

## Precise atmospheric oxygen measurements with a paramagnetic oxygen analyzer

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**Abstract.** A methodology has been developed for making continuous, high-precision measurements of atmospheric oxygen concentrations by modifying a commercially available paramagnetic oxygen analyzer. Incorporating several design improvements, an effective precision of 0.2 ppm O<sub>2</sub> from repeated measurements over a 1-hour interval was achieved. This is sufficient to detect background changes in atmospheric O<sub>2</sub> to a level that constrains various aspects of the global carbon cycle. The analyzer was used to measure atmospheric O<sub>2</sub> in a semicontinuous fashion from air sampled from the end of Scripps Pier, La Jolla, California, and data from a 1-week period in August 1996 are shown. The data exhibit strongly anticorrelated changes in O<sub>2</sub> and CO<sub>2</sub> caused by local or regional combustion of fossil fuels. During periods of steady background CO<sub>2</sub> concentrations, however, we see additional variability in O<sub>2</sub> concentrations, clearly not due to local combustion and presumably due to oceanic sources or sinks of O<sub>2</sub>. This variability suggests that in contrast to CO<sub>2</sub>, higher O<sub>2</sub> sampling rates, such as those provided by continuous measurement programs, may be necessary to define an atmospheric O<sub>2</sub> background and thus aid in validating and interpreting other O<sub>2</sub> data from flask sampling programs. Our results have also demonstrated that this paramagnetic analyzer and gas handling design is well suited for making continuous measurements of atmospheric O<sub>2</sub> and is suitable for placement at remote background air monitoring sites.

### 1. Introduction

Despite several decades of study and many recent advances in our understanding of the physical and geochemical processes involved, significant uncertainties still exist in the magnitude of terrestrial and oceanic sources and sinks in the global carbon cycle and in the processes affecting it [Schimel *et al.*, 1995]. For example, the impact of marine biota is poorly constrained and interannual variations are not quantified nor are their reasons understood [Bender *et al.*, 1996]; the concentration of atmospheric CO<sub>2</sub> is rising at a slower rate than predicted by the rate of increasing fossil fuel usage [Keeling *et al.*, 1995]; anthropogenic land changes are adding significant but uncertain amounts of CO<sub>2</sub> to the atmosphere [Schimel *et al.*, 1995]; and the oceans and undisturbed parts of the land biota are CO<sub>2</sub> sinks of uncertain magnitude. Vigorous debate continues as to the relative magnitude, spatial distribution, and physical processes involved in the partition-

ing of these CO<sub>2</sub> sources and sinks [e.g., Ciais *et al.*, 1995], and in global marine productivity estimates [e.g., Bender *et al.*, 1996].

One method for improving our understanding of the contemporary carbon cycle involves measuring changes in atmospheric O<sub>2</sub> concentrations [Bender *et al.*, 1996; Keeling *et al.*, 1993, 1996; Keeling and Shertz, 1992]. Photosynthesis and respiration processes produce coupled changes in O<sub>2</sub> and CO<sub>2</sub> concentrations from both the land and marine biota. However, differences in the physical and chemical interactions of these gases with seawater cause the fluxes across the air-sea interface to be largely decoupled. Because of these differences, information about the fluxes can be gained from measurements of both atmospheric O<sub>2</sub> and CO<sub>2</sub> that is not achievable from CO<sub>2</sub> measurements alone. There are two key differences. First, atmospheric CO<sub>2</sub> uptake by the oceans can occur with no corresponding O<sub>2</sub> flux, both because O<sub>2</sub> is relatively insoluble in seawater and because uptake of CO<sub>2</sub> by the oceans in response to increasing atmospheric CO<sub>2</sub> levels involves inorganic reactions that do not involve O<sub>2</sub>. This implies that on interannual timescales, land and marine biotic sinks for the excess atmospheric CO<sub>2</sub> can be separated and quantified from measurements of O<sub>2</sub> [Keeling and Shertz, 1992; Sarmiento *et al.*, 1998]. Second, pertinent to seasonal timescales, air-sea CO<sub>2</sub> exchange due to marine biotic activity is heavily suppressed by the seawater chemistry that interconverts dissolved CO<sub>2</sub> with other dissolved carbonate forms.

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An analytical measurement precision and accuracy of about 1 ppm O<sub>2</sub> is required [Keeling *et al.*, 1993] to be able to put useful constraints on these carbon and oxygen fluxes and to address the issues mentioned above (note that by ppm O<sub>2</sub>, we mean  $\mu\text{mole O}_2$  per mole of dry air on a CO<sub>2</sub>-free basis). To date, two independent measurement techniques have been developed which can measure atmospheric O<sub>2</sub> to this level of precision. Keeling [1988a] developed an interferometric method, where small variations in the refractive index of air are measured and related to changes in air composition. Correcting for a CO<sub>2</sub> interference effect and with some plausible assumptions on the other gases in whole air, changes in the refractive index can be related to atmospheric O<sub>2</sub> concentration and expressed in terms of changes in the O<sub>2</sub>/N<sub>2</sub> ratio [Keeling *et al.*, 1998]. Bender *et al.* [1994] developed a second method, modifying a Finigan MAT 251 isotope ratio mass spectrometer to simultaneously measure atomic masses 29 (<sup>15</sup>N<sup>14</sup>N) and 32 (<sup>16</sup>O<sub>2</sub>), also effectively measuring atmospheric O<sub>2</sub>/N<sub>2</sub> ratios. Both of these techniques require relatively expensive, dedicated instruments and, with their current design, require flask samples to be collected in order to make remote background atmospheric O<sub>2</sub> measurements.

Atmospheric O<sub>2</sub> has also been previously measured using paramagnetic oxygen analyzers [Machta and Hughes, 1970; Taylor, 1968]. However the best precision achieved (based on multiple aliquots from a flask sample) was of the order of 10 ppm, and due to the reproducibility obtained from reference gas calibrations, these workers were unable to report data with an accuracy better than 60 ppm. In this paper we describe a methodology which incorporates high precision gas handling techniques, allowing us to make substantial improvements to the analytical precision of a paramagnetic analyzer and achieving better than the required level of precision of 1 ppm O<sub>2</sub>. This new method complements the two existing methods and provides certain advantages such as lower cost and allows for continuous remote background atmospheric O<sub>2</sub> measurements.

The remainder of this paper is divided into two main sections. The first discusses the operating principle of the paramagnetic analyzer, the design improvements we have made to it, and results from experimental testing of the method. The second presents preliminary results and interpretations from ambient air sampled in a semicontinuous fashion from the end of Scripps Pier, La Jolla, California.

## 2. Paramagnetic Analyzer System Design and Testing

### 2.1. Paramagnetic Analyzer and Gas Handling Descriptions

The commercially available "Paramagnetic Oxygen Sensor, Paramax 101" from Columbus Instruments International Corporation measures oxygen concentrations by utilizing the paramagnetic properties of molecular oxygen, first discovered by M. Faraday in 1851 [Kocache, 1986]. The heart of the oxygen sensor is in fact a "PM1155B" oxygen transducer cell manufactured by Servomex Limited and described in detail by Kocache [1986]. This cell contains a small glass dumbbell suspended in a strong, nonuniform magnetic field. Paramagnetic molecules tend to align their mag-

netic moments with the field and to be attracted to areas of higher field strength. This attraction creates an air pressure gradient in the cell, which produces a torque on the dumbbell. The PM1155B employs a "self-nulling" mechanism whereby deflections of the dumbbell are detected and used to regulate an electric current flowing through a wire wrapped around the dumbbell, which produces an electromagnetic force resulting in a countervailing torque, thereby keeping the dumbbell in its original position. The output signal of the PM1155B is essentially equal to this regulating current, which is linear to the magnetic susceptibility of the airstream (the net effect from all paramagnetic and diamagnetic molecules). Table 1 shows that the O<sub>2</sub> molecule has by far the largest magnetic moment of common molecules in air, and variations in O<sub>2</sub> will dominate the variation in magnetic susceptibility of dry air. Taking into consideration typical ambient concentration changes, CO<sub>2</sub> is the next most important gas, contributing an interference effect typically  $\leq 0.6\%$  (mol per mol) that of O<sub>2</sub>. Hence to a good approximation, we can directly correlate the electric current to the paramagnetic susceptibility of O<sub>2</sub> alone and hence to the O<sub>2</sub> partial pressure of the incoming airstream.

The factory specifications for the Columbus Instruments paramagnetic analyzer quote a repeatability of  $\pm 1000$  ppm O<sub>2</sub> and a drift rate of 100 ppm O<sub>2</sub>/h, whereas in our work we need a precision in O<sub>2</sub> mole fraction of 1 ppm or better. Paramagnetic susceptibilities are inversely proportional to absolute temperature [Kocache, 1986], and clearly, O<sub>2</sub> partial pressure is directly proportional to the total pressure in the cell; so to improve the precision of the analyzer, the temperature and pressure in the cell and the flow rate of the inlet airstream need to be controlled to a very high degree of constancy. In addition to these dynamic parameters, the analyzer has a very high sensitivity to vibration and a long memory effect from shock, hence it must be carefully protected against these to reduce instrumental noise.

We interfaced the Columbus Instruments paramagnetic analyzer to the gas-handling system shown in Figure 1. The cell pressure was kept constant by using active differential pressure control. We maintained the cell at about 200 torr above ambient because it is easier to establish and maintain control at a pressure somewhat above ambient pressure. As shown in Figure 1, the required pressure elevation was achieved by passing sample gas through a diaphragm compressor pump (Neuberger, model N05). Any incoming airstream had been predried, but to ensure that all samples enter the analyzer with a common dewpoint, we passed the airstream through a cryogenic, stainless steel cold trap at -80°C. The airstream then passed through a preliminary, or "coarse," active pressure control which acts as protection against pressure "pulsing" effects from the compressor. For independent reasons, we maintained this coarse pressure regime at about  $1800 \pm 10$  torr, achieved using a 10,000 torr differential pressure gauge (Sensotec) and a solenoid valve (V1 in Figure 1; MKS, 248 Control Valve) servoed to an electronic controller (MKS, Type 250C Controller).

After passing through a four-way valve (V2; discussed below), the sample gas passed through a manual needle valve (V3 in Figure 1). This valve served two purposes; first, it isolated the two pressure control regimes from each other, and second, it protected the paramagnetic analyzer against any

**Table 1.** Molar Magnetic Susceptibilities of the Primary Constituents in Air

Species	Mole Fraction in Dry Air/ppm <sup>a</sup>	Molar Magnetic Susceptibility/ $\times 10^{-6}$ cgs <sup>d</sup>
N <sub>2</sub>	780,840	-12.0
O <sub>2</sub>	209,460	3449.0 (at 293 K)
Ar	9,340	-19.6
CO <sub>2</sub>	354 <sup>b</sup>	-21.0
Ne	18.18	-6.74
He	5.24	-1.88
CH <sub>4</sub>	1.72 <sup>b</sup>	-12.2
Kr	1.14	-28.8
H <sub>2</sub>	0.5	-3.98
N <sub>2</sub> O	0.310 <sup>b</sup>	-18.9 (at 285 K)
CO	0.02-0.25	-9.8
O <sub>3</sub>	0.0-0.1	6.7 (liquid)
NO	0.028 <sup>c</sup>	1461.0 (at 293 K)
NO <sub>2</sub>	0.035 <sup>c</sup>	150.0 (at 408 K)
H <sub>2</sub> O	0-30,000	-12.97 (liquid, at 293 K)

<sup>a</sup> Concentration data taken from Keeling [1988a], unless otherwise noted.

<sup>b</sup> From Graedel and Crutzen [1993].

<sup>c</sup> From Logan et al. [1981].

<sup>d</sup> Data taken from Lide [1992]. Gives the molar magnetic susceptibilities of the listed element or compound expressed in cgs units. A positive value indicates a paramagnetic element or compound whereas a negative value indicates a diamagnetic element or compound. Measurements at 1 atm, 298 K, unless otherwise noted.

transient flow pulses above the maximum allowable flow rate of 200 std mL/min, which could extensively damage the paramagnetic cell. Further protection was provided by the relief valve and V4 at the outlet of the analyzer.

Pressure control of the paramagnetic analyzer cell was established with a  $\pm 1$  torr (full scale) differential pressure gauge (MKS, Baratron 223BD) and a solenoid valve (V5 in Figure 1, MKS, 248 Control Valve) servoed to a second electronic controller (MKS, Type 250C Controller). The reference side of the differential pressure gauge consisted of a "Pressure Reference" volume filled with air to about 960 torr (V8 normally closed). The MKS controller maintained a zero pressure differential (precise to 0.0005 torr) across the pressure gauge by adjusting the solenoid control valve, V5. The flow design maintained constant pressure at the inlet to the analyzer by means of an adjustable bypass flow. Controlling in this way ensured that differences in the delivery pressures of reference gases or sample air would not affect the flow rate or pressure in the analyzer. V3 and V4 were set so that the flow rate through the analyzer was 120 mL/min and the bypass flow rate was 15 mL/min, as measured by downstream rotameter type flowmeters. An additional mechanical pressure gauge was located at the outlet of the analyzer as a diagnostic measure of cell pressure.

The paramagnetic analyzer, the  $\pm 1$  torr differential pressure gauge, and the "Pressure Reference" volume were all housed in a well-insulated enclosure, with the "Pressure Reference" volume further packed in polyurethane insulation. With this arrangement the analyzer response drifted on a quasi-diurnal cycle with an amplitude of about 400 ppm O<sub>2</sub>, apparently linked to the diurnal temperature cycle in our laboratory of 1°C. To reduce the effect of this instrumental drift, the sample gas was replaced every 2.5 min with a reference gas, by means of a pneumatically operated four-way valve (V2).

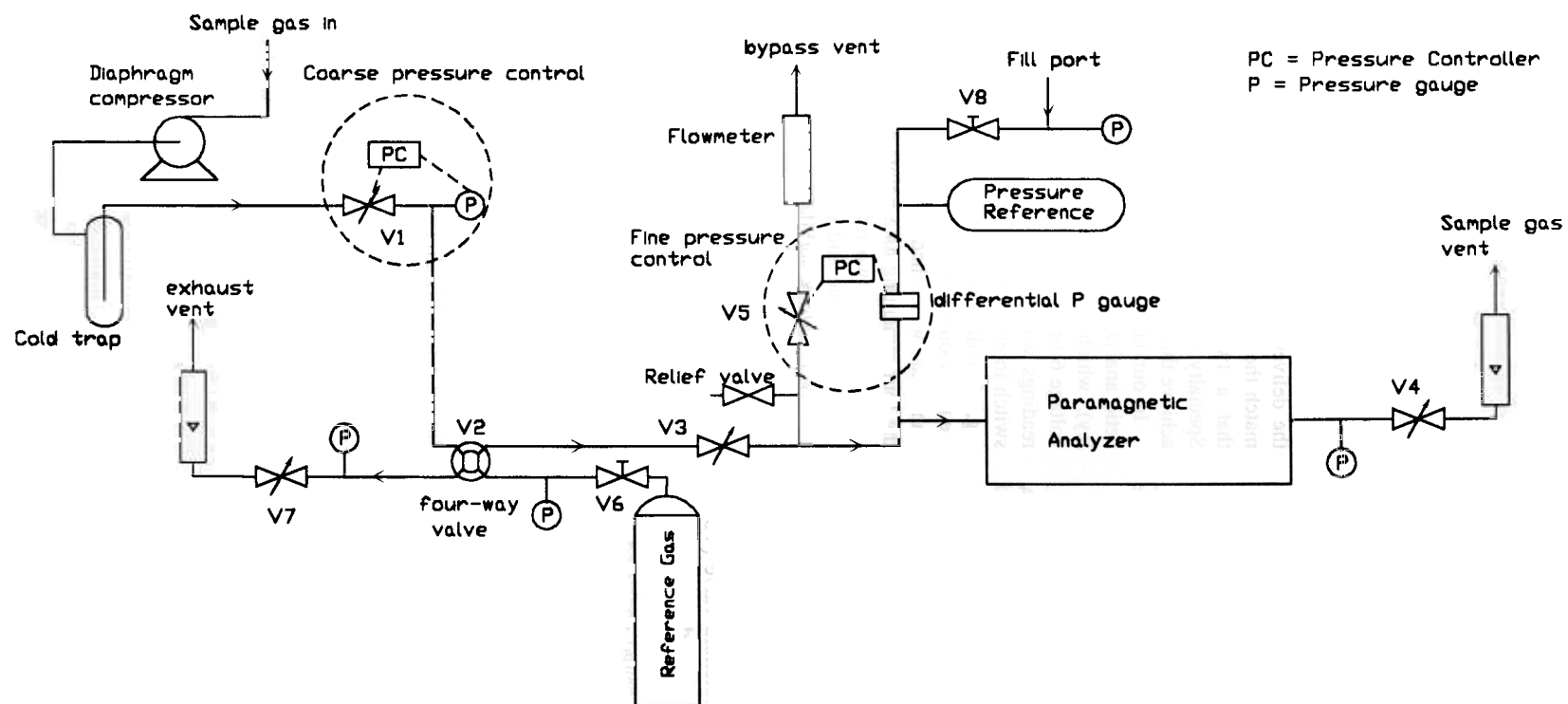
A solenoid valve, triggered by a computer to switch every 2.5 min controlled the pneumatic actuator. By computing concentration changes relative to the reference gas, we were able to null out the effect of analyzer drift on timescales longer than approximately 5 min. The gas stream not passing through the analyzer at any given time was vented through the second exit port of the four-way valve. This switching technique reduced transient pressure fluctuations induced by switching between two gas streams and maintained constant conditioning of the walls of all inner tubing surfaces. A manual needle valve (V7) was adjusted to balance the venting flow rate to the flow rate through the analyzer. In addition, the delivery pressure of the reference tank was adjusted to match the 1800 torr delivered by the sample line. We found that a two-stage high pressure cylinder regulator (Scott Specialty Gases, Model 14 series) was sufficiently precise to achieve this.

In our laboratory, data were acquired from the paramagnetic analyzer with a computer-interfaced voltmeter (Keithley), which was programmed to read the analyzer output voltage 6 times in each 30-s interval. The average of the six readings was stored in an output file. Hence in a 2.5-min switch interval, which we call a "sample jog" or a "reference jog," five data points were stored. When processing the data we threw out the first data point of each jog to avoid sweepout transients, which had a duration of about 20 s, and averaged the four remaining data points of each jog. We then linearly interpolated the two reference gas values on either side of a sample gas value and computed the difference between this interpolated value and the sample gas value.

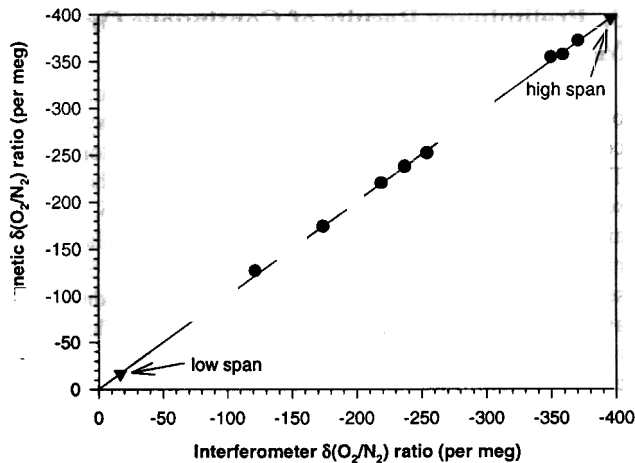
## 2.2. Fine-Tuning Improvements

To improve the flushing characteristics of the differential pressure gauge, we placed a length of capillary tubing inside the 1/8th inch tubing, forcing any incoming airstream to travel to the pressure gauge diaphragm and eliminating most of the dead volume. The paramagnetic analyzer was so sensitive to pressure changes that very small leaks on the reference volume side of the  $\pm 1$  torr differential pressure gauge, of the order of  $10^{-7}$  mbar L s<sup>-1</sup>, were problematic. Welding all fittings on this reference side eliminated these leaks. From extensive testing, we showed that the model N05 compressor did not detectably alter either the O<sub>2</sub> or CO<sub>2</sub> composition of an airstream passed through it. However, as supplied by the factory, these pumps were found to leak at the Teflon flapper plate seals, so we modified the pump heads, sealing the leak using four Viton O-rings, two on either side of the flapper plate at the inlet and outlet bore holes of the pump head.

During the design-testing phase, we discovered a source of noise with a period of about 17 s and an amplitude of 3.2 ppm O<sub>2</sub>, which was present when sample gas was passing through the analyzer but not when reference gas passed through (during which time the baseline noise was about 0.8 ppm). We eliminated this source of noise simply by adding a short coil of 1/4 inch diameter polyethylene-aluminum composite tubing (Dekoron) between the N05 compressor and the cold trap which added approximately 10 mL of buffer volume. We speculate that the noise was caused by interactions between flow pulsations attributable to the compressor and thermal diffusive fractionation within the cold trap [Severinghaus et



**Figure 1.** Schematic showing the gas-handling system used for making continuous atmospheric oxygen measurements with the Columbus Instruments paramagnetic oxygen analyzer. The "sample gas in" was either air from the Scripps Pier or a calibration gas. The "reference gas" was switched in and out with the sample gas every 2.5 min and was used to correct for the analyzer drift problem discussed in the text.



**Figure 2.** Results from a test on the linearity of the response of the paramagnetic analyzer for the range of  $O_2/N_2$  ratios expected in ambient air. The solid line is  $x = y$ . Triangles indicate the paramagnetic “high span” and “low span” cylinders, which were used to define the span of the analyzer, hence they were forced to be equal to the interferometer-defined ratios. The ratios of the other eight cylinders were then determined from this span.

*al.*, 1996]. This resulted in concentration differences between adjacent “parcels” of air, and because the flow was laminar, these concentration differences were maintained and propagated through to the paramagnetic analyzer cell.

### 2.3. Experimental Testing

To test the precision, accuracy, and linearity of the paramagnetic analyzer system described above, we conducted two main experiments. The first experiment was primarily a linearity test. Reference gas from a suite of ten gas cylinders spanning a range of  $O_2$  concentrations was passed through the sample side of the paramagnetic system for a period of 1 hour each. As with normal sampling protocol, the pneumatic four-way valve switched between a reference tank and sample gas at 2.5-min intervals. In this manner, twelve 2.5-min averaged values of  $O_2$  concentration differences from the reference tank

were obtained for each cylinder. The interferometric oxygen analyzer also concurrently analyzed gas from each cylinder. In an extensive array of tests, described by Keeling [1988b] and Keeling *et al.* [1998], the interferometric analyzer has been proven to be both highly linear and accurate at reporting atmospheric  $O_2$  concentrations. Additionally, the  $CO_2$  concentration for each gas was determined from analysis on a Siemens Ultramat II  $CO_2$  analyzer.

Variations in  $O_2$  concentrations are typically reported as changes in the  $O_2/N_2$  ratio according to methods described by Keeling *et al.* [1998]. Values are expressed in per meg units, where

$$\delta(O_2/N_2) \text{ (per meg)} = \frac{(O_2/N_2)_{\text{sam}} - (O_2/N_2)_{\text{ref}}}{(O_2/N_2)_{\text{ref}}} \times 10^6,$$

where  $(O_2/N_2)_{\text{sam}}$  is the ratio of the sample gas and  $(O_2/N_2)_{\text{ref}}$  is the ratio of an arbitrary reference gas cylinder. In these units, 4.8 per meg are essentially equivalent to 1 ppm (i.e., 1  $\mu\text{mole } O_2$  per mole of dry air). To express the paramagnetic analyzer output in per meg units, we use the formula:

$$\delta(O_2/N_2) \text{ (per meg)} = aV + \frac{\delta X_{CO_2}}{(1 - X_{O_2})}$$

where  $V$  is the voltage output from the paramagnetic analyzer, expressed as a difference between sample gas and a reference gas as described above,  $a$  is the span factor in units of per meg/V, calculated from analyzing two cylinders with known  $O_2$  concentrations (called “high span” and “low Span”),  $\delta X_{CO_2}$  is the difference in  $CO_2$  mole fraction of the sample from an arbitrary reference gas, in ppm, and  $X_{O_2}$  is the standard mole fraction of  $O_2$  in dry air (here we use 0.20946 [Machta and Hughes, 1970]). The  $\delta X_{CO_2}$  term accounts for the dilution effect of  $CO_2$  changes on the  $O_2$  partial pressure in the analyzer cell, at constant total pressure. This formula assumes that dilution caused by variations in trace gas species other than  $CO_2$  is negligible.

Results from this linearity test are shown in Figure 2 and Table 2 and show that the paramagnetic analyzer is highly linear ( $r^2 = 0.999$ ) over at least the range of 0 to -400 per meg, covering the range of concentrations observed in atmospheric oxygen due to natural and most anthropogenic perturbations. Table 2 also provides secondary information on the precision

**Table 2.** Results From Linearity Test of the Paramagnetic Analyzer

Tank I.D.	Interferometer $O_2/N_2$ Ratio, per meg	Paramagnetic $O_2/N_2$ Ratio, per meg	Difference, per meg <sup>c</sup>
ND01540 (high span)	-16.6	-16.6 <sup>a</sup>	-
ND02729 (low span)	-395.8	-395.8 <sup>a</sup>	-
ND02702	-237.3 <sup>b</sup>	-237.8	0.5
ND02701	-174.2 <sup>b</sup>	-174.2	0.0
635872	-359.6	-357.8	-1.8
ND06875	-219.6	-220.1	0.5
CC106697	-254.4	-252.2	-2.2
ND02705	-371.1	-372.7	1.6
ND01598	-121.5	-127.2	5.7
465062	-350.3	-354.8	4.5

<sup>a</sup> These two values were forced to be equal to the interferometer values, to define the span of the paramagnetic instrument. All other values were then calculated from this defined span.

<sup>b</sup> These two tanks are used to define the span for the interferometer. As such, their measured interferometer  $O_2/N_2$  ratios given here are not in fact values measured on the day of the test but rather are predetermined values that have been assigned to these two tanks based on the calibration protocol in the Scripps  $O_2$  laboratory [Keeling *et al.*, 1998].

<sup>c</sup> The mean difference of all cylinders is  $1.1 \pm 2.8$  per meg.

of the paramagnetic analyzer system. The average difference between the two instruments for the eight gas cylinders was 1.1 per meg, with a standard deviation of 2.8 per meg. These values incorporate inherent measurement errors in both analytical instruments.

The second series of experiments we called the "null" experiments. In one such experiment, reference gas was passed through the system continuously with no switching of the four-way valve. Data were then processed as if the four-way valve had been switching between a sample and reference gas. A series of 214 "sample jogs" were distributed about a mean difference of -0.2 per meg with a standard deviation of  $\pm 3.1$  per meg. This result corresponds to the theoretical precision that can be achieved by the paramagnetic transducer itself and how well a 2.5-min switching rate can null out the effect of sensor drift, assuming that no noise is introduced by the valve switching.

We also examined the possibility of a modified switching protocol that would double the lifetime of the reference gas. Analyzing the same data as above but assuming a switching protocol of 2.5 min of reference gas, followed by 7.5 min of sample gas, then 2.5 min of reference gas, etc., we obtained a mean difference of 0.1 per meg and a standard deviation of  $\pm 3.5$  per meg. To statistically compare these two results, we calculated the standard error based on a frequency of reporting data once per hour, resulting in  $\pm 0.9$  per meg for the 2.5-2.5 min switching scheme and  $\pm 1.4$  per meg for the 2.5-7.5 min switching scheme. This suggests that it is worthwhile investigating such reference gas saving methods further.

Another type of null experiment was designed to place a limit on the precision achievable with the entire gas handling system and not merely the analyzer transducer and the sample switching scheme. In normal operation, the pneumatic four-way valve shown in Figure 1 was used to switch between sample gas and a reference gas, whereas in this null experiment, gas derived from the same reference tank entered on both sides of the four-way valve. From previous work [Keeling *et al.*, 1998], we have found dividing the flow from a high-pressure gas line into two pathways to be problematic, with measured  $O_2/N_2$  differences between the two pathways resulting from fractionation. This problem was minimized by constructing a "T" made from a monolithic block of brass, connected directly to the reference cylinder with two high-pressure gas regulators connected to the block [Keeling *et al.*, 1998]. This reduced thermal gradients where the gas path divides in two, reducing  $O_2/N_2$  fractionation.

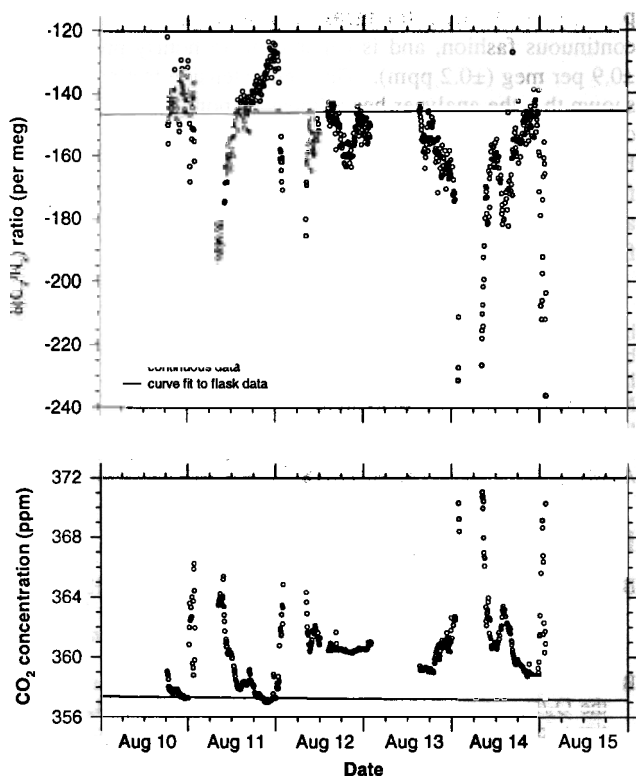
Data for this "T" experiment were processed in the same manner as before, using a 2.5 min/2.5 min switching protocol and determining the difference in concentrations between two nominally identical gas streams. A series of 208 sample jogs were distributed about a mean difference of -4.7 per meg with a standard deviation of  $\pm 3.1$  per meg (and a standard error of  $\pm 0.9$  per meg if reporting data hourly). This standard error shows that effectively no additional imprecision was introduced by our gas handling system. The offset of -4.7 per meg shows that there was, however, a systematic offset introduced in dividing the flow. We did not identify the source of this offset, but it is clear that it involved the gas-handling system upstream of the analyzer and was not intrinsic to the paramagnetic analyzer itself.

### 3. Preliminary Results of Continuous Oxygen Measurements

One of the foreseeable applications of this paramagnetic oxygen analyzer is in measuring atmospheric oxygen in a continuous fashion at remote background air-monitoring sites. To test the feasibility of this application, we ran the analyzer semicontinuously for a period of 3 months in 1996. Ambient air was drawn from the end of Scripps Pier, La Jolla, California, located about 300 m from the shoreline and 15 m above sea level. Air was drawn into our lab, a total distance of approximately 490 m from the end of the pier, through 1/2 inch outside diameter polyethylene-aluminum composite tubing (Dekoron). The air flowed first through the Siemens Ultramat II  $CO_2$  analyzer, then divided into two streams, one of which went to the paramagnetic analyzer, the other to the interferometric analyzer. All three instruments were calibrated daily during a 4-hour calibration procedure in the early morning. A 10-min calibration was additionally carried out every hour on all three instruments, and for the paramagnetic analyzer, a reference gas was switched in every 2.5 min as described above. A computer controlled all necessary valve switching and data acquisition.

We present here a sample of the data, from August 10-16, 1996. Figure 3 shows  $O_2$  data measured by the paramagnetic analyzer and converted to  $O_2/N_2$  ratios and also concurrent  $CO_2$  data from the same airstream. The  $O_2/N_2$  data exhibit large daily variations, and the rapidity of these variations indicate that local sources and sinks are the predominant influences on the air. The daily pattern observed is most likely due to the prevailing on-shore, off-shore wind pattern present at La Jolla. In the night and early morning, off-shore winds bring air impacted by local fossil fuel combustion with low- $O_2/N_2$  ratio and high- $CO_2$  concentration, whereas during the day cleaner on-shore winds are present, driving up  $O_2/N_2$  ratios and driving down  $CO_2$  concentrations. As expected, changes in these two gases anticorrelate, as is shown more clearly in Figure 4, and the data have an  $r^2$  value of 0.88. The slope of the best-fit line through the data of Figure 4 is  $-6.22 \pm 0.09$  per meg/ppm, or  $1.30 \pm 0.02$  mol  $O_2$  consumed per mol  $CO_2$  produced. The high variability of the data in Figure 3 indicates that all of the air sampled in this week (with the possible exception of the end of August 12) was polluted or contaminated air, and the expected largest source of pollution in the La Jolla area is from the combustion of "liquid" fossil fuels, which when fully combusted have a ratio of  $1.44 \pm 0.03$  mol  $O_2$  consumed per mol  $CO_2$  produced [Keeling, 1988a]. The lower value we observed of 1.30 can most probably be explained by small dilution effects from exchanges with either land biota ( $O_2:C = 1.1$  [Severinghaus, 1995]) or oceans. Figure 3 also shows curve fits to the La Jolla flask data series. A comparison of these curves with the actual day to day variability in  $O_2$  and  $CO_2$  concentrations highlights the somewhat ambiguous nature of flask sampling methods.

The scatter of the residuals from the linear fit to the data in Figure 4 represents more than instrumental scatter and illustrates that  $O_2/N_2$  ratios and  $CO_2$  concentrations in ambient air are not always anticorrelated. The most significant example of this can be seen in Figure 3 on August 12 from approximately 1500-0000 local time. During this period, the  $CO_2$  concentration was relatively steady, while the  $O_2/N_2$  ratio first



**Figure 3.** Continuous  $O_2/N_2$  and  $CO_2$  measurements sampled from the end of the Scripps Pier for a 1-week period in August 1996. The y axes have been scaled so that  $O_2/N_2$  and  $CO_2$  changes can be compared visually on a mole to mole basis. Data points shown are 2.5-min averages, with one point every 5 min. Gaps in the data are during 4-hourly daily calibration runs or downtime for other logistical reasons. Also shown are the curve fits to the La Jolla flask data (collected at 1-2 week intervals and analyzed on the interferometric oxygen analyzer), based on a four harmonic seasonal cycle and a stiff spline interannual trend.

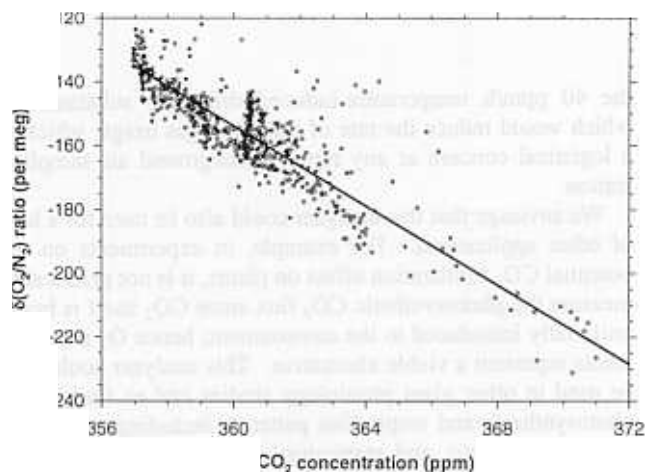
sharply decreased and then increased again to close to its earlier value. Such phenomena can be explained only by influences from oceanic sources or sinks. For example, there may have been a local upwelling event that brought oxygen-depleted waters to the surface, or there may have been a shift in air mass circulation. Because for air-sea gas exchange the  $CO_2$  equilibration time is an order of magnitude longer than the  $O_2$  equilibration time [Keeling *et al.*, 1993], only  $O_2$  would have been affected by such an event.

Figure 5 shows the  $O_2/N_2$  ratios derived from the paramagnetic analyzer and the concurrent  $O_2/N_2$  ratios derived from the interferometric analyzer. As can be seen, there is a small systematic offset of approximately 2.1 per meg. This offset is most likely another manifestation of the offset discovered above in the null test using the brass "T", and is clearly the result of gas-handling difficulties rather than analyzer problems. The two analyzers show the same features in the data with similar precision.

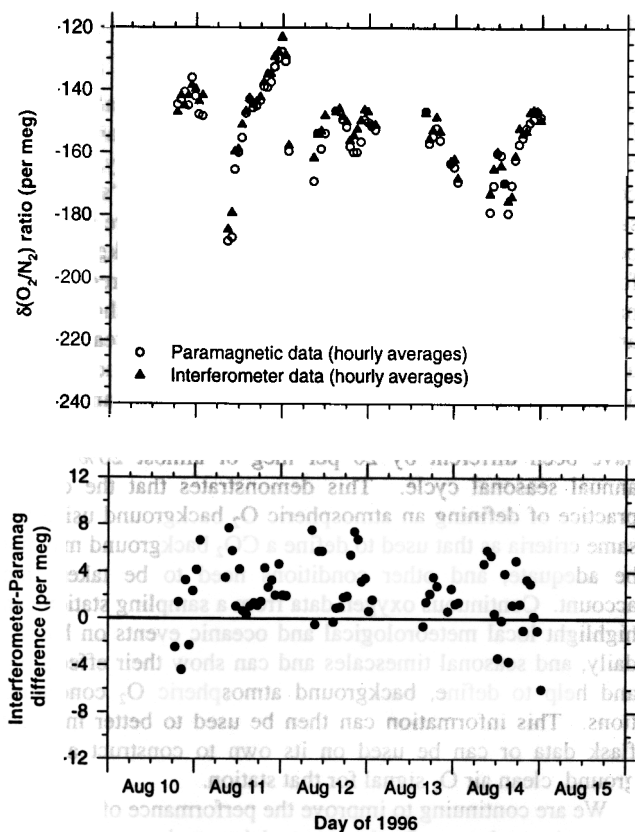
#### 4. Discussion and Conclusions

The event on August 12 discussed in section 3 highlights one of the advantages of a continuous oxygen dataset over flask sampling programs that are currently in operation [Bender *et al.*, 1996; Stephens *et al.*, 1998; R. Francey, personal communication, 1997]. Flask samples take a "snap-shot" sample and are to some extent "blind" to the nature of the air being sampled. The criteria used in collecting background air for  $O_2/N_2$  flask samples typically stipulate wind direction in a particular sector and greater than a certain threshold speed and stipulate ambient  $CO_2$  concentration being steady. The afternoon of August 12 may well have satisfied such criteria at La Jolla, but depending on whether a flask sample was collected at 1500 or 1800 local time, the  $O_2/N_2$  ratio could have been different by 20 per meg or almost 20% of the annual seasonal cycle. This demonstrates that the current practice of defining an atmospheric  $O_2$  background using the same criteria as that used to define a  $CO_2$  background may not be adequate, and other conditions need to be taken into account. Continuous oxygen data from a sampling station can highlight local meteorological and oceanic events on hourly, daily, and seasonal timescales and can show their effects on, and help to define, background atmospheric  $O_2$  concentrations. This information can then be used to better interpret flask data or can be used on its own to construct a background, clean air  $O_2$  signal for that station.

We are continuing to improve the performance of this paramagnetic analyzer. In the most elaborate improvement we hope to create a precisely controlled constant temperature environment by means of an active temperature control system. We are optimistic that this modification will reduce



**Figure 4.**  $O_2/N_2$  and  $CO_2$  data from Figure 3 plotted against each other. The correlation is good, with an  $r^2$  of 0.88. The slope of the best-fit line is  $-6.22 \pm 0.09$  per meg/ppm, or  $1.30 \pm 0.02$  mol  $O_2$  consumed per mol  $CO_2$  produced, close to but lower than a value of 1.44 that would be expected if all the air was polluted by fossil fuel combustion from petroleum based fuels only. The residuals from the linear fit are larger than expected from instrumental imprecision, illustrating that  $O_2/N_2$  and  $CO_2$  are not always anticorrelated in ambient air.



**Figure 5.** For the same period of continuous data collection on the paramagnetic analyzer, concurrent interferometer  $O_2/N_2$  data were collected. Apart from a small calibration offset, the two analyzers show the same features with similar precision. Note that the interferometer outputted one data point per hour, so the paramagnetic data were binned and averaged accordingly for this graph.

the 40 ppm/h temperature-induced drift rate substantially, which would reduce the rate of reference gas usage, which is a logistical concern at any remote background air sampling station.

We envisage that this analyzer could also be used for a host of other applications. For example, in experiments on the potential  $CO_2$  fertilization effect on plants, it is not practical to measure the photosynthetic  $CO_2$  flux since  $CO_2$  itself is being artificially introduced to the environment; hence  $O_2$  measurements represent a viable alternative. This analyzer could also be used in other plant physiology studies and to study plant photosynthesis and respiration patterns, including measuring the photosynthetic and respiratory quotients. Finally, from analysis of the anticorrelation between  $O_2$  and  $CO_2$  concentrations (see Figure 4), it may be possible to separate effects of fossil fuel and natural  $CO_2$  emissions from a region or country (assuming minimal complications from ocean influences). The analyzer is not suited, however, for measurements from a moving platform because of vibration and motion sensitivity.

In summary, the paramagnetic oxygen analyzer, when incorporated with the gas-handling design discussed in this

paper, is well suited for measuring atmospheric oxygen in a continuous fashion, and is capable of an hourly precision of  $\pm 0.9$  per meg ( $\pm 0.2$  ppm). Through extensive testing we have shown that the analyzer has a linear response for oxygen concentrations in the range of variations observed in ambient air. Finally we have shown that the analyzer can operate successfully for many months at a time with little or no maintenance and that resultant data are in good agreement with results from the interferometric oxygen analyzer.

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