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# ANALYTICAL FLUIDIC SAMPLING SYSTEMS*

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## SUMMARY

Fluidic logic sampling systems have been developed for analytical detectors such as the plasma chromatograph and flame ionization detector. Automated systems are reported for gases and vapor-phase samples which are rapid, quantitative and reproducible. Sample modulation systems, multiplexers, parallel-to-serial converters and sequential samplers have been developed which give no leakage or cross-talk signals. Other applications in analytical chemistry are proposed.

## INTRODUCTION

Representative, reproducible and quantitative sampling is a critical and formidable consideration in analytical chemistry. The development of new measurement methods such as plasma chromatography, enhancement of the state of the art of existing analytical techniques such as high-performance liquid chromatography (HPLC), and increasing demands on analytical sensitivity for trace analyses (*e.g.*, environmental sampling, analysis of pharmaceuticals and food products, and clinical and toxicological analyses) emphasize the importance of sampling.

High-efficiency HPLC columns operating at a plate height of 40 $\mu$m, and thereby generating 25,000 theoretical plates/m, will be limited by the width and symmetry of the input peak profile[1]. Without high-speed sampling systems which can reproducibly inject symmetrical sample profiles of minimum width, the ultimate efficiency of HPLC cannot be obtained. An additional requirement for sampling systems can be found in trace analysis, where it is imperative that contamination of samples be minimized and reduced to very low levels, which is without precedent in analytical chemistry. The analysis of aromatic hydrocarbons in sea water at the parts per $10^{12}$ level is an example of the need to use inert, non-adsorptive and sealed components that can readily be cleaned, but which must be a functional, rapid, reproducible, versatile, modular, automated sampling system.

The need for new sampling techniques is obvious in plasma chromatography

* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental work. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

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where the maximum total sample size is often $10^{-8}$ g and the best analytical results are usually obtained below the $10^{-10}$ g level. The sample entering the instrument must react completely with the reactant ions and yet not saturate the instrument by using all of the reactant ions. Only under these conditions can one be assured of relating the total number of ions measured to the original sample concentration. To take advantage of the high sensitivity and rapid clearing time of the plasma chromatograph, it is further imperative that the amount of sample be controlled and well defined. The amount of sample which will meet these conditions depends on (a) the reactivity of the sample with the reactant ions, (b) the mass or concentration of the sample, and (c) the vapor pressure of the sample in the inlet of the plasma chromatograph.

GC was successfully demonstrated to be one approach to controlled sampling for plasma chromatography[2,3]. The gas chromatograph has the advantage of being able to elute single components in a nitrogen matrix into the plasma chromatograph. In this manner, plasma chromatography is a means of peak identification and ultrasensitive GC detection. The combination of GC and plasma chromatography does not require any form of molecular separator or vacuum inlet and the response of the plasma chromatograph has been shown to be independent of the flow-rate of the carrier gas in GC for Freons[2]. However, extensive column conditioning must be used in order to eliminate stationary phase bleed from the gas chromatograph because of the very high sensitivity of the plasma chromatograph.

The concentration of the sample entering the plasma chromatograph cannot always be adequately controlled so as to avoid saturating the plasma chromatograph. Saturation of the plasma chromatograph by sample overloading and accompanying adsorption on the wall markedly increases the clearing time and may complicate the analysis of subsequent peaks. For example, there is seldom any need to identify or quantitate a solvent peak, and its concentration is always too high for it to be introduced directly into the plasma chromatograph. Thus a simple sample switching system between the gas chromatograph and the inlet of the plasma chromatograph would enhance the analytical utility of the plasma chromatograph. Similarly, the plasma chromatograph could be used for more extensive or complicated analytical problems if precise, controlled switching and sampling systems were available. For example, it would be desirable to multiplex several gas chromatographs or other sample sources into one plasma chromatograph. It should also be possible to sample many different sources, either serially or simultaneously, for plasma chromatographic analysis and these experiments will be discussed.

Fluidics were shown by Wade and Cram[4] to be an effective sampling system for GC. They proposed other analytical experiments and applications based on the control, sensing, logic, memory, timing and interfacing capabilities of fluidics, such as analytical sampling, solution and vapor-phase kinetics, stop-flow experiments, flame photometry, atomic absorption, plasma chromatography, titrators, sample and/or flow modulation, stream splitting, column switching, trapping, GC interface to mass spectrometer and IR spectrophotometer, automation and control, gas-phase separators, oscillators for fluid flow, and compensation for noise and baseline drift.

The results of their work indicated that the advantages of fluidic logic include (1) rapid and reproducible switching times; (2) dead volumes of the sample element in automated systems could be as low as 10 $\mu$l; (3) no moving parts or sliding seals; (4)

sampling systems can be automated for precision and/or routine sampling; (5) chemically inert, stable and can withstand temperatures of up to 800°; (6) they can be operated in all environments; (7) not subject to electrical noise or drift; (8) circuits have a wide dynamic range of timing variables; and (9) they are simple, versatile, reliable, of low cost, easily maintained and compact, and no special tools or supplies are required.

These advantages have been realized in industrial applications and used for displays, density measurements, frequency-to-analog conversion, frequency decoupling, phase discrimination, proportional control devices, velocity measurement, etc. However, fluidics are limited by being subject to clogging, active circuits components must be tuned, and the interconnecting tubing gives rise to timing delays. The principal problem to be overcome in gas chromatography was the fact that fluidic components are designed to operate at high volumetric flow-rates and low pressure drops (or loads). Obviously, the converse is true in GC.

The number of published analytical applications of fluidics is very limited. Fleet and Von Storp[5] reported liquid sampling experiments using water, aqueous solutions and volatile organic solvents. They were able to operate their logic system successfully with liquid flow-rates as low as 80 ml/min and predicted that even lower flow-rates could be achieved by reducing the dimensions of the flow channels.

It was therefore thought that fluidics could act as a nearly ideal analytical sampling system for many analytical detectors, such as the plasma chromatograph, where flow-rates of carrier gas of 100 ml/min or more are commonly used. Thus a number of different fluidic sampling systems have been developed for plasma chromatography to:

(a) Introduce very short duration sample pulses (*e.g.*, 10 msec with a monostable multivibrator). This is particularly advantageous in studying the fundamental processes in ion–molecule reactions, the response time of the instrument, and in generating low sample concentrations.

(b) Vary the sample concentration entering the plasma chromatograph by generating a preset number of sample pulses with a one-shot multivibrator. In this manner, the linear dynamic range, clearing time, and lower limits of detection of the plasma chromatograph could be measured.

(c) Selectively switching GC peaks into the plasma chromatograph.

(d) Introduce different reactant ions into the plasma chromatograph to enhance the chemical selectivity of the instrument.

(e) Multiplex one or more sample sources or gas chromatographs into the plasma chromatograph.

(f) Periodically sample in a serial mode from different sample sources, *i.e.*, digital multiplexing between chemical reactors, production streams, pollutant sources, etc.

(g) Sample a number of different sources simultaneously, such as reactant and product concentrations, with subsequent analysis by plasma chromatography. Such a device is analogous to a parallel-to-serial converter in digital logic.

The purpose of the present study was to demonstrate the operation of multicomponent fluidic systems, and their analytical utility and versatility as sampling systems into analytical detectors, *e.g.*, a hydrogen flame ionization detector or a plasma chromatograph.

## EXPERIMENTAL

The fluidic components used in this work were all active circuit elements. The sampling elements were mounted on a manifold such that each of the sampling fluidic components had independent 1/8-in. O.D. stainless-steel inlet tubes for the power supply ($P_s$), control ports and outlets. The control fluidics were mounted on a Corning mounting manifold (Model 191601), where all of the power supply ports were in common. PTFE tubing (1/8 in. O.D.) was used for all sample transfer and control connections on the manifold. All of the fluidic components referred to in this work are commercially available from Corning Fluidic Products (Corning, N.Y., U.S.A.): OR/NOR gates (Model 191453), AND/NAND gates (Model 191455), flip-flops (Model 191454), binary counters (Model 191464), back-pressure switch (Model 191491), one-shot multivibrator (Model 191458), interval timer (Model 191954) and time delay relay (Model 191466); and from Northeast Fluidics (Bethany, Conn., U.S.A.): electronic interface valve (Model 2013).

A plasma chromatograph (Model Beta VII; Franklin GNO, West Palm Beach, Fla., U.S.A.) which had been previously silanized with hexamethyldisilazane was used for these studies under the following operating conditions: carrier gas (air) flow-rate, 100 ml/min; drift gas (air) flow-rate, 500 ml/min; carrier inlet temperature, 280°; plasma chromatograph housing temperature, 188°; high voltage, $\pm$ 3000 V; grid gate pulse width, 0.2 msec; and scan time, 20 msec.

All of the gases into the plasma chromatograph or the gas chromatograph were filtered through 500-ml 13X molecular sieve traps, which were followed by particulate filters.

The plasma chromatograph inlet system was modified so that a minimum-dead-volume, all-stainless-steel (1/16-in. O.D.) system was used. The quartz sample inlet tube of the plasma chromatograph was removed and replaced with the stainless-steel tubing so that it extended 2 in. into the plasma chromatograph tube housing. A 2-in., 25-gauge needle was silver-soldered into the 1/16-in. connecting tubing to act as a flow restrictor to impedance match the GC flame ionization detector (FID) and the plasma chromatograph. The plasma chromatograph carrier gas was brought in through a Swagelok "T" downstream from the restrictor such that there were no unswept volumes in the interface and connecting tube.

The experimental fluidics–plasma chromatographic measurement system is shown in Fig. 1. It should be noted that the sampling logic is remote from the control logic so that it can be placed in heated zones and to reduce the dead volume of the sampling system to a minimum. A 125-ml gas scrubbing tower was arranged like an exponential dilution flask. Nitrogen was used as the carrier gas at a flow-rate of 6.8 l/min, and the test sample was dimethylformamide (DMF).

## DISCUSSION OF EXPERIMENTAL SAMPLING SYSTEMS

### *Monostable*

The fluidic one-shot multivibrator is the simplest conceivable automatic sampling system. It is shown schematically with a timing diagram in Fig. 1. The monostable converts the manual control signal, which is of indeterminant duration, into a 10-msec pulse. If no signal is present at control port $C_1$, the output is normally through

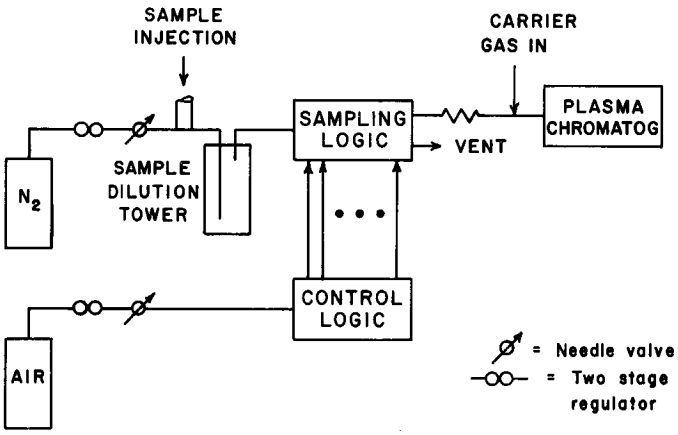


Fig. 1. Block diagram of the experimental system for fluidic sampling systems interfaced to a plasma chromatograph.

$O_2$. When a logical "1" ($\geqslant$ 5 p.s.i.) control signal is applied at $C_1$, the output switches $O_1$ "on" for 10 msec and then returns to $O_2$, the stable state. Output $O_1$ remains "off" until the signal at $C_1$ is removed and applied again. If $C_1$ is "high" for less than 10 msec, $O_1$ remains "high" only as long as $C_1$ is at a logical "1".

The monostable sampling system was used to study the clearing time of the plasma chromatograph. By switching a positive pressure of 10–30% of $P_s$ to the control arm, $C_1$, the monostable injected 10-msec pulses of DMF vapor into the plasma chromatograph. The sample size was varied by timing the delay after injection of DMF in the dilution tower. By using a restrictor in the plasma chromatograph inlet, the pressure drop across the fluidic sampling component was increased so that smaller flow-rates could be used.

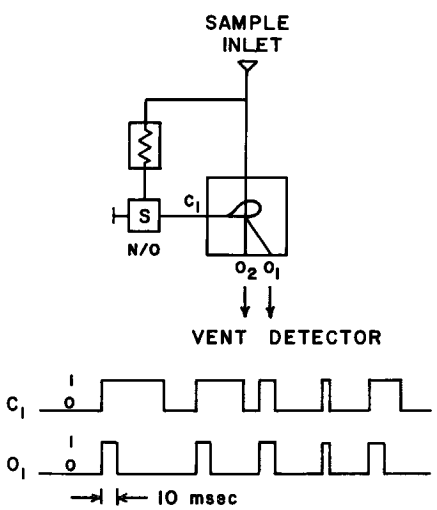


Fig. 2. Monostable fluidic sampler and timing chart. The output signal at $O_1$ shows the response to control signals applied at $C_1$ which are of random duration and frequency.

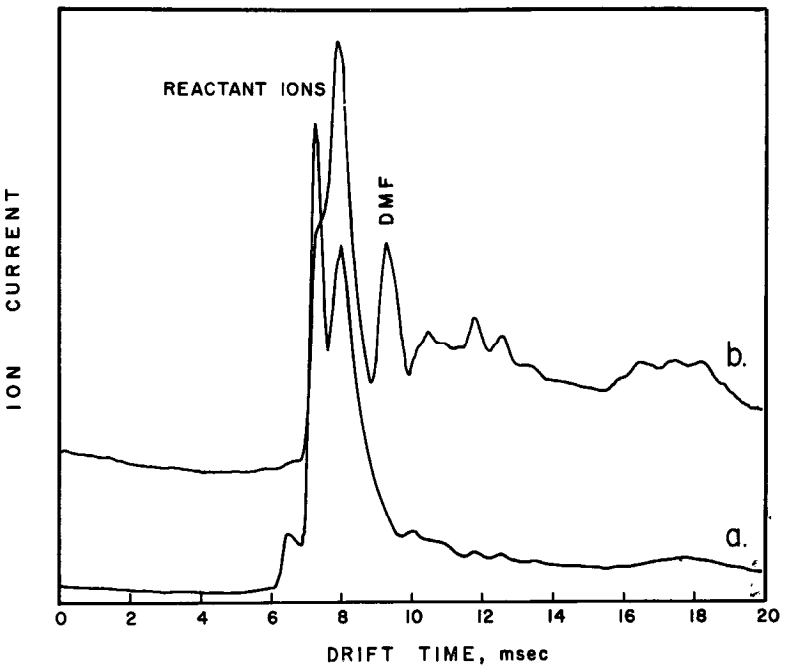


Fig. 3. Negative ion plasmagrams of (a) background signal from fluidic sampling system and plasma chromatograph, and (b) DMF vapor samples pulsed into the plasma chromatograph. Reactant ions are shown at drift times of 7.3 and 8.0 msec, and DMF ion-molecule drift time is 9.2 msec.

Fig. 3 compares the negative ion plasmagrams of (a) the plasma chromatograph background for the sampling system shown in Fig. 2 vented to the atmosphere, and (b) a negative ion plasmagram of DMF after twenty sample pulses were injected into the plasma chromatograph at intervals of 250 msec. The DMF ion–molecule peak at 9.2 msec represents a total concentration of about $10^{-9}$ g, assuming that there were

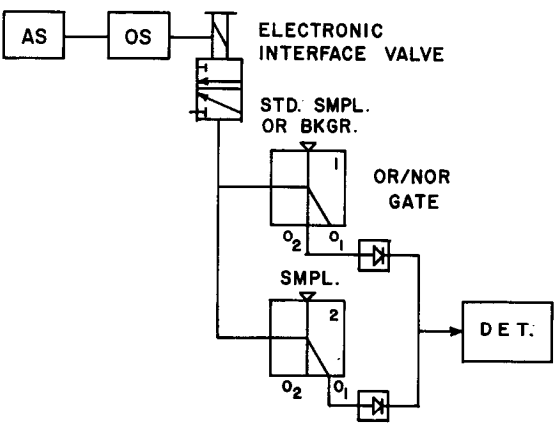


Fig. 4. Sample modulation system for chopping between a standard sample, reference signal or background entering OR/NOR gate 1, and the analytical sample flowing through gate 2. STD. = Standard; SMPL. = sample; BKGR. = bacground; DET. = detector; AS. = astable; OS. = one shot multivibrator.

no adsorption or condensation losses in the fluidics or connecting tubing. It is significant to note that the plasmagram shows the presence of the reactant ion in the presence of the sample and therefore the plasma chromatograph is not driven to saturation or overloaded. The peak height for DMF was found to vary with the number of pulses injected and the rate at which the monostable was pulsed. Under these conditions, the clearing time of DMF in the plasma chromatograph reaction chamber and drift tube was 3.5–5.5 sec, depending on the sample size injected.

*Sample modulation*

Sample input pulses are therefore advantageous for calibrating the plasma chromatograph as a detector, evaluating the linear dynamic range of the detector, measuring the lower limit of detection and studying the nature of the ion–molecule reactions. A fluidic sample modulation system was developed by using an electronic interface valve, two OR/NOR gates and a variable frequency oscillator, as shown in Fig. 4, to chop between a sampled input and a reference or background source. As the output of the interface valve goes "high", the standard, background or reference sample is vented to the atmosphere through $O_1$ and OR/NOR gate 2 is enabled so that the unknown sample is switched to $O_1$ and into the plasma chromatograph or other analytical detector. As long as the output of the interface valve is "low", the unknown sample will be vented and the effluent from gate 1 will flow into the plasma chromatograph. The pneumatic diodes prevent back-streaming from one gate into the other and have a very low forward bias. The oscillator circuit shown in Fig. 5 consists of an astable multivibrator followed by a one-shot or monostable squaring circuit which drives the electronic interface valve. The output of the square-wave oscillator is adjusted to give 20-msec pulses at continuously variable frequencies between 0.12 and 50 Hz. Thus the sampling frequency is variable in order to compensate for the response time of the detector and/or the sampling system. Binary counters may be added to this system to generate a pre-set number of sample pulses. In this manner, the sample size can be digitally controlled and totally automated. These systems may be either "hard-wired", in the case of fluidic logic, or controlled with an up-counter after the monostable.

An all-fluidic sample modulation system is shown in Fig. 6. The system differs

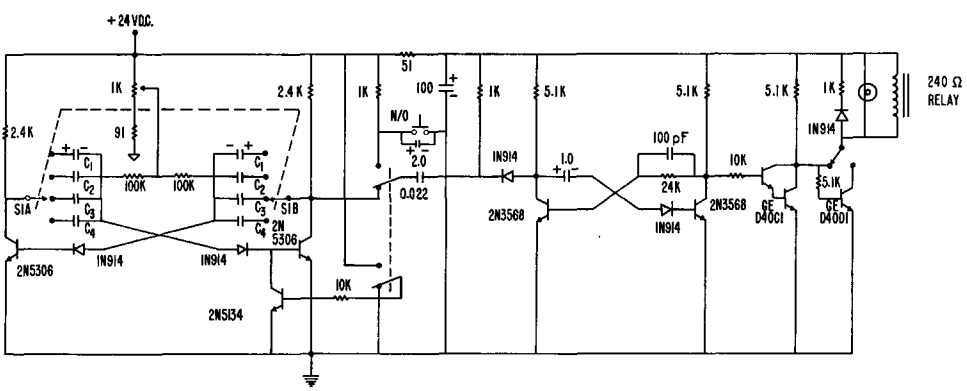


Fig. 5. Schematic diagram of the variable frequency oscillator circuit to drive the electronic interface valve.

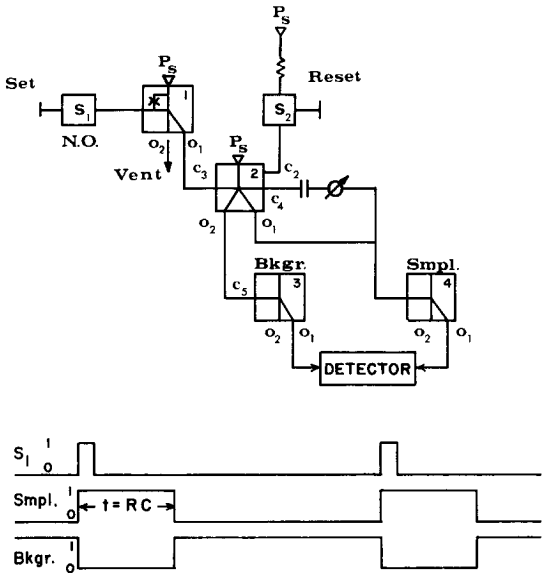


Fig. 6. Single-sample fluidic modulation system. Sampling period is variable and is activated by $S_1$. $P_s$ = Supply gas; Bkgr. = background signal/sample; Smpl. = analytical sample.

from the hybrid circuit described above in that it controls the duration of the sampling period by the *RC* time constant and is designed for the introduction of single samples. The power supply gas, $P_s$, to the back-pressure switch, gate 1, is normally vented through outlet $O_2$ and thus $C_3$ is a logical "0" on gate 2 such that the control signal, $C_5$, on gate 3 is "high". Thus the background, or reference signal, is delivered to the detector continuously until switch $S_1$ changes the state of the back-pressure switch. Upon switching its output to $O_1$, the output of flip-flop FF 2 is switched to $O_1$ and the vapor-phase sample entering $P_s$ on gate 4 is switched to $O_1$. The control signal at $O_1$ from gate 2 is also fed back through an *RC* network to control port $C_4$ such that as long as $t < RC$, outlet $O_1$ on gates 2 and 4 will be "high". When $t \geqslant RC$, the sample is turned off by re-setting FF 2, thereby removing the control signal to gate 4 and re-enabling gate 3 with a logical "1" at $C_5$. The pneumatic *RC* time constant consists of a 10-in.$^3$ buffer capacitor (C) and an adjustable needle valve (R). The connecting tubing represents an additional delay line component of 1 msec/ft. The timing diagram and logic levels for this sequence are also shown in Fig. 6. Switch 2 is used to re-set the logic system after it is first enabled; once operational, the only control needed is at $S_1$.

*Four-channel sample multiplexer*

Fig. 7 schematically illustrates the design and timing diagram of a four-channel sample multiplexer (MLPX). The system allows four independent sample inputs (A–D) through OR/NOR gates 4–7. Gates 1–3 are OR/NOR and binary counter control gates for automation of the system. The input control to gate 1 from the oscillator and interface valve toggles the gate 1 outputs into the binary counters, gates 2 and 3. The binary counters are clocked through the counting inputs $C_3$ and $C_4$ and switch the complementary binary outputs $O_1$ and $O_2$ alternately "on" and "off" in response

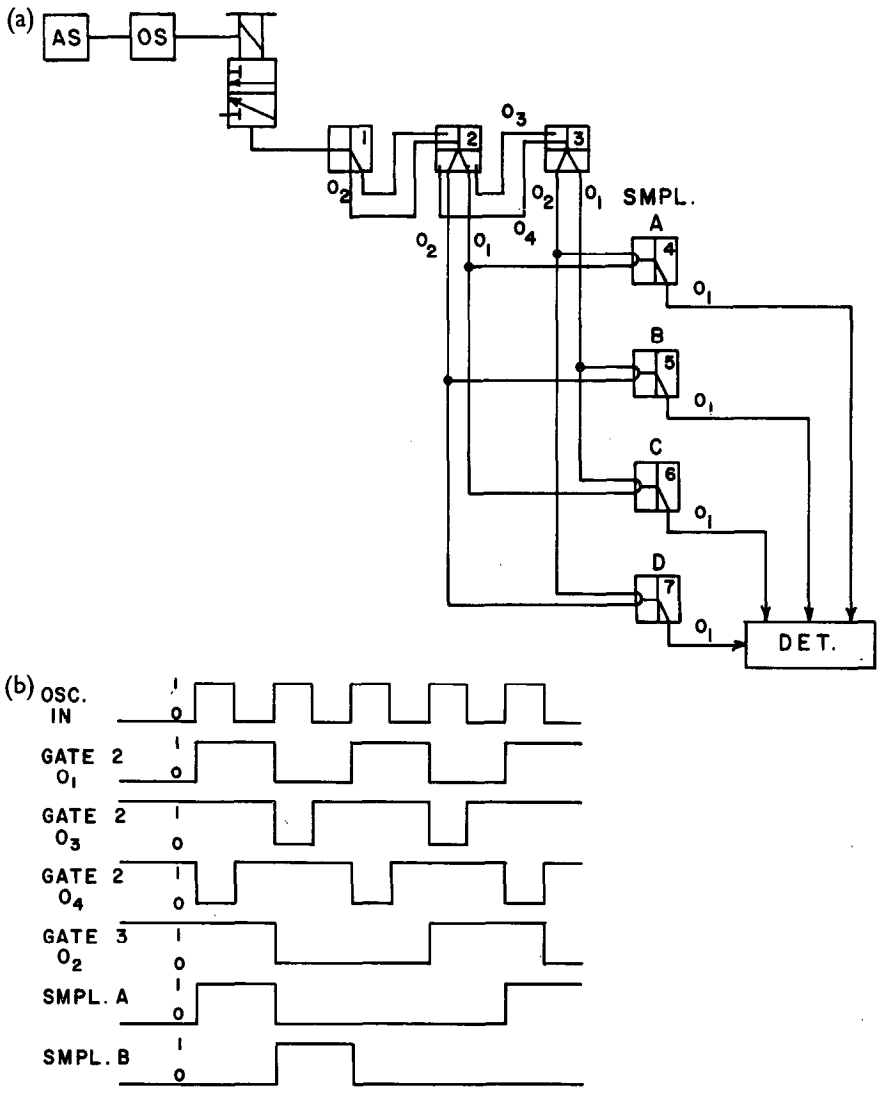


Fig. 7. (a) Four-channel sample multiplexer, using fluidic binary counters. (b) Timing diagram for synchronization of the principle logic elements in the four-channel multiplexer. AS = Astable; OS = one shot multivibrator; SMPL. = sample; DET. = detector.

TRUTH TABLE FOR THE FOUR-CHANNEL SAMPLE MULTIPLEXER

| *Input pulse* | *Outputs* | | *Sample input to detector* |
|---|---|---|---|
| | *Gate 2* | *Gate 3* | |
| *set* | *X* | *X* | *X* |
| 1 | $O_1$ | $O_2$ | A |
| 2 | $O_2$ | $O_1$ | B |
| 3 | $O_1$ | $O_1$ | C |
| 4 | $O_2$ | $O_2$ | D |
| 5 | $O_1$ | $O_2$ | A |

to each pair of input signals. Outputs $O_3$ and $O_4$ are provided for staging connections between counters.

Initially the counters are "set" with a logical "1" at the "set" control ports, which makes the $O_2$ outputs "high". Therefore, the first input clock pulse sets the output of gate 2 at $O_1$ and gate 3 remains at $O_2$, which enables OR/NOR gate 4 so that sample A is switched to the detector. The second clock pulse disables gate 4 because the control inputs are no longer both "true" and enables gate 5. Each succeeding clock pulse sequences through the MLPX and the fifth pulse received by the counter will re-enable gate 4 to begin a new sampling sequence.

The switching time of the system is limited by the number of logic elements and the delay lines. The switching time of each of the gates and counters is at least 10 times faster than the switching frequency of the system as configured in Fig. 7. The sample size entering the detector depends on the sampling time, flow-rate through the gate and the vapor-phase concentration in the gas stream. Therefore, it is imperative that the timing of the input control signal should be variable over a large range because the other parameters are usually fixed by the flow-rate requirements of the logic and by the nature of the sample itself. The switching frequency is thereby dictated by the sensitivity of response of the detector, the response time of the detector and the requirements for frequency of repetitive sampling.

*Multichannel multiplex system for analysis*

A larger multiplexing system was designed and built that has the additional features of a variable sample delay, measurement of the background signal after every sample and the introduction of an external standard between samples. The simplified timing diagram for this system is shown in Fig. 8. It can be seen that a positive going pulse from the interface valve clock circuit enables sample A to be introduced into the detector after a delay time ranging from zero up to the period of the oscillator, depending on the width of the sample input desired. The second positive-going pulse turns "off" the sampling gate and turns "on" a gate representing the blank or background signal for reference purposes and/or to purge the detector. This sequence is followed by the sampling of the external standard, another background/purge, and sampling of the second sample, which could be either a different sample, B, or sample A with an internal standard.

The logic for this system is also shown in Fig. 8. The first MLPX in the sequence serves as a controller for the sampling MLPX, enables the background gate (No. 5) on every second and fourth clock pulse, and turns "on" the external standard gate (No. 6) on the third pulse. The variable delay, D, uses a needle valve as a variable resistor to adjust the delay time from 1 to 10 sec. Gate No. 8 serves as a fan-out element to drive gates 16–19. These gates are required in order to isolate the sample MLPX gates from the detector line, *i.e.*, the sample MLPX will always be "on", regardless of the status of gates 5 and 6, and therefore the control lines to gates 16–19 must all be "low", except during sampling. The timing considerations for this system are similar to those described for the MLPX above.

*Parallel sampler*

The fluidic analog of a parallel-to-serial converter is shown in Fig. 9, which allows samples A–D to be collected simultaneously and then analyzed sequentially.

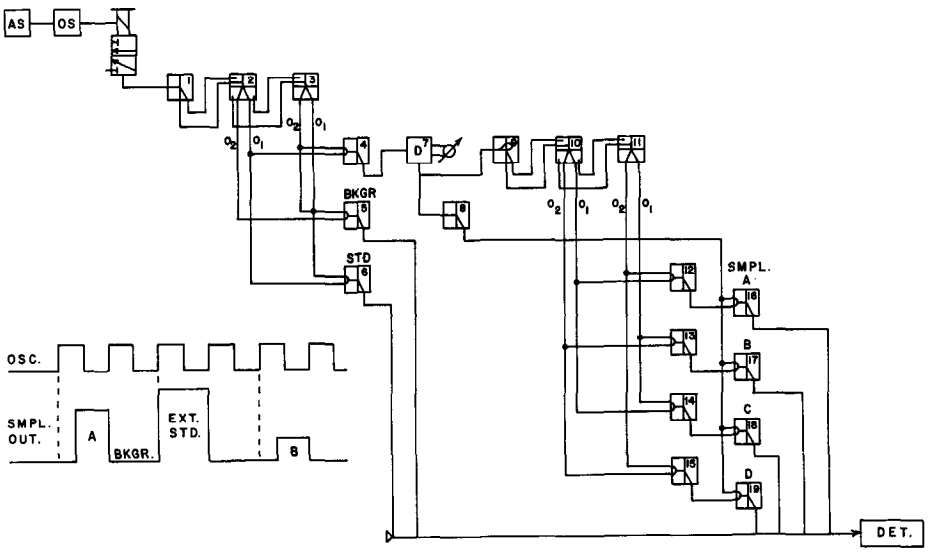


Fig. 8. Schematic diagram of a multichannel multiplex system for analysis. Timing chart shows the sequencing of the system. AS = Astable; OS = one shot multivibrator; D = time delay relay; BKGR. = background; STD. = standard; SMPL. = analytical sample; DET. = detector.

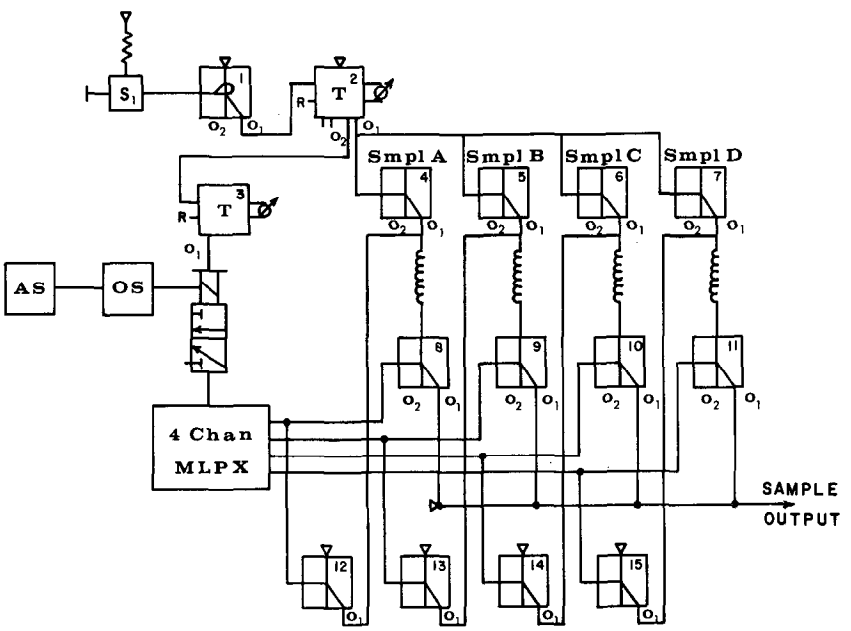


Fig. 9. Fluidic parallel-to-serial sampler for sampling four different inputs (A–D) simultaneously. AS = Astable; OS = one shot multivibrator; T = interval timer.

The system is manually activated through switch $S_1$ for sample collection. By activating the monostable (gate 1), the interval timer (T) for sample collection is initiated. Gates 4–7 are all "on" simultaneously as long is $O_1$ is at a logical "1". Intervals up to several minutes can be effected by adjusting the external resistance of the interval timer.

Outputs $O_1$ and $O_2$ are complementary. Therefore, the second interval timer is enabled when the first cuts off and determines the total "on" time of the MLPX. Samples A–D are collected in the sample storage coils. Gates 4–11 act as valves so that the sample appears to be in a flow-through system of defined volume and yet is isolated from the detector. At the end of the pre-set time interval, output $O_1$ on the timer goes "low" which disables the sampling gates, turns the second interval timer "on" and thereby enables the interface valve. At that stage the four-channel MLPX sequences each of the samples into the detector by enabling gates 8–11 in turn. As the first output of the MLPX goes "high", gates 8 and 12 switch to output $O_1$ so that the $P_s$ to gate 12 acts as a sweep gas and moves the sample through the sample coil and into the detector. The second clock pulse into the MLPX disables sample channel A and the associated gates, and enables an identical system for sample B. The MLPX will continue to sequence until it is disabled by the second timer. Thus timers $T_1$ and $T_2$ need to have independently large ranges in time. These elements are repeatable to $\pm 2\%$ between 1 and 15 sec. In addition, pneumatic diodes may need to be added to the system in order to prevent back-flow through the gates, depending upon the type and design of gates used.

*Serial sampler*

Fig. 10 represents a serial sampling system for cyclic sequencing through two or more different sample systems. Upon activation of the interval timer, T, by the switch and monostable, output $O_1$ goes "high" and switches sample A into the detector. The delay timer, D, is started simultaneously, which holds off sequencing to the second stage. Note that gate 7 is latched to the $O_2$ output at the start of the sampling period for A by the $O_4$ pulsed output of the interval timer. After the pre-settable delay period, FF 7 is set to the $O_1$ output by the output of the delay timer. This level change initiates the second monostable, sampling of the second sample (B), and FF 7 is reset back to $O_2$. This sequence will be continued until the last sampling stage is reached. The flip-flop in that sequencer is fed back to the first stage so that sampling is continued in a cyclic manner.

By varying the interval timers $T_4$ and $T_5$, and their associated time delays, samples A and B can be analyzed sequentially; with a purge interval in between the

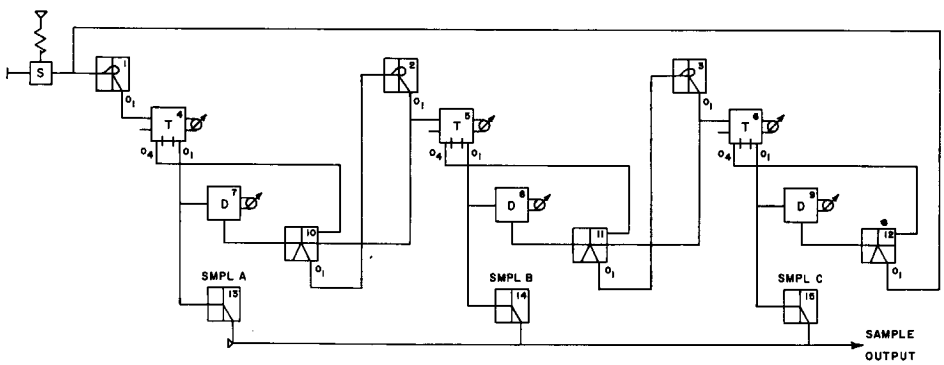


Fig. 10. Serial sampler for cyclic sequential sampling. T = Interval timer; D = time delay relay.

two samples, a differential or summation signal of A and B can be obtained, depending upon the detector configuration. Guiochon[1] suggested that one or more of these systems could be used in order to automate high-precision vacancy chromatography.

*General*

It should be noted that in all of the logic systems described, the sample passes through only one logic gate, which is the last gate before the detector. This is necessary in order to minimize sample contamination, cross-contamination and adsorption on tubing walls, and because it is desirable to have the maximum timing and flow-rate control on the sampling element. Therefore, it is not satisfactory for the sample logic components to serve also as control elements. In this manner, the total effective dead volume to which the sample is subjected is less than 10 $\mu$l, the inside volume of an OR/NOR gate.

Leakage of DMF vapor through control ports and logic outputs which were "off" was checked with the high-sensitivity plasma chromatograph, and no measurable signals were detected. Similarly, cross-talk between logic elements could not be detected, which indicates that fluidics can be a very quantitative sampling system when operated within specifications.

Integrated fluidic circuits are beginning to appear which offer the advantages of miniaturization, decreased delay times and lower dead volumes, and the need for "troubleshooting" will be greatly reduced. Therefore, we expect that fluidics will be used in a greater number of analytical applications in the future.

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