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Introduction

The ever-increasing use of flow injection analysis (FIA) in monitoring and analysis has lead to the development of more complex flow injection (FI) manifolds. Development of these manifolds has traditionally sought to optimize the relationship between the two kinetic processes occurring in a FI manifold namely the physical process of zone dispersion and the chemical kinetics resulting form the reaction(s) between sample and reagent (Ruzicka and Hansen, 1998). A key component of the FI manifold involved in this optimization is the mixing coil (reactor). This component, to a large extent, determines the radial mixing, hopefully maximizing the mixing of the reagent with the sample, and the longitudinal dispersion, hopefully minimizing the laminar flow dispersion of the sample into the reagent/carrier stream (Ruzicka and Hansen, 1998). The use of an appropriate reactor plays a significant role in determining important analytical parameters, such as sensitivity and detection limit, for it defines the amount of time spent in the reactor, which in turn determines the amount of dilution and extent of reaction that can occur. Finally, the mixing chamber also determines the homogeneity of the flow stream after solution merging at confluence point.

Up until this point optimization of the length (volume) of the mixing coil required obtaining a balance of the throughput and sensitivity: maximum sensitivity commonly involves injection of large sample volumes at slow flow rates, which gives less than optimal throughput. Conversely, high throughput generally involves small samples and high flow rates where sensitivity is limited. Achieving this balance through the use of a reactor of appropriate length and volume involves the time-consuming experimentation with different reactors through physically removing/inserting mixing coils. Not only does this create a possibility of affecting analytical reproducibility; it also puts a good deal of wear and tear on parts of the FI manifold.

The need to change components also limits the ability to use FIA systems in completely automated or remote settings. This trend toward "remote instrumentation" (not to be confused with field portable instrumentation) is perfectly addressed by FIA techniques assuming a complete automated instrument is possible. Currently, all common components of FIA instruments can be controlled via computer except one - the mixing coil.

Recognizing a need for an improved mixer/reactor, the continuously variable volume reactor (CVVR) was developed to address the need for remote unattended FIA manifold operation and the issue of manifold optimization. Development of the CVVR allows fully automated FIA analysis, and through its design allows the volume of the mixing coil to be changed dynamically as the sample bolus travels through the mixing coil to the detector. This is the first time this approach has been demonstrated in the literature.

Background

The first prototype of the CVVR was developed in our laboratory in 1997 (Lipe and Chalk, 1998; Lipe and Purinton, 1998) and is shown in Figure 1. The body was a four-inch long cylinder made of Peek, with a maximum inner volume of 1650 μL with the
piston fully out. Into the open end of the CVVR body was inserted a piston, also made of Peek. Thus, the volume of the CVVR (mixing chamber) is determined by the position of the piston in relation to the body. This piston was driven by a computer controlled linear-actuator stepper motor. Using the piston, the volume of the chamber could be adjusted from 50 µL to 1650 µL in increments of 0.8 µL (1/1000" step). This volume could be changed at rates of 0.8 µL/s (1 step/s) to 160 µL/s (200 steps/s).

Initial experiments with the first prototype CVVR showed that the device worked well as a replacement for a traditional mixing coil. Variation of the volume of the chamber in "static" mode (i.e. the chamber is set at one volume as the sample bolus traveled through it - a traditional FIA experiment) gave variable dispersion of a dye solution (bromothymol blue) and variable reaction conditions (iron(II) and o-phenanthroline). In addition, variation of the chamber volume as the sample bolus traveled through the chamber - "program" mode give double peaks with injection of a dye (Figure 2). These peaks showed that the sensitivity and the throughput (peak width at base) could be more independent, as once the peak maximum has passed through the detector the chamber volume can be decreased to push the rest of the peak out of the manifold. Subsequently, the patent for the CVVR was applied for (4).

However, when the program mode was used with a chemical reaction system (iron(II) and o-phenanthroline), irreproducible peaks were obtained that were not useful analytically. This was thought to be due to variable mixing patterns occurring in the chamber. For this and many other reasons a second prototype was designed, detailed in this paper.

**Experimental**

The second prototype of the CVVR was developed as depicted in Figure 3 (Medeiros and Harrell, 2000). Like the first prototype, it is a four-inch long cylinder made of PEEK, with a maximum volume of 2050 µL (2" linear travel of piston). Inserted in one end of the CVVR is a piston, also made of PEEK. As with the first CVVR, this piston is driven by a computer-controlled linear-actuator stepper motor from Hayden Switch and Instrument Inc. (Waterbury, CT). Using the piston, the volume of the chamber can be adjusted from 50 µL to 2050 µL in increments of 0.8 µL (1/1000" step). This volume can be changed at rates of 0.8 µL/s (1 step/s) to 160 µL/s (200 steps/s). An improvement over the design of the first CVVR is the connector used to attach the piston to the linear-actuator motor. This bracket helps maintain stability of the piston and prohibits the piston from axial rotation around the motor drive shaft, the result of which would restrict linear motion and cause a loss of precision movement.
As an improvement over the first chamber, the end opposite the piston is no longer a single inlet. Rather, it now contains two ports for multi-line analyses and a small internal rotor that can be used to force mixing as the sample and reagent enter the chamber. This rotor is independently controlled by a rotary stepper motor from Hayden Switch and Instrument and can be used to mix at rates of 100-300 rpm. The body, piston, rotor end, and other pieces of the CVVR were manufactured by PlasTech P.M. (Houston, TX).

The program (Virtual Instrument - VI) used to control both the linear and rotary stepper motors was developed with LabView 5.0 from National Instruments (Austin, TX). This program affords the ability to vary not only the speed and rate of chamber movement, but also the rate of speed at which the rotor turns. Programs that define the variation of the parameters for the device (speed, volume, enable/disable, forward/reverse) are generated by a separate LabView VI.

At the start of an experiment the program is loaded into the controller VI and signals are sent every second to move the chamber/actuate the mixer. The VI's are run on a PowerPC 4400/200 Macintosh computer (Apple Inc., Cupertino, CA). Signals are sent through a National Instruments PCI-1200 data acquisition (DAQ) card and into drive cards (Hayden Switch and Instruments Inc.) for each motor.

The housing of the second prototype was made of Delrin. The design of this housing was done on AutoCAD R13 (Autodesk, San Rafael, CA) and Canvas 5.0 (Deneba Software, Miami, FL).

The housing was designed to keep the electrical components separate from the chamber, preventing damage in the event of a chamber leak, and also to minimize effects of external vibrations on the CVVR.

Additional features of the second CVVR also include: location feedback sensors for the piston position, control of the injection of the sample, which allows computer co-ordination of the chamber program with the sample injection (previously manual), and two outlets to send the sample to two detectors if required. Program design has also been improved over the first prototype by incorporating curved variations of the volume of the chamber between setpoints.

The pump used while optimizing the system was a peristaltic pump manufactured by Labconco (Kansas City, MO). The sample injection was made using an electronically actuated six port injection valve (Valco, Houston, TX).

Results/Discussion

The second design of the CVVR has proven to be a significant advancement over the first. The construction of the rotor assembly shows no solution leaks and the interface to the rotary stepper motor is stable since redesigning the rotor spindle without the notch (weak joint).

Control of both motors has been redesigned due to problems with the smoothness in rotation of the rotary stepper motor. Previously, the controller VI would send out the speed signal to both motors by on-the-fly generation of
square waves at the appropriate frequencies (every iteration). This caused a small but significant processing delay that did not allow the signal to be part of every cycle. This problem has been overcome by using the outputs of the PCI-1200 onboard timer clocks, which do not require much processor time.

Construction of a new housing for the CVVR was necessary due to the additional electronics needed to control the CVVR. The design is such that any possible leak of fluid from the chamber will fall to the base of the housing and drain out thus saving the electronics. Additionally, improved alignment of the chamber piston, body, and two motors will lead to less wear and tear, thus providing better long term reproducibility in the speed of the rotor and movement of the piston.

The electrical requirements of the new CVVR are obviously greater (e.g. two motors) and a new power supply has thus been used. Power is now fed to three separate voltage regulators, two to supply 13.5 V to each of the two motors and one to provide 5 V for the potentiometers that feedback the position of the chamber. Also, problems encountered previously with blowing control pins on the PCI-1200 board (TTL signals) has prompted the use of optoisolators on each of these four lines (enable/disable and direction on each motor) to allow control yet eliminate too much current draw.

Initial experiments with the second prototype using bromothymol blue dye and the iron(II) o-phenanthroline reaction system show the same functionality as the first prototype in the static mode. Experiments with variation of the rotor speed have been inconclusive (not much different from no stirring) and additional experiments will look at the design of the rotor paddle (on the end of the spindle) to improve the mixing characteristics. No experiments have yet been performed in the program mode.

**Conclusions**

Although many concerns of the first CVVR were addressed and corrected in the development of the second CVVR, the second CVVR has also shown a need for further development. Because the ultimate goal for the CVVR is use in fully automated sampling and testing environments, more specifically, water-monitoring systems at remote locations, ruggedness and reliability must be maximized in design and operational features. This includes proper control of the environment inside the CVVR housing and sturdiness in the moving parts of the CVVR, as well as alignment and feedback control.

**References**


