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# A PULSE DILUTION SYSTEM FOR THE PRODUCTION OF DILUTE CONCENTRATIONS OF ATMOSPHERIC TRACE GASES

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A pulse dilution system in which small volumes of gas are injected into an air flow, by means of a standard 6-port G.C. valve, is described. This system is shown to produce the expected dilution, and to be able to produce gas mixtures whose concentrations can be varied by an order of magnitude simply by varying the injection frequency.

**KEY WORDS:** Gas calibration mixtures, trace gas.

## INTRODUCTION

The production of trace gas mixtures, at typical atmospheric concentrations, is an essential requirement of most experimental atmospheric chemistry programs. Such mixtures are necessary to calibrate monitoring instruments at ambient levels, to test instrument linearity, to test the ability of an inlet system to transport a trace gas from the atmosphere into an instrument, and to test the stability of gases within sampling containers. Since ambient concentrations are usually low, often in the part per trillion by volume (pptv) range, the production of ambient level concentrations that are stable and quantifiable requires a good deal of attention to detail and sophisticated dilution systems.

For stable compounds very dilute mixtures can be made using static systems<sup>1</sup>. For example, a small volume of the trace gas can be injected into a bag or vessel containing a large volume of air. More common, especially for less stable species, is the use of a dynamic flow dilution system. A known flow of an already dilute mixture, from a calibrated cylinder or from a small flow over a permeation device, is further diluted by mixing it with a much

larger flow of air. The dilution factor is then the ratio of the two flows. This technique can be used for a large number of species and concentrations, but is limited in the extent to which very low concentrations can be achieved. Commercially available trace gas standards are available for concentrations above 5 ppmv, which is similar to the concentrations achievable with slow flows over low permeation rate tubes. The production of sub ppbv concentrations therefore still requires dilutions of  $10^4$  or so from these levels. Commercially available flow controllers work reliably to  $1 \text{ ml min}^{-1}$ , so flows of the order of  $10 \text{ l min}^{-1}$  are necessary to achieve the desired dilution. This represents a large, often inconvenient, use of purified air. Two stage dilution systems can overcome this limitation, but for many gases the quantitative passage of sub ppm levels through flow meters and controllers is a problem. To avoid exposing the reactive species to a flow control element, these systems usually monitor the flow into the second stage as the difference between the total first stage flow and the vented flow. This method can only reliably produce dilutions of a few percent if the measured flow difference is to have sufficient precision. These systems have been applied successfully<sup>2</sup> to give dilutions of up to  $2 \times 10^{-5}$ , but still require an air flow of  $10 \text{ l min}^{-1}$ . Thus, methods to produce high precision gas dilutions at moderate gas flows are still needed.

In this note, we report on the construction and testing of a pulse dilution system capable of achieving high degrees of dilution with modest air usage. It is a modification of the Wösthoff gas-dosing system described in Nelson<sup>1</sup> and Axelrod et al.<sup>3</sup>, where a small volume of the trace gas is periodically injected into an air flow using a standard 6-port G.C. valve. In this way, much smaller amounts of gas can be added, than would be possible with a

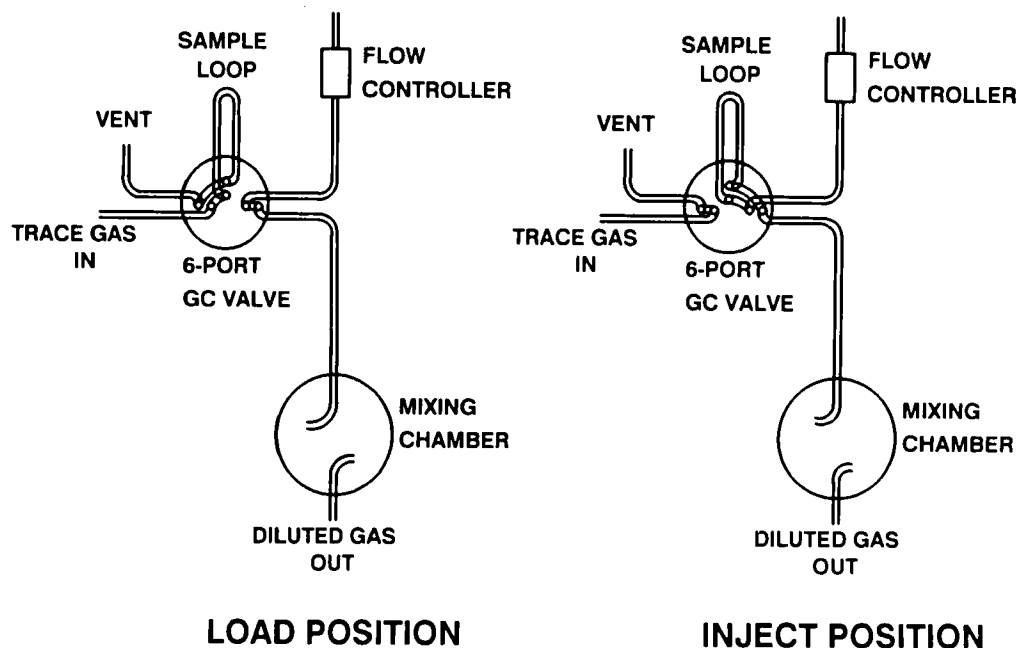
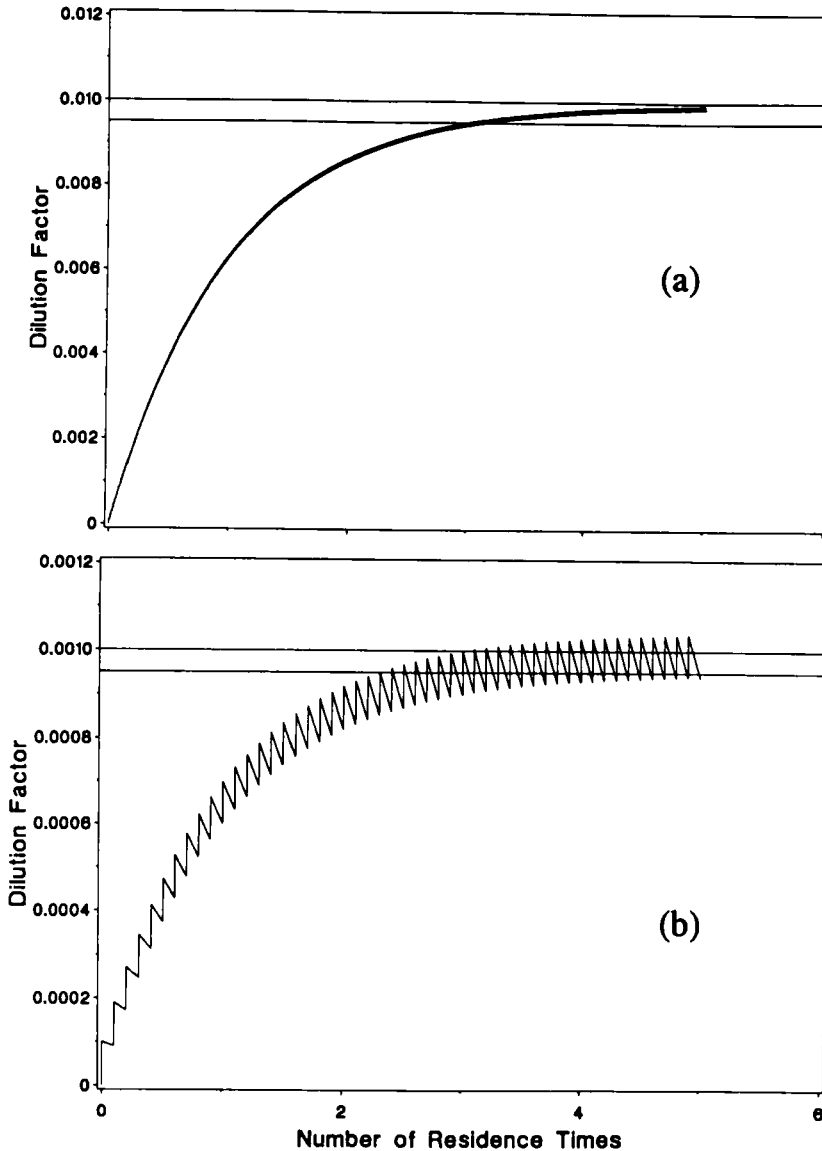


Figure 1 Schematic diagram of the dilution system.

flowmeter, so much higher dilutions are possible for the same air flow. It has the additional advantages that the gas is maintained at ambient temperature, is not forced through an orifice, and only contacts the relatively inert materials within the valve.



**Figure 2** The concentration leaving the mixing chamber as a function of time, expressed as a dilution factor, and assuming a zero initial concentration. (a) 100 injections per residence time, (b) 10 injections per residence time. The horizontal lines represent the expected dilution from equation (1) and 95% of that expected.

## EXPERIMENTAL

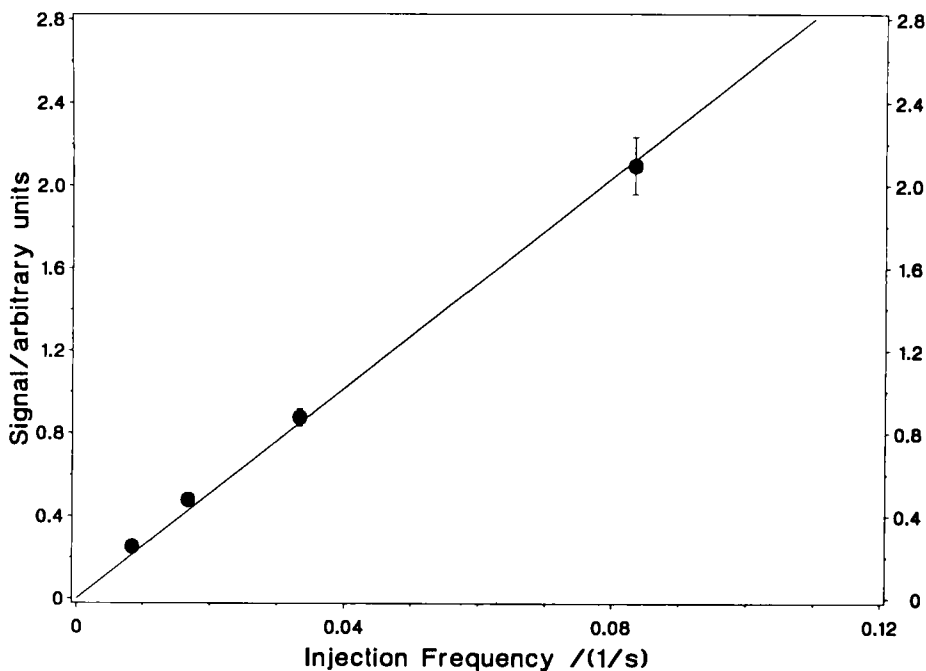
A schematic of the dilution system is shown in Figure 1. A known flow of air flows through a 6-port G.C. valve and a mixing chamber. The valve is kept primarily in the load position where the trace gas to be diluted flows through the sample loop and is vented. The valve is periodically moved to the inject position. This allows the small volume of "concentrated" gas contained in the sample loop to be added to the air flow. The average dilution achieved by this system is then given by:

$$\frac{C_d}{C_c} = V \frac{\nu}{F} \quad (1)$$

where  $C_d$  and  $C_c$  are the concentrations of the diluted and concentrated gas, respectively;  $V$  is the volume of the sample loop;  $\nu$  is the frequency at which the valve is switched; and  $F$  is the flow rate of the air. When using this equation, care must be taken to correct the volume  $V$  to the same temperature and pressure conditions for which the flowmeter was calibrated.

Since the trace gas is added to the air as a high concentration pulse, the concentration of the diluted gas leaving the valve will vary with time. The purpose of the mixing chamber is to allow each pulse of gas to mix with the air and so reduce these fluctuations to an acceptable level. We have calculated the concentration of the trace gas exiting the mixing chamber, as a function of time, assuming perfect mixing within this chamber. For the simulations, short pulses of concentrated gas were admitted to the mixing chamber, at intervals that were 100 (or 10) times shorter than the mixing chamber residence time. The results of these simulations are shown in Figures 2a and b respectively. As expected the average concentration of the diluted gas is 10 times higher in the first case, because 10 times as much gas was added, and concentration rises to 95% of the average concentration calculated above in 3 residence times. The most notable feature is the much greater variation in the concentration in the second case, where there is a significant time for dilution of the gas in the mixing chamber between gas additions. This shows the need to "tailor" such a dilution system to the application. When filling a bag or other large sample container, where additional mixing could occur, the concentration variation in 2b would be acceptable. This would not be the case if the gas was being used to determine the detection limit of a fast response analyzer where a system with a performance similar to 2a would be required. Axelrod et al.<sup>3</sup> have pointed out there would be a smaller concentration variation if a series of smaller chambers of the same total volume were used. This modification would be desirable when using a fast response detector.

The system used in the test study had a 1000 cm<sup>3</sup> mixing chamber and a flow rate of 82.5 cm<sup>3</sup> min<sup>-1</sup> and so a residence time of 12.1 min. The 6-port G.C. valve was coupled to a nominal 0.25 cm<sup>3</sup> sample loop, the actual volume was determined to be 0.23 ± 0.005 cm<sup>3</sup>, and was activated by a Valco model E90 electrical actuator controlled by a timer (ChronTrol model CD). This allowed the valve to be repetitively switched from the load to inject positions from 6 to 60 times per mixing chamber residence time. Since the valve actuator was not designed for such intensive use it was found to be necessary to blow air through the housing to prevent overheating. The valve was held in the inject position for 2 s and in the



**Figure 3** Results of the dilution test experiment. Each point is the mean and standard deviation of 8-10 replicate measurements

load position for at least 8 s. This allowed the gas in the sample loop to be replaced a minimum of 5 times each cycle, which was sufficient to ensure that all gas in the loop was displaced. The trace gas used was cyclohexane, obtained by bubbling  $\sim 10 \text{ cm}^3 \text{ min}^{-1}$  of air through a solution of cyclohexane in dodecane held at  $0^\circ\text{C}$  in an ice/water bath. Samples of the gas for analysis were taken by syringe from septums at the outlets of the mixing chamber and the bubbler. Analysis was performed on a Delsi model Di200 gas chromatograph with a flame ionization detector, using a 2 m glass column packed with 10% 1,2,3-tris (2-cyanoethoxy) propane on 100/120 Chromosorb PAW. The G.C. was coupled to a PE Nelson 950 interface and a computer running PE Nelson integration software which was used to determine peak areas. Data reported below are the averages of 8 to 10 replicate measurements.

## RESULTS

Two tests of the dilution system were performed. The actual dilution for a particular frequency  $\nu$  was measured to assess the accuracy of equation (1). The ability of the system to deliver a range of concentrations for a fixed loop size was tested by varying the frequency of the injections.

The actual dilution achieved by the system was checked by measuring the concentration of cyclohexane leaving the bubbler, and after dilution at a fixed rate of 5 injections per minute ( $\approx 60$  per residence time). The expected dilution factor, including errors from the air flowmeter and the volume, was  $1.34 \pm 0.03 \times 10^{-2}$ . However, the experimentally derived dilution factor was only  $1.25 \pm 0.07 \times 10^{-2}$ , where the error was derived from the  $1\sigma$  values of the measured means. The measured and expected dilution factors are within  $2\sigma$  error limits and, while the difference is not significant, it does suggest it may be prudent to calibrate each individual system rather than rely solely on Equation 1.

The ability of the system to produce a range of concentrations, using a fixed loop size, was tested by varying the frequency of injections by a factor of 10. Figure 3 shows the means and standard deviations of these measurements as a function of the injection frequency. We note here that when measuring the lowest concentration, (1 injection in 6 residence times) the standard deviation of the 8 measurements was 7.3% whereas it was only 4.5% for the higher concentrations. This indicates an additional source of variation at the lower frequencies, probably as illustrated in 2b. There is good linearity over the concentration range and this shows that once a concentration range is set by the loop size, an order of magnitude concentration variation can be readily produced using this system. The linearity also shows that the deviation from the predicted dilution is due to a systematic error which can be removed by a one-time calibration of the system.

We have shown that the pulse dilution system described here can produce significant levels of dilution,  $10^{-2}$ - $10^{-3}$ , for air flows below  $100 \text{ cm}^3 \text{ min}^{-1}$ . Within a single system, an order of magnitude concentration variation can also be achieved. Higher dilutions than reported here are easily possible using smaller sample loops and/or higher flow rates. An order of magnitude change in both of these would produce variable, single step dilutions of  $10^{-4}$ - $10^{-5}$  using an air flow of only  $11 \text{ min}^{-1}$ . Such a system could find widespread use in the production of trace gas mixtures for a number of atmospheric chemistry applications.

### Acknowledgement

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