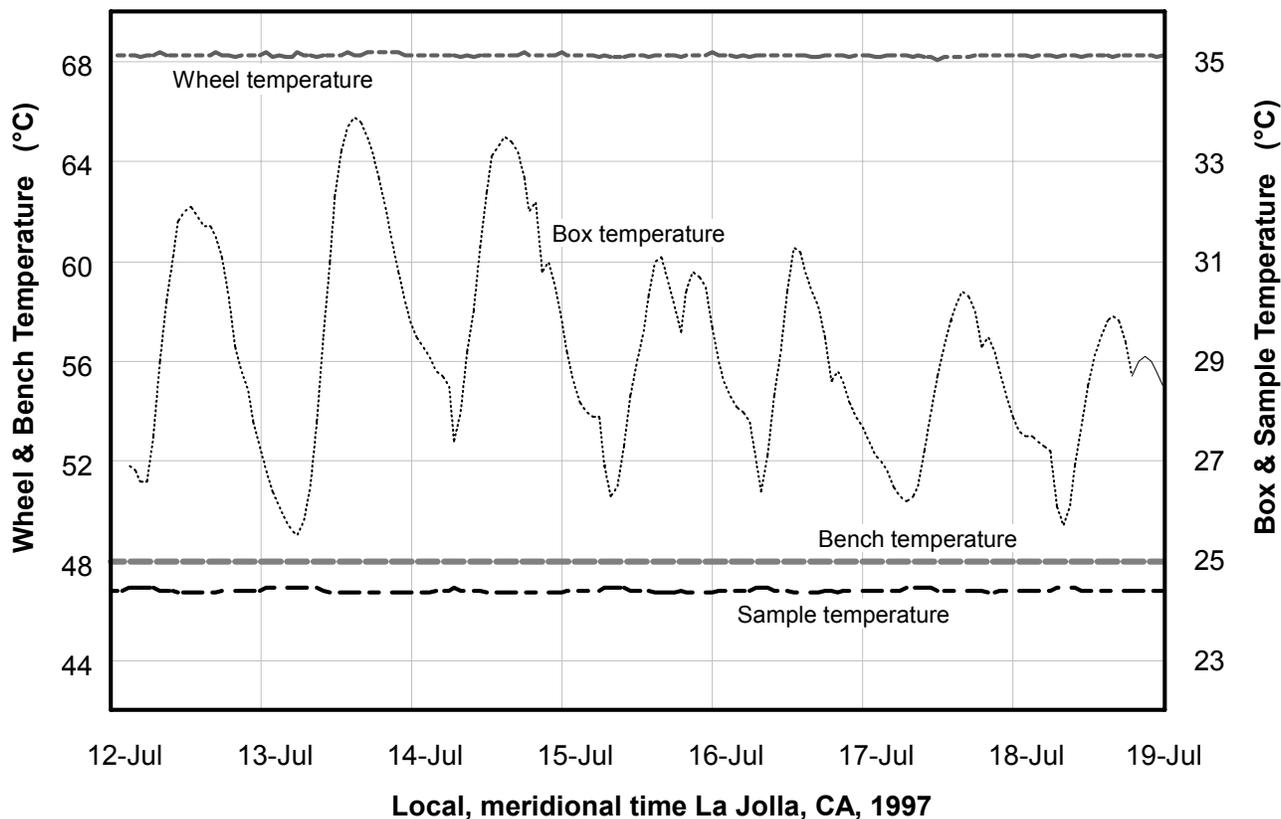


FIG. 2: One hour averages of instrument temperatures for the GFC wheel, the air sample at the exit of the measurement cell, the optical bench and the instrument box during one week of operation in La Jolla. The stability for the three fixed components is excellent and less than 0.01%, while the box temperature reflects ambient temperature changes.

ZERO DRIFT

Instrument drift about the zero point as shown in Figure 2 is acceptable in urban monitoring applications with CO mixing ratios in the ppm range, but overwhelms the measurement when CO drops below 1 ppm. The device used in this experiment has a published zero drift specification of $<0.1 \text{ ppm day}^{-1}$ ($<0.2 \text{ ppm per week}$). With a targeted lower detection limit (LDL) of $<50 \text{ ppb}$, this would equal a 200% drift in 24 hours.

As mentioned above, zero drift can be best minimized by stabilizing the ambient temperature around the instrument and drift of less than 20 ppb should be achievable over short-term periods. Any signal offsets from true zero can be kept to within 20 ppb by resetting the zero signal at the end of a 15 minute zero check, which was done in our measurements following a 30 minute measurement cycle. The zero reset (and also span calibration) can be automated by utilizing the analyzer's operating software. Upon exiting the calibration mode, the analyzer can automatically adjust the zero offset and resume CO analysis after a five minute hold-off period, which allows the sample stream to stabilize to ambient mixing ratio. This method accomplishes the goal of frequent zero drift adjustment without the need for manual intervention and minimizes drift correction.

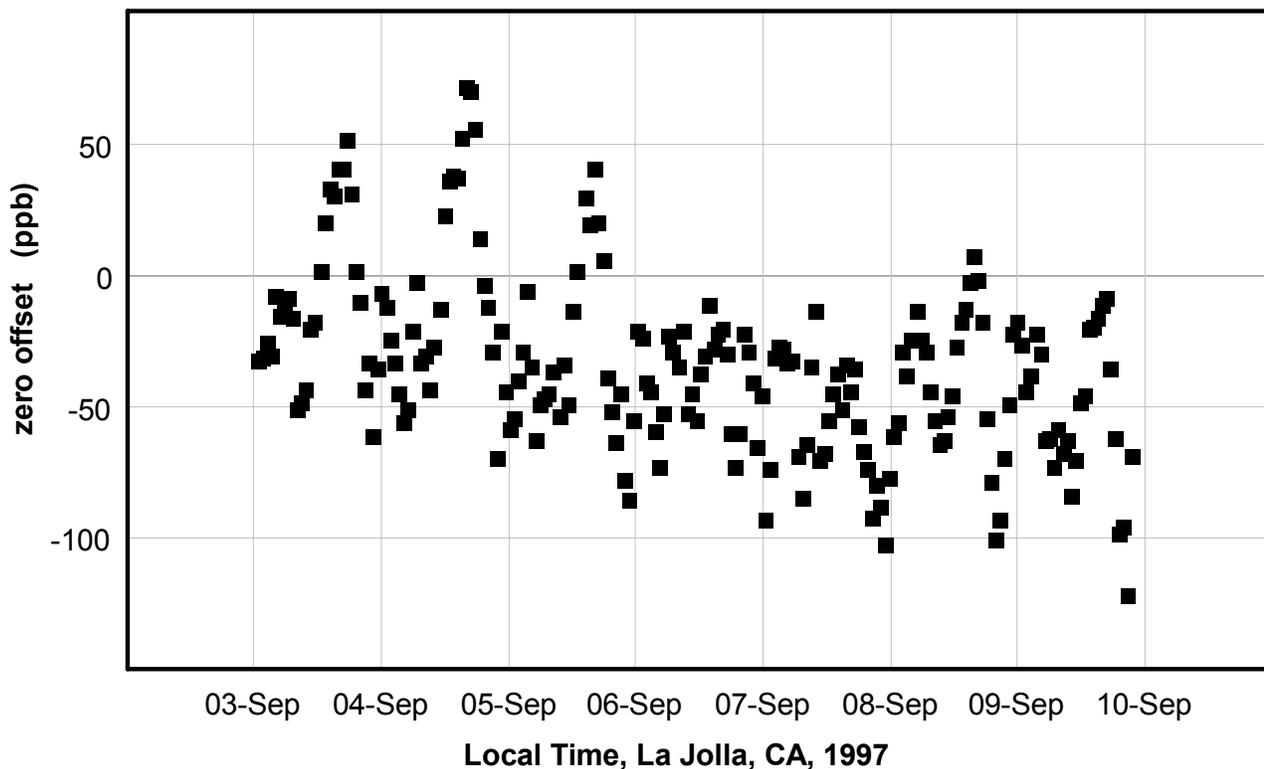


FIG. 3: Zero drift as a function of time during operation in La Jolla. The zero level was not adjusted during this period and reflects a dependence on ambient laboratory temperature.

CONCLUSION

The effectiveness of the described design modifications on instrument sensitivity can be seen in Figure 4, which is a plot of the instrument's stability figure. Each data point is composed of the standard deviation of twenty-five instantaneous measurements of the CO mixing ratio taken ten seconds apart while sampling CO-free, ambient air (with the internal zero-span option). This is, in fact, the standard US EPA method of measuring instrument related signal noise in ambient air analyzers. During our experiments in La Jolla, the stability was 5.0 ± 2.3 ppb. Defining the lower detection limit (LDL) to be twice the noise (the stability figure), yields an LDL of 10 ppb, which is well below the target range of 50 ± 10 ppb ambient CO mixing ratio found in remote, non-polluted environments.

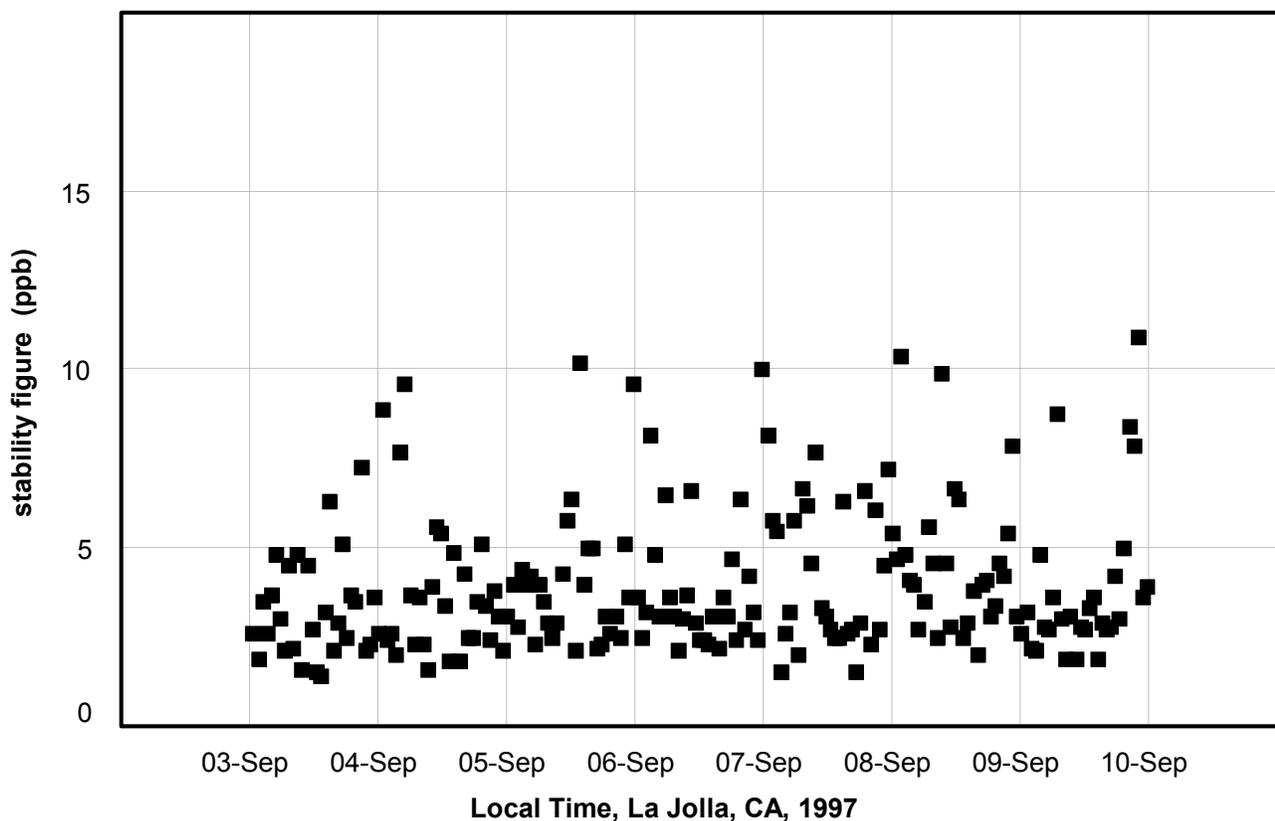


FIG. 4: Stability figure as a function of time during operation in La Jolla. The stability is a measure for the instrument precision during zero air operation.

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