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MODIFICATION OF A COMMERCIAL DUAL CHANNEL VALVE TO BE USED IN A STOPPED-FLOW INJECTION ANALYSIS SYSTEM

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The commercially available variable-volume dual channel Tecator V-200 injection valve can also be implemented in stopped flow injection analysis systems, with some modifications in its bypass loops. The new configuration of the valve is reported. The features and reproducibility of halting the flow when different portions of the sample plug were located in the flow cell, for three FIA manifolds, were studied. With this modified valve, as it was expected, a steady state signal was obtained much more quickly than by the conventional procedure involving the halting of the peristaltic pump.

Keywords: Flow injection; stopped-flow; injection valve

Although the very nature of Flow Injection Analysis (FIA) allows all its possible measurement modes to be considered kinetic methods of analysis, from a more restrictive point of view, this denomination is only applied to those methods involving measurement of the rate of a chemical reaction. According to this definition, the stopped-flow variant is the FIA mode most commonly used in kinetic analytical methods. Essentially, it involves halting the carrier stream at some point along the manifold, which

in turn stops the dispersion of the sample plug and allows the rate of the reaction - proportional to the analyte concentration - to be readily measured.

The flow is usually halted in one of two ways, namely by stopping the peristaltic pump at a fixed delay time after injection and using a single three-way rotary valve between the injection systems,[1], or, as reported more recently, by using a newly designed multifunction HPLC-FIA injection valve.[2]

This paper shows the possibility of modifying the bypass loops of a commercially available variable volume dual channel Tecator V-200 injection valve for a twofold purpose: injection and halting of the flow. This recently marketed valve has already been employed in simultaneous analysis and in implementing zone-sampling and merging-zones FIA approaches.[3]

EXPERIMENTAL

Apparatus and manifolds

The different manifolds used were made up of a Gilson Minipuls-2 peristaltic pump, a variable-volume dual channel Tecator V-200 injection valve, a quartz flow cell (18 ul inner volume, 10 mm optical path length) and a Hewlett-Packard HP-8451A diode array spectrophotometer. The peristaltic pump was connected to a relay which, like the injection valve, was governed by an HP-8924 GPIO interface connected to the spectrophotometer HP-85 computer. All tubing and injection loops were 0.5 mm ID PTFE. A piece of back pressure tubing (200 cm long, 0.3 mm ID) was always kept after the detector flow-cell.

The stopped-flow mode was implemented on the conventional single, dual and three-channel manifolds depicted in Fig. 1 - for simplicity, the control system is only shown in the first manifold.

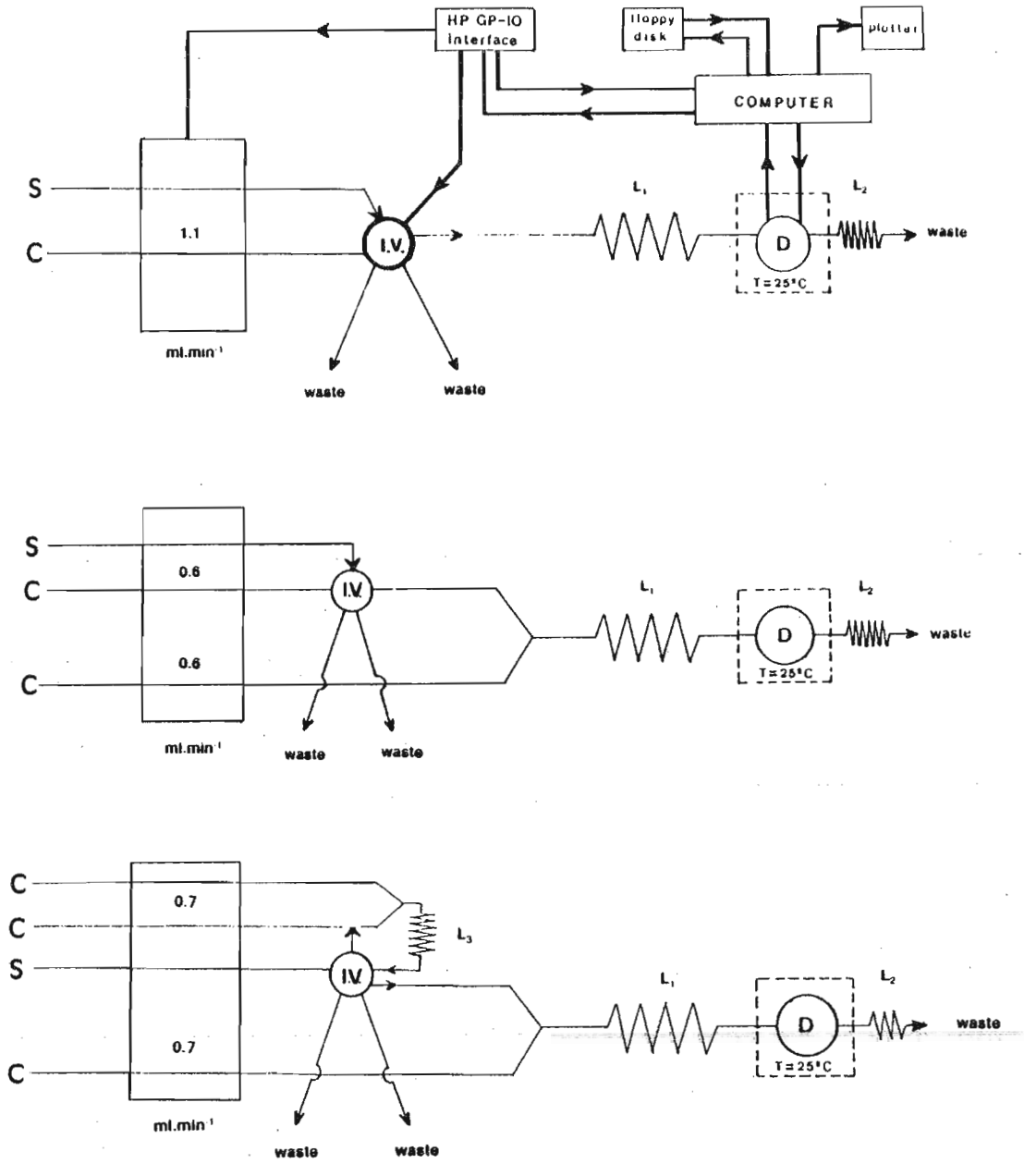

Figure 1. FIA manifolds used. Sample: Potassium dichromate 0.4 g l^{-1}, 0.01 mol dm^{-3}. Carrier: deionized water. V_{in} = 100 ul.

L_1 = 2 m, 0.5 mm ID; L_2 = 2 m, 0.3 mm ID; L_3 = 0.8 m, 0.5 mm ID

The experimental set-up was evaluated by using a 0.4 g/l solution of potassium dichromate in 0.01 mol dm^{-3} KOH and de-ionized water as carrier, and monitoring the absorbance at 374 nm.

Modifications in the injection valve

The Tecator V-200 valve used is a commercially available dual channel injection valve furnished with bypass loops. Roughly, it can be regarded s a combination of two conventional injection valves (V_1 and V_2). Figure 2 shows the schemes of their configurations for application of the stopped-flow mode. Compared with the standard configuration, V_1 is used for the usual purpose of injecting the sample, while V_2 is used without its bypass loops after linking its **H** and **G** positions. Under these conditions, if the carrier outlet of V_1 (**D**) is connected with the inlet of V_2 (**H**), the flow towards the detector is stopped at the loading position of V_1 (Fig. 2a) and restarted upon injection of the next sample (Fig. 2b).

Procedure

To test the applicability and performance of the proposed new arrangement of the bypass loops in the valve, the residence time (T_r) of each manifold was initially determined from four replicate injections of the dichromate solution. Then the flow was halted by switching the valve or stopping the peristaltic pump once the residence time - plus a preset delay time in some cases- had elapsed from injection. The absorbance was then measured every 2 s for 2 minutes. The reproducibility of the system was evaluated from 11 consecutive injections.

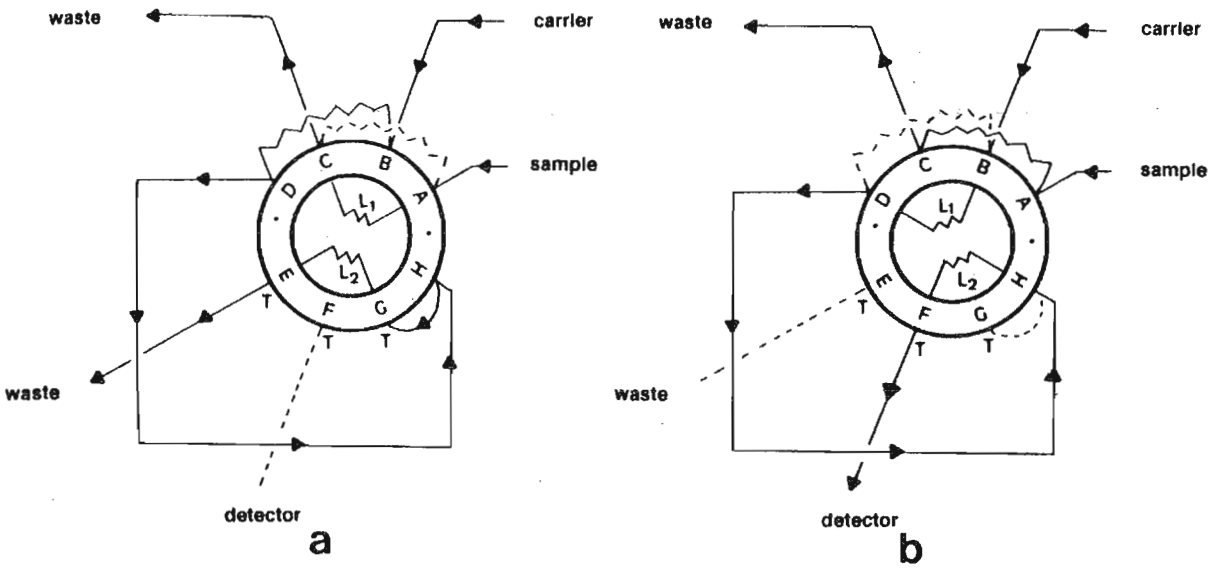

Figure 2. Injection valve arrangement. a) Load sample and stopped-flow position. b) Inject position.

L_1 and L_2: Injection loops. T: Sealed entries.

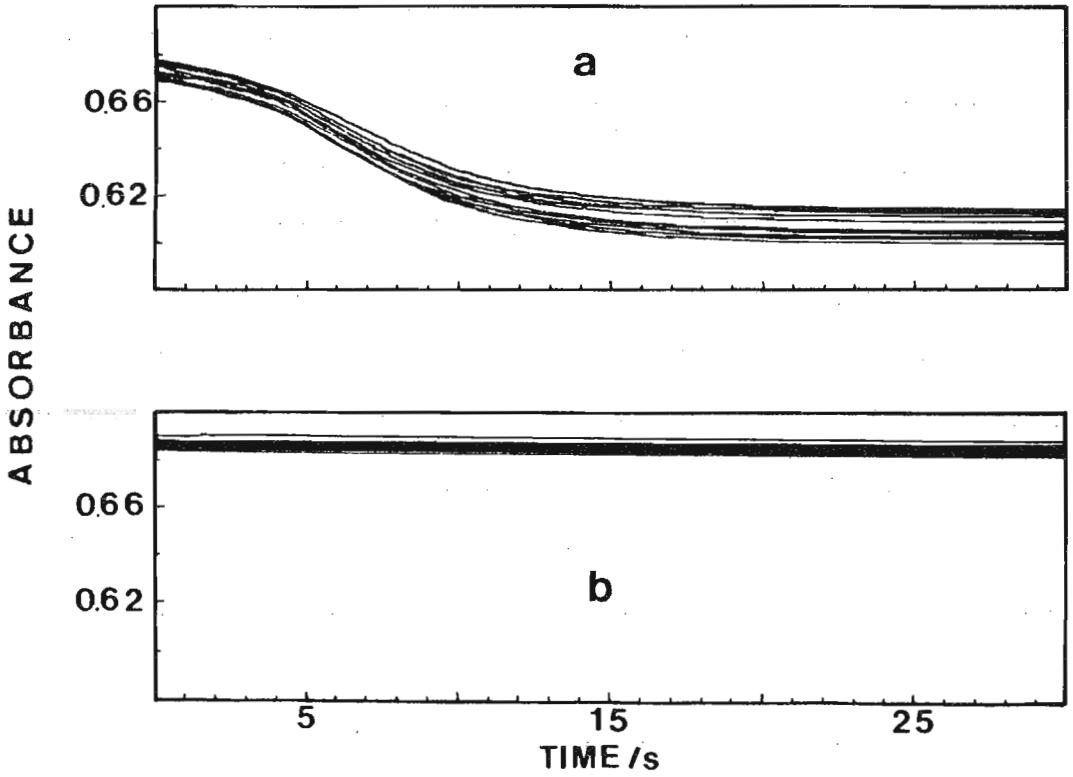

Figure 3. Absorbance vs. time for 11 injections, using manifold 3 and halting the flow at the maximum of the FIA peak. a) Stopping the peristaltic pump. b) Using the valve.

RESULTS AND DISCUSSION

The FIA stopped-flow technique, introduced by Ruzicka and Hansen in 1980,[4] is one of the most promising and widely used in implementing flow-injection kinetic methods. Basically, it involves halting the flow while a portion of sample plug is in the detection cell. Under these conditions, the effect of the only active force, namely axial diffusion, is virtually negligible, so that any change in the measured parameter (normally the absorbance) is exclusivelly due to the chemical reaction(s) involved and the disturbing effect of background and matrix signals is avoided as a result.

The fraction of the sample plug which must be in the flow-cell at detection depends on the nature of the system concerned. The analyte concentration -and hence the analytical sensitivity - is maximum at the maximum of the FIA peak and decreases along its tail. Thus, the dispersion along the FIA peak can be exploited to find a zone resulting in an optimal relation between the analyte and reagent concentrations or, simply, to adapt the sensitivity of the analytical process to the unknown concentration without the need to vary the injected volume or dilute the sample.

All these possibilities were considered in evaluating the performance of the proposed stopped-flow system by studying the reproducibility of the procedure in halting the flow at different positions along the tail of the FIA peak. Table 1 lists the results obtained (mean and relative standard deviation) from 11 replicate injections into the different manifolds by halting the flow at the peak maximum (H_m) and at different points corresponding to absorbance values of about 0.9, 0.5 and 0.2 H_m. only the data obtained in the first 20 s were considered as the absorbance did not vary significantly after that time.

As can be seen, the valve allows the flow to be stopped virtually instantaneously, which allows the obtainment of constant absorbance values with any of the manifolds; on the other hand, halting the flow by means of the pump results in

Table 1. Mean Absorbance values and relative standard deviations (%) obtained in 11 replicate injections by stopping the flow at different positions of the FIA peak using the injection valve (V) or the peristaltic pump (P). V_i = 100 ul

		Time (s)									
		0		6		10		14		20	
Position	**Mode**	**A**	**rsd**	**A**	**rsd**	**A**	**rsd**	**A**	**rsd**	**A**	**rsd**
						Manifold 1					
H_m	V	0.715	0.81	0.712	0.76	0.711	0.75	0.711	0.72	0.711	0.75
	P	0.700	0.47	0.681	0.59	0.679	0.66	0.678	0.68	0.677	0.72
						Manifold 2					
H_m	V	1.285	0.68	1.282	0.69	1.282	0.71	1.281	0.66	1.281	0.68
	P	1.236	0.70	1.158	1.21	1.147	1.22	1.145	1.22	1.145	1.22
						Manifold 3					
H_m	V	0.687	0.23	0.687	0.26	0.686	0.23	0.686	0.22	0.685	0.23
	P	0.673	0.45	0.617	0.79	0.608	0.82	0.607	0.84	0.608	0.83
0.9 H_m	V	0.628	0.48	0.626	0.49	0.627	0.49	0.627	0.49	0.627	0.49
	P	0.643	0.28	0.537	0.59	0.526	0.65	0.525	0.63	0.526	0.62
0.5 H_m	V	0.369	0.35	0.362	0.39	0.362	0.39	0.362	0.36	0.364	0.38
	P	0.362	0.86	0.252	1.03	0.244	1.07	0.242	1.11	0.245	1.10
0.2 H_m	V	0.205	1.75	0.203	1.67	0.203	1.62	0.203	1.57	0.204	1.57
	P	0.196	2.45	0.128	2.75	0.123	2.77	0.122	2.78	0.124	2.74

an appreciably decrease in the absorbance in the first few seconds. This is even more outstanding in Fig. 3, which shows the 11 curves obtained with manifold 3 by stopping the flow at the maximum of the FIA peak. With the peristaltic pump, the steady state is not reached until 15 s after it is stopped. This has been attributed to the inherent inertia of this element.[5]

The precision achieved was very good; in fact, the relative standard deviation was greater than 1% only when the flow was stopped at the end of the tail of the FIA peak. The best precision was obtained at the peak maximum; in addition, it was better for the valve than for the pump -except for the single-channel manifold, which yielded similar values.

From the results above, it can be concluded that the behaviour of the modified Tecator V-200 valve, is comparable with any injection valve suitable to be used in stopped flow injection analysis.

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