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Note

Continuous monitoring of a changing sample by multiplex gas chromatography

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Multiplex gas chromatography (MGC) is a technique in which multiple samples may be introduced into a chromatographic system regardless of the elution time of the individual components [1]. Although the output obtained from a MGC experiment is not directly interpretable, computational techniques can be used to obtain the chromatogram from the detector output data. This is done by calculating the impulse response function from the multiplexed output data.

The impulse response function is defined as the response of a system to an applied impulse input signal. The impulse response function is related to the output and input modulation signal by the following equation [2]:

$$h(\tau) = FT^{-1} [FT(Output)/FT(Input)] \quad (1)$$

where FT is the Fourier transform, "Output" is the detector output signal, "Input" is the modulation or injection signal, and $h(\tau)$ is the system impulse response function. For a single injection or pulse, $h(\tau)$ is the chromatogram of the sample that is directly obtained from the output data. For a long modulated signal composed of multiple sample injections, eqn. 1 is used to calculate the chromatogram. This technique is well summarized by Phillips [1].

Some of the most promising applications of this technique are either in areas where more data are needed to improve the detection limits of a detector or where continuous monitoring of a sample stream is required. Specifically, for NASA, this technique is being investigated as a way of conducting GC analyses from a descending spacecraft through a planetary atmosphere [3]. Under such a scenario the time available to complete a gas chromatographic analysis will be very limited. If conventional gas chromatography (*i.e.*, one single injection for each sample) is used, then, there will only be time for analysis of just a few samples before the spacecraft reaches the surface of a planet. Under such scenario, no information will be obtained from altitudes the spacecraft passes while it is involved in GC analysis.

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One of the most important restrictions for using MGC on a descending spacecraft is that the data collected will be representative of a sample whose composition varies as a function of altitude. The concentration of any given component of the atmosphere may increase or decrease as a function of altitude. In addition, a given component may appear unexpectedly during the sampling period. These changes in composition can deteriorate the signal-to-noise ratio (S/N) of the final calculated chromatogram due to variations in the baseline. These variations will contribute noise to the final calculated chromatogram. This type of noise as been defined as correlation noise by Annino and Bullock [4]. The degree of correlation noise is proportional to the rate of change in the sample. If a change occurs rapidly then the calculated signal will be completely incomprehensible [1,4,5].

In this work, the technique of exponential dilution (ED) [6] was used to change the composition and concentration of a gaseous mixture to emulate the changes in the atmospheric composition that a descending spacecraft will sample. The sample was introduced using MGC and the chromatogram computed using eqn. 1. The ED technique has previously been used by Koel *et al.* [5] to calibrate a GC system with a flame ionization detector using a sample containing methane as the only component which was determined.

In the ED technique, a flask of known volume is filled with a gas sample. Then a diluent is introduced into the flask at a constant rate. The diluted sample mixture then flows from the flask into the GC injection valve. The sample inside the flask is diluted exponentially as a function of time. At any time the concentration of the sample inside the flask can be calculated using the following equation [6]:

$$C_t = C_0 e^{-ft/v} \tag{2}$$

where C_t is the concentration of the sample at time t, C_0 is the initial concentration, f is the diluent flow-rate and v is the volume of the flask. The ED technique can also be used to make changes in sample composition by introducing a new sample in the flask instead of a diluent. After an experiment is completed, the collected data are divided into equal time segments.

It is the purpose of this paper to report results obtained while applying MGC to an environment of changing sample composition. Also the errors that resulted with various degrees of change in the sample concentration were determined by performing a calibration of the MGC system with four different rates of sample dilution.

EXPERIMENTAL

The GC system used in this work is shown in Fig. 1. The GC detector was a Model PI-52 02 photoionization detector (HNU Systems, Newton, MA, U.S.A.) with a 11.70-eV lamp. The column was a 1.5 m × 1.1 mm I.D. stainless-steel tube packed with *tert.*-butyl isocyanate bound to Porasil C (100–150 mesh). The column temperature was 25°C. The GC injection assembly was composed of an 8-port Valco valve with two 100-μl sample loops and a Valco electric actuator (Alltech, Deerfield, IL, U.S.A.) for computer control of the valve. A Datametrics Type 1511 Controller and three Model 825 Datametrics mass flow controllers (MANCO, Santa Clara, CA, U.S.A.) with orifices for 10.0, 20.0 and 100.0 ml/min were used to regulate and measure the flow of all the gases used.

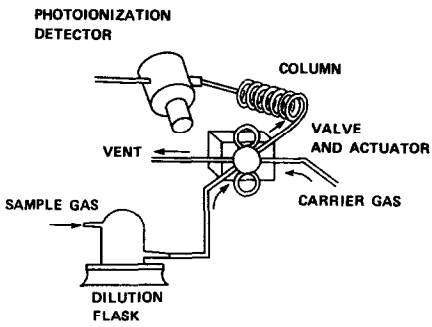

Fig. 1. Schematic diagram showing the major components of the multiplex exponential dilution flask gas chromatographic system.

Testing of the multiplex ED system was conducted with three different gas mixtures. One of them contained methane, ethane, propane and butane at 100.00 ppm in helium (Matheson). Another mixture contained those same components but at 1000.00 ppm (Matheson). A third mixture prepared manometrically contained ten hydrocarbons at the following concentrations: methane and ethane at 71.1 ppm, propane and butane at 142.3 ppm, isobutane and ethylene at 213.4 ppm, acetylene and propene at 227.6 ppm, propyne and propadiene at 355.7 ppm, all in helium. The carrier gas was 99.999% helium (Matheson). The flow-rate through the column was 16.0 ml/min.

In order to emulate the variations in sample concentration, the 100.00 ppm gas mixture was used. An ED flask of known volume was connected upstream of the sample valve. This flask is a glass vessel of accurately determined volume (239.6 ml) equipped with openings to permit continuous gas flow. It contains a magnetically-driven stirring vane to guarantee complete mixing. This flask was fabricated following the same specifications used for the ED flasks made by Varian during the early 1970s. Similar ED flasks were used during the late 1970s to calibrate the GC system that was used on board the Pioneer Venus probe for determining the gaseous components in Venus' atmosphere [7]. These flasks are still in use in our Branch and are very reliable for calibration of newer GC's being developed for use in other missions. Before starting each experiment, the flask was filled with the sample to be used at a rate of 10.0 ml/min for a period of 2 h. To ensure that the flask was completely filled with the sample, a few test injections of the sample entering the sample loop were made and no change in intensity of the GC signal was detected. Four dilution experiments were performed using the following diluent flow-rates: (1) 12.0 ml/min, (2) 18.2 ml/min, (3) 32.2 ml/min and (4) 61.6 ml/min. Before starting with the dilution, the multiplex experiment was run for an 18.0 min period to determine the intensities of the GC peaks for the 100.00-ppm concentration mixture. That peak intensity was used as reference to calculate the concentrations that were used for the exponential dilution plots. The data obtained from the experiments were used to calculate the impulse response functions using eqn. 1 followed by generation of the exponential dilution curves of concentration with respect to time for both propane and butane. To monitor this concentration as a function of time, the time corresponding to the aver-

age concentration was calculated by integrating over the interval of each data segment and using eqn. 1. The four dilution experiments were run for approximately 40, 75, 40 and 18 min, respectively. Four theoretical dilution curves using those same diluent flow-rates were also generated. The natural log of the concentrations of each experiment was plotted *vs.* Time followed by calculation of the relative error between these curves and the theoretical ones. An additional plot of % relative error with respect to diluent flow-rate in ml/min was also generated.

A study was also conducted to test the multiplex ED technique while changing the sample mixture as a function of time. In this experiment, the flask was filled with the ten hydrocarbon mixture described previously. This was followed by the introduction of a mixture containing methane, ethane, propane, and butane, all at 1000.00 ppm in helium. The four hydrocarbon mixture was introduced at a constant rate of 9.0 ml/min for a period of 140 min. A total of 1272 injections were generated during that period.

The multiplex ED system was operated using a System 1800-Model B high-speed microcomputer (Integrated Image Systems, Santa Clara, CA, U.S.A.) through an IEEE 488 interface attached to a Nelson Analytical 900 Series analog-to-digital interface (Cupertino, CA, U.S.A.) both providing the modulation signal and acquiring the detector signal. The software used for modulating the frequency of injections and acquiring the output data was supplied by Nelson Analytical and it is written in Basic. This program will only work for single-injection chromatograms. We added a random generator program to perform the multiplex ED experiments. The probability of injection was 14%. The data acquisition rate was one point per second. After all the experimental data were collected, it was transferred to a MicroVax II (Digital Equipment Corporation, Santa Clara, CA, U.S.A.) to calculate the impulse response function using eqn. 1. All the data collected in each experiment were divided in segments of 15.0-min lengths (900 data points) to monitor the dilution of the sample as a function of time for each second of the experiment. Each 15.0-min segment had the same injection sequence. That sequence was chosen from preliminary MGC experiments in which the injection or input sequence changed as a function of probability of injection. The sequence that resulted in a chromatogram with the highest S/N was the one chosen for this work.

RESULTS AND DISCUSSION

Fig. 2a and b illustrates exponential dilution plots of concentration with respect to time for the theoretical case, and for propane and butane at the starting concentrations of 100.00 ppm for the experiment with a diluent flow-rate of 18.2 ml/min. The sample used also contains methane and ethane at 100.00 ppm but these two components are not detectable by the photoionization detector used. The differences between the experimental values and the ones calculated using eqn. 1 are higher during the first 16.0 min of the dilution due to the faster change in concentration from 100.00 ppm to 30.00 ppm for both propane and butane. After that period of time the experimental values gradually becomes much closer to those predicted by eqn. 2.

Fig. 3a and b shows the plots of % of relative error between the experimental and theoretical curves as a function of diluent flow-rate for propane and butane for four separate experiments. For both propane and butane the relative error is directly

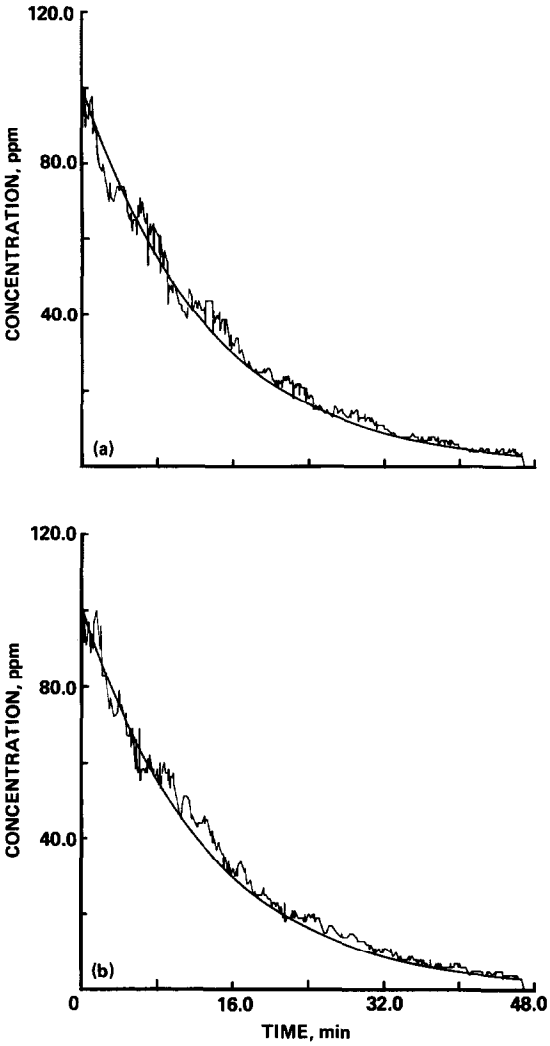

Fig. 2. Exponential curves showing an exponential decrease in concentration for (a) propane and (b) butane both at an initial concentration of 100.00 ppm, and a theoretical curve calculated using eqn. 2 for comparison with the experimental ones using a diluent flow-rate of 18.2 ml/min for a period of 75 min. A total of 670 injections were generated during that period. Each experimental point for both propane and butane represents 15.0 min. of data determined by computation of the impulse response function using eqn. 1. Volume of dilution flask = 239.6 ml.

proportional to the rate of dilution. for propane, the lowest relative error was 5.5% for a diluent flow-rate of 12.0 ml/min corresponding to a dilution time of 64.3 min from 100.00 ppm to 0.35 ppm. The highest relative error was 19.8% for a diluent flow-rate of 61.6 ml/min corresponding to a dilution time of 18.0 min from 100.00 ppm to 0.35 ppm. For butane the lowest relative error was 6.0%, and the highest

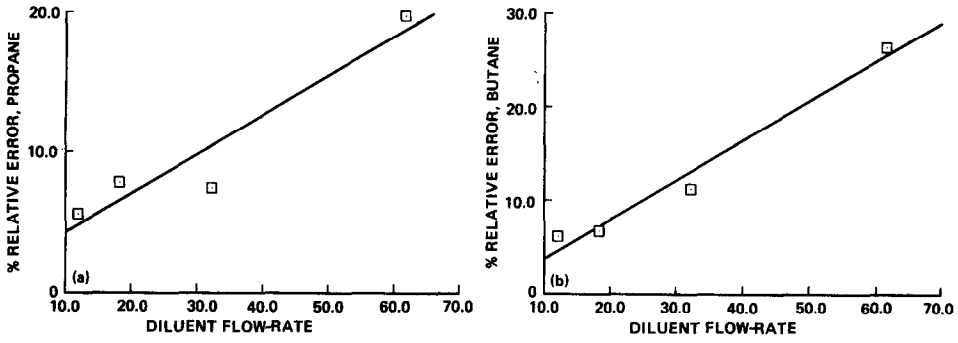

Fig. 3. Plots of % of relative error between the experimental and theoretical curves as a function of the four diluent flow-rates (in ml/min) used for (a) propane and (b) butane. For propane the slope was 0.28 ± 0.07, intercept = 1.4 ± 0.4, and coefficient of determination = 0.90. For butane the slope was 0.42 ± 0.05, intercept = 0.6 ± 1.7, and coefficient of determination = 0.98.

26.3%. The differences between the experimental values and the theoretical ones are due to (1) variations in the gas flow-rate when the injection valve is switched to introduce the sample, (2) non-linear chromatographic effects that contribute more to baseline instabilities if the dilution rate is faster and (3) the fact that Fourier transforms can be used only for stationary systems or slow changing systems. All these effects will result in baseline variations in the calculated chromatogram defined as correlation noise (discussed briefly in the introduction).

Fig. 4 shows the chromatograms obtained for the study in which one mixture containing methane, ethane, propane, and butane, all at 1000.00 ppm, was used to change a mixture of different composition (methane, ethane, ethylene, propane, acetylene, isobutane, butane, propene, propadiene and propyne) by the multiplex ED technique. All the chromatograms were obtained by calculating the impulse response function as defined in eqn. 1. Fig. 4a is the chromatogram of the mixture containing 10 components before the beginning of the dilution. Methane and ethane are not detectable by the photoionization detector used. Propyne is strongly retained in the column and appears as a very low, broad peak beyond the end of the chromatogram. Propene and propadiene elute at the retention time represented by peak 6 in Fig. 4a. In addition, a negative pressure peak, sporadically present in the data (Fig. 4b and c), originated from a change in pressure when the valve turns at the time of injection. Fig. 4b is a chromatogram obtained by calculating the impulse response function after 20.5 min of the dilution experiment. After that period of time, propane and butane increased in concentration to 602.3 ppm, while all other components had decreased. Finally, 116.5 minutes after the experiment began the only detectable components were propane and butane at concentrations close to 1000.0 ppm (Fig. 4c).

This study shows that a multiplex ED technique can be used to simulate environments where a sample is changing with time as long as the composition changes slowly with time. As discussed above, the errors calculated are a combination of uncertainties due to correlation noise. At present, additional data analysis techniques

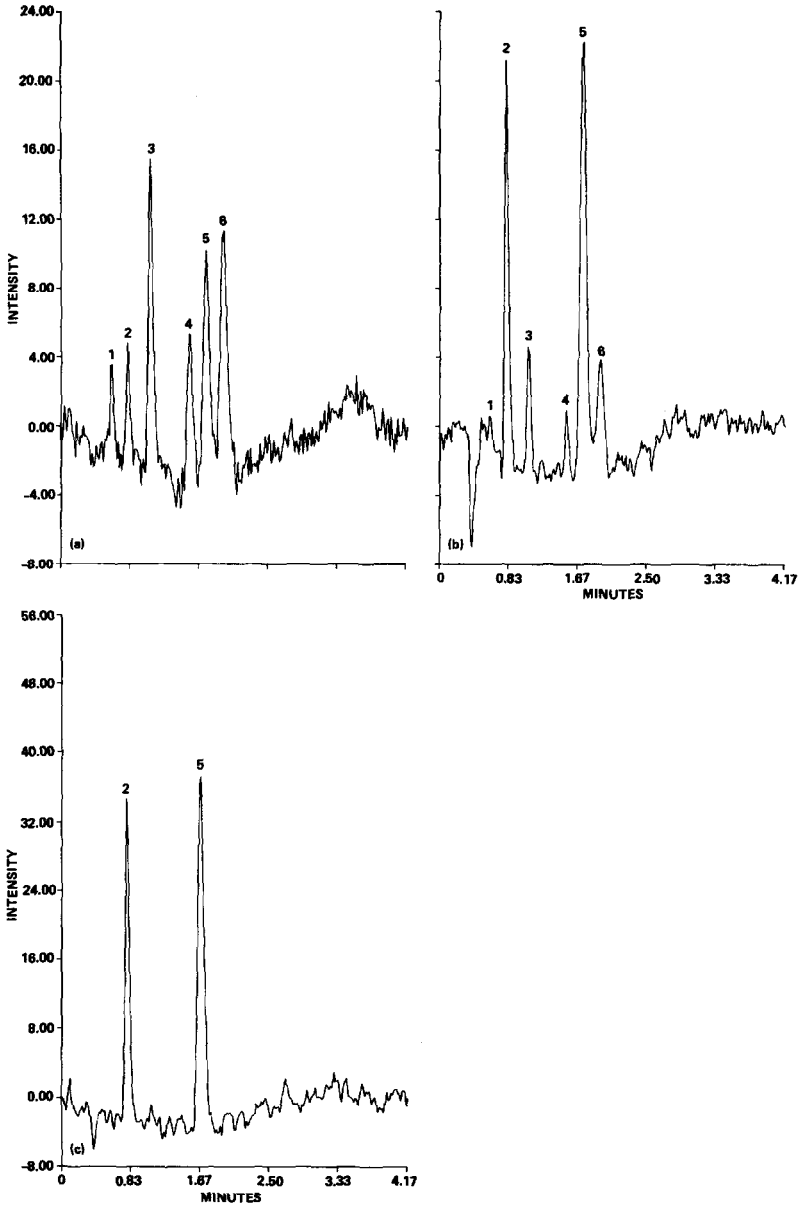

Fig. 4. Chromatograms obtained from the calculation of the impulse response function at three stages during the change in sample composition. The column temperature was 25°C and the flow-rate was 9.0 ml/min. Intensity is in arbitrary units. (a) First 15.0 min of the experiment where no change in sample composition occurred (dilution time = 0.0 min). The six peaks correspond to 1 = ethylene (213.4 ppm), 2 = propane (142.3 ppm), 3 = acetylene (227.6 ppm), 4 = isobutane (213.4 ppm), 5 = butane (142.3 ppm), and 6 = propene (227.6 ppm) and propadiene (355.7 ppm). Not detected: methane, ethane and propyne. (b) Chromatogram obtained from the calculation of the impulse response function 20.5 min after the multiplex ED experiment started. The six peaks correspond to 1 = ethylene (66.0 ppm), 2 = propane (602.3 ppm), 3 = acetylene (105.5 ppm), 4 = isobutane (99.0 ppm), 5 = butane (602.3 ppm), and 6 = propene (105.5 ppm) and propadiene (164.9 ppm). (c) Chromatogram obtained from the calculation of the impulse response 116.5 min after the multiplex ED experiment started. The two peaks correspond to 2 = propane and 5 = butane, each component present at a final concentration of 989.2 ppm.

are being developed to monitor an environment where a sample analyzed changes more rapidly than the one reported in this paper.

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