reaction between the amine component in Hydranal and the carbonyl compounds.

CONCLUSIONS

The proposed FIA method is capable of reducing the influence of large variations in the physical properties of the samples on the results. However, care must be taken in the choice of the solvent for the standard solutions to keep the matrix effect low. A standard solvent with a viscosity as similar as possible to that of the sample solvents seems to be the most favorable. Although the method has not been optimized with respect to kinetic discrimination between the Karl Fischer reaction and interfering side reactions such as the ketal reaction, slower side reactions have no influence on the results. Besides, the FIA technique offers some general advantages when compared to conventional titrations, for instance, high sampling rate, over 250 samples per hour; low consumption of the reagent, about 0.5 mL per sample; low sample volumes, 2–10 μL; a closed system, which means minimum contact with the toxic reagent; good reproducibility, typical values for the standard deviation in percent (v/v) H_2O were 0.0004 (coil reactor) and 0.0007 (SBSR), with peak area measurements; no need for calibration of the Karl Fischer reagent; no problems with the humidity of air in the reaction chamber. The main drawback with the FIA method results from the requirement for standards which have to be regularly determined with an alternative method. However, one possibility to minimize this disadvantage could be the use of electronic calibration according to Olsen et al. (*23*), where only one standard solution is needed. The linear range obtained for a conventional 7 mM Karl Fischer reagent is 0.001–0.100% (v/v) H_2O, which is suitable for the determination of water in organic solvents. A change in the strength of the Karl Fischer solution with a high buffer capacity is all that is required for use in a different concentration range.

Registry No. H_2O, 7732-18-5; 2-propanol, 67-63-0; diethyl ether, 60-29-7; benzene, 71-43-2; acetonitrile, 75-05-8; ethanol, 64-17-5; propyl acetate, 109-60-4; chloroform, 67-66-3; dichloromethane, 75-09-2; acetic acid, 64-19-7; isopropyl acetate, 108-21-4; triethylamine, 121-44-8.

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Monosegmented System for Continuous Flow Analysis. Spectrophotometric Determination of Chromium(VI), Ammonia, and Phosphorus

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A system for continuous flow analysis in which the sample is introduced in the flow manifold between two air bubbles is described. The characteristics of the system were evaluated in the absence of chemical reactions and have shown that the proposed approach can be employed for determinations that require long residence times. The system was tested in the spectrophotometric determination of ammonia, phosphorus, and chromium(VI). The results demonstrate that the proposed system can replace the classical segmented continuous flow analysis or flow injection analysis in many determinations with advantages in sampling rate, sensitivity, and reagent and sample consumption. The detection limits for determination of ammonia, phosphorus, and chromium(VI) are 5, 20, and 3 ng·mL^{-1}, respectively at 99.7% confidence level. The precision is better than 1% for all determinations and samples can be introduced at rates of 120 per hour or more.

Automated analysis with continuous flow systems can be classified into two major categories, one using segmented and the other using nonsegmented flowing streams. Skeggs' (*1*) classic work introduced the general technique of segmented continuous flow analysis (SCFA) with air-segmented streams. The function of air segmentation is to reduce longitudinal dispersion of sample along the flow path, which in turn decreases sample interaction and permits a long residence time for the sample, favoring sensitivity and enabling the use of relatively slow reactions. However, the air bubbles introduced into the fluid stream must be removed prior to measurement. The usual method employs aspiration of the bubbles before detection (*2*). This operation always removes some fluid, causes a delay in the half-wash time, and also disturbs the concentration profile of the sample zone. In order to avoid these shortcomings, SCFA systems work with signals at 90%, or more, of the steady state. Some other approaches, such as electronic identification of the bubbles, have been proposed to overcome this interference (*3–5*). In addition, SCFA systems usually require more complex and expensive instrumentation.

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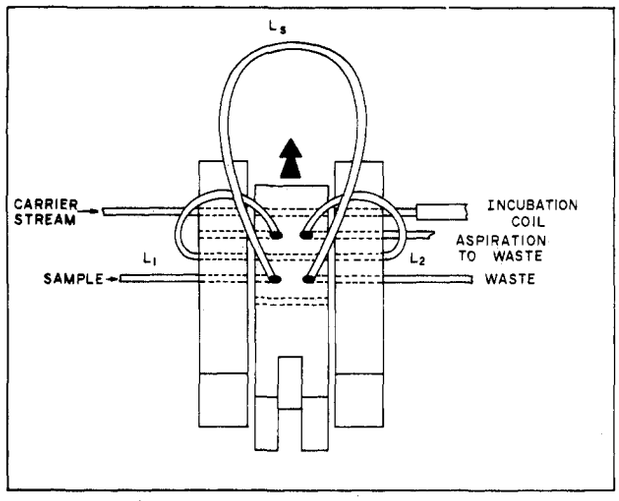

Figure 1. Injection valve. The arrow indicates the direction in which the central part is moved in order to introduce the sample in the carrier stream.

Nonsegmented continuous flow analysis, as described by Ruzicka and Hansen (*6*) and Stewart et al. (*7*), is termed flow injection analysis (FIA). This is presently the most used nonsegmented approach. In this case the sample is introduced as a plug via a valve, mixing is mainly by dispersion-controlled processes, and the response curves do not reach the steady-state plateau. FIA is capable of use with a high sampling rate, with good reproducibility and versatility. The instrumentation required is very simple and less costly. However, the residence time of the sample in nonsegmented streams is much shorter than in air-segmented systems and this seems to be an obstacle for analytical methods involving slow reactions, mainly if high sensitivity is required.

In the present paper, a system for continuous flow analysis is described in which the sample, between two air bubbles, is introduced in the flowing stream. The components of the system are those of common FIA apparatus and the air bubbles are removed with a permeation membrane before reaching the detector. The purpose for the development of this system was to sum up the good characteristics of the FIA technique, such as simplicity, reproducibility, versatility, and high sampling frequency with the possibility of working with slow-reaction methods. The proposed technique is called monosegmented continuous flow analysis (MCFA). It was first studied in the absence of chemical reactions and was then used for the spectrophotometric determination of chromium(VI), ammonia, and phosphorus.

EXPERIMENTAL SECTION

A diagram of the injection valve used to introduce the sample and the air bubbles is shown in Figure 1. The valve was built with acrylic blocks and its design is similar to that described by Bergamin et al. (*8*). Introduction of sample, between two air bubbles, is accomplished when the central part of the valve is moved forward and remains in this position until the second bubble leaves the L_2 loop. Then, it returns to the sampling position and stays there for the time necessary to pump a suitable volume of the wash fluid through the incubation coil. The volume of sample depends on the length of tubing L_S (1.5 mm i.d.). The volume of the air bubbles was 50 μL, obtained with two polyethylene tubes (L_1 and L_2, of 0.9 mm i.d.) of appropriate length. The injection valve was operated by means of two solenoids controlled by a microcomputer system (Telematic, TSI-1000).

The permeation cell used to remove the air bubbles from the flowing stream is schematically shown in Figure 2. The unit consists of two parts (A and B) made of acrylic and held together by four screws (not shown in the figure). A piece of commercial PTFE tape (Vedarosca, Incoflon Ind. Com., Ltda., São Paulo, Brazil; $d = 1.3 \pm 0.1$ g·cm^{-3}) of about 68 μm thickness was placed

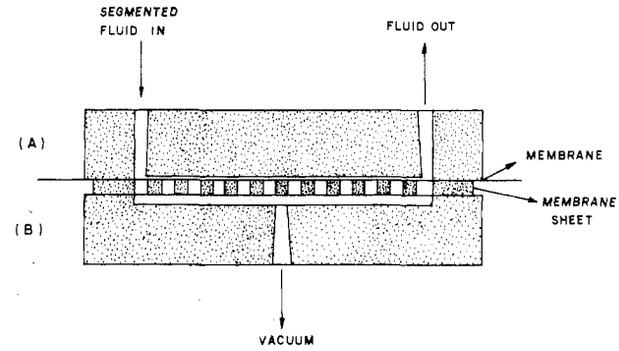

Figure 2. Air permeation cell for debubbling the flowing stream.

Table I. Values of D, t_B, and the Precision of Measurements as a Function of Sample Volume

introduced vol, μL	t_B, s	V, sample·h^{-1}	D	% rel std dev
50	12.5	288	2.68	1.2
100	15.0	240	2.14	0.7
200	20.0	180	1.34	0.3
300	22.5	160	1.16	0.1
400	25.0	144	1.14	0.1
500	27.5	130	1.11	0.1

over an acrylic sheet between the two parts of the cell. Part A has a shallow groove (volume of about 12 μL) through which the fluid flows. Part B has a groove (volume of about 60 μL) through which vacuum from a water aspirator was applied. The polytetrafluoroethylene membrane lasts about 6 h, working at liquid flow rates of 4.0 mL·min^{-1}.

The fluids were impelled with a peristaltic pump (Ismatec MP13 GJ4) and Tygon pumping tubes are employed. The spectrophotometric measurements were performed by use of a flow cell (volume of 80 μL) with a light path of 1 cm, installed in a spectrophotometer (Zeiss, PM2A) connected to a strip chart recorder (ECB, RE 101).

The flow diagrams used are shown in Figure 3. The mixing columns M were built with Tygon tubes (2 mm i.d., 4 cm long) packed with glass beads of 50–60 mesh. The incubation coils T_1–T_4 were polyethylene tubes (2 mm i.d.) wound with 15 cm diameters and with the following lengths: T_1, variable; T_2, 150 cm; T_3, 100 cm; T_4, 300 cm. The reagents and solutions used were as follows: R_1, 5×10^{-3} M ammonium molybdate in 0.2 M nitric acid; R_2, 0.5% (w/v) ascorbic acid; R_3, 2 M sulfuric acid; R_4, 0.2% (w/v) diphenylcarbazide in 25% (v/v) acetic acid; R_5, 0.2% (w/v) sodium hypochlorite; R_6, 2% (w/v) phenol and 1% (w/v) sodium prussiate; R_7, masquing solution of 5% (w/v) EDTA and 0.5 M sodium hydroxide. Reagent-grade chemicals were used throughout, except in the case of the hypochlorite solution where a commercial bleach was used. An aqueous copper(II) sulfate solution containing 1.25 g·L^{-1} of the metal was used to evaluate the monosegmented system in the absence of reaction.

RESULTS AND DISCUSSION

Characteristics of the System. The first experiments were performed with the purpose of evaluating the peformance of the monosegmented system in the absence of reactions. By use of the flow system shown in Figure 3A, the interdependence among sensitivity, sampling rate, and residence time was evaluated. Sensitivity was correlated to the dispersion coefficient, defined as $D = A_0/A_p$, where A_0 is the absorbance of the Cu(II) solution measured by introducing it directly into the flow cell and A_p is the peak absorbance obtained by introducing the same solution into the flow system. The residence time t_I (seconds) is defined as the time interval elapsed between the instant of sample introduction and the appearance of the signal. The sampling rate V (samples per hour) is given by $V = 3600/t_B$, where t_B (seconds) is defined as the time interval between the instant of appearance of the signal and its return to the base line.

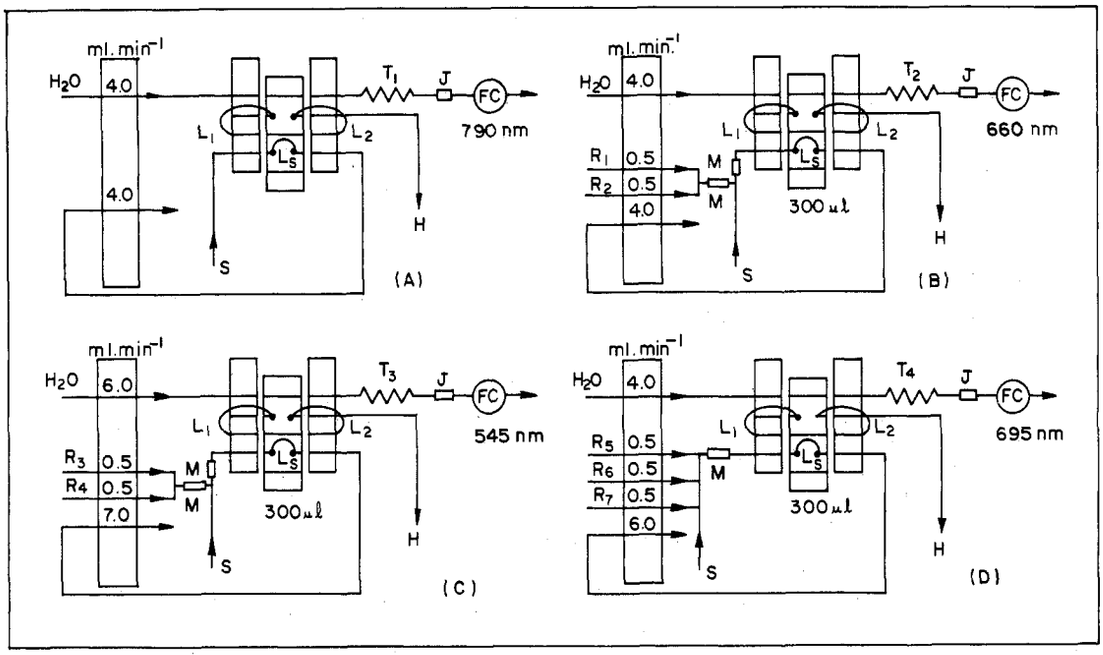

Figure 3. Monosegmented flow manifolds: (A) for evaluating the system; (B) for determination of phosphorus; (C) chromium(VI); (D) ammonia. FC denotes the flow cell where detection is made, at indicated wavelength. J is the permeation cell. H is the conection to water aspirator. See Experimental Section for other definitions.

Table II. Effect of the Length of the Incubation Coil on the Parameters D, t_B, and t_I and the Precision of t_I

incubation coil, cm	t_I, s	% rel std dev of t_I	t_B, s	D
50	28.2	0.4	20.0	1.11
90	51.7	0.3	21.0	1.13
150	84.3	0.4	21.5	1.14
300	163.1	0.1	22.5	1.14
600	328.1	0.1	27.5	1.15

Table I shows the results of the effect of sample volume on dispersion coefficient and sampling rate. The relative standard deviations of the values of absorbance (ten replicates) are also given in Table I. For these measurements the value of t_I was 58 s, obtained by using an incubation coil of 2 mm i.d., 100 cm long with a flow rate equal to 4.0 mL·min^{-1}. The results of Table I show that the system is capable of yielding high sampling rates and good sensitivities. It is also observed that better precision is obtained with sample volumes larger than 100 µL. This observation was expected because small volumes suffer more disturbance in the debubbling procedure. According to the results of Table I, the precision of the monosegmented system compares favorably with that for second-generation SCFA (AutoAnalyzer II) and FIA systems (*9*).

Results of experiments in which the length of the incubation coil (T_1) was varied are given in Table II. these results were obtained by using a flow rate of 4.0 mL·min^{-1} and a sample volume of 300 µL. As can be seen in this table, the monosegmented system permits the use of long residence times with little loss in sensitivity, as can be observed by the small values of D. Also, the results indicate that sampling rates higher than 120 samples per hour can be obtained with negligible carryover, even with residence times as long as 328 s, for the sample volume and flow rate indicated. This certainly represents the major advantage of the MCFA system described here over the FIA system in which to maintain acceptable sensitivity and sampling rates the residence time of the sample is limited to about 30 s. Table II also shows the precision (expressed as the relative standard deviation) of five measurements of t_I, for each example. These results show that the system can work with reactions that do not reach equilibrium in the flow system, provided that timing reproducibility is assured.

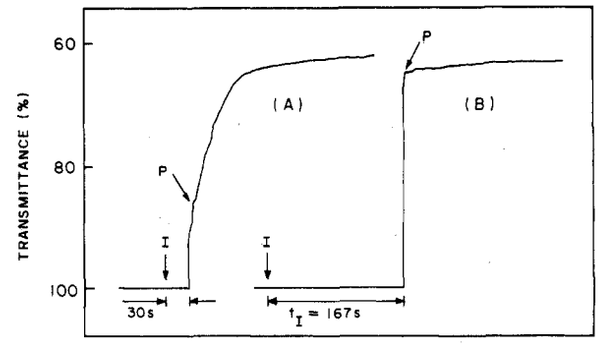

Figure 4. Magnitude of the signal as a function of time for the determination of ammonia. Incubation coil was 54 cm long (A) and 300 cm long (B). I denotes the instant of sample introduction and P represents the instant when the carrier stream was stopped.

Experiments were also performed where the flow rate was varied and its influence on D was found. The effect is negligible (D = 1.06–1.09) when a 300-µL sample solution is introduced in an incubation coil 100 cm long with the carrier stream flowing from 0.8 to 6.0 mL·min^{-1}.

After the performance of the proposed system in the absence of reactions was established, it was applied to the spectrophotometric determination of chromium(VI), phosphorus, and ammonia. These determinations were chosen because these procedures encompass relatively slow as well as relatively fast reactions and thus could serve well to test the monosegmented system.

Determination of Ammonia. A spectrophotometric procedure using a modified Berthelot reaction catalyzed by sodium nitroprussiate was employed for the determination of ammonia with the MCFA system described in Figure 3D. In order to find the time required for complete color development, preliminary experiments were performed by stopping the flow when the sample zone reaches the detector. Typical results are shown in Figure 4 and indicate that a residence time equal to 167 s suffices.

Figure 5C shows a calibration run obtained with standard solutions of ammonia (as ammonium chloride). Linearity was

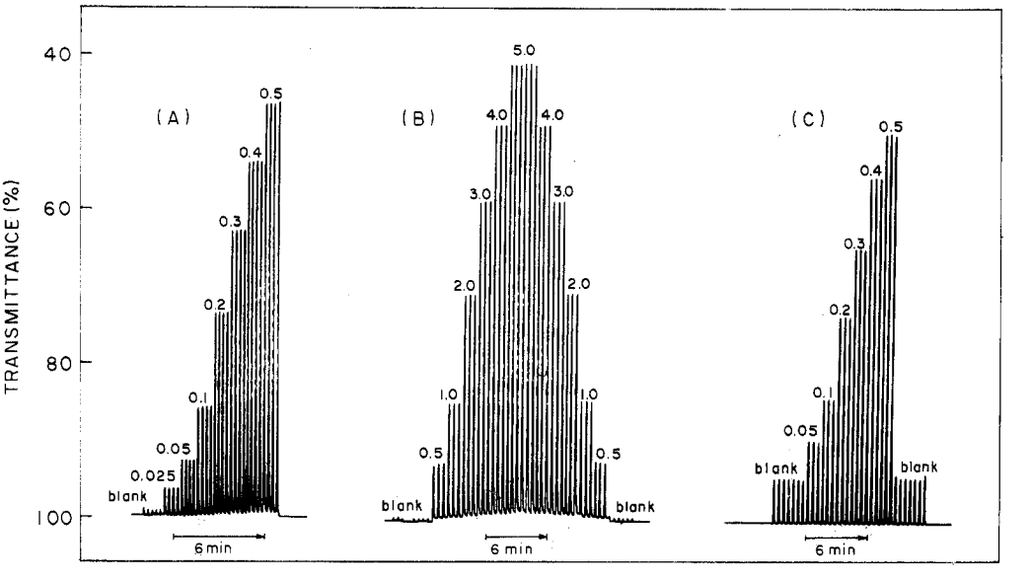

Figure 5. Photographic reproduction of calibration runs for determination of chromium(VI) (A), phosphorus (B), and ammonia (C). The numbers over the peaks represent the concentration of the species micrograms per milliliter.

obtained in the concentration range 0–1 $\mu g \cdot mL^{-1}$. The absorbance values A are related to the concentration of ammonia C_{NH_3} ($\mu g \cdot mL^{-1}$) by the equation: $A = -(8.0 \times 10^{-3}) + 0.5879C_{NH_3}$ with a correlation coefficient equal to 0.9998. The estimate for the standard deviation from 14 blank measurements is 9×10^{-4} absorbance units. This value enables calculation of a detection limit for ammonia equal to 5 $ng \cdot mL^{-1}$ at a confidence level of 99.7%. The standard deviation for the signal was ±5 and ±1 $ng \cdot mL^{-1}$, for ten replicates of, respectively, 1 and 0.05 $\mu g.mL^{-1}$ standard solutions. A sampling rate of 120 samples per hour can be obtained with negligible carry-over, as shown in Figure 5C.

A comparison between the performance of MCFA and that of a FIA procedure recently described (*10*) for determination of ammonia shows that the MCFA system allows a sampling rate and sensitivity about 30 and 40% higher, respectively. In addition, the MCFA system is simpler and does not employ a thermostatic bath operating at high temperature, which can hydrolyze nitrogen compounds and cause interference.

The proposed method was applied to the determination of ammonia in samples of natural water and the results are compared with the value determined by the accepted procedure (*11*) in Table III. A correlation coefficient of 0.997 was obtained and the results are related by the expression $C_{MP} = -3.0 + 1.007C_{MR}$ where C_{MP} and C_{MR} are the ammonia concentration found by the proposed and the reference method, respectively.

Determination of Phosphorus. Spectrophotometric determination of phosphorus with the MCFA system described in Figure 3B was carried out using classic reactions which form a heteropolyacid between molybdate and phosphate, following reduction of molybdenium(VI) to molybdenium(V) by ascorbic acid. Preliminary experiments, such as those described for the determination of ammonia (Figure 4) showed that a residence time of 84 s is sufficient for the development of color.

Linearity was observed in the range 0–8 $\mu g \cdot mL^{-1}$. The equation $A = -(4.1 \times 10^{-3}) + 0.07670C_p$ relates the absorbance value A with the phosphorus concentration, C_p, in the range 0–5 $\mu g \cdot mL^{-1}$ with a correlation coefficient of 0.9998. The standard deviation of 15 blanks is 6×10^{-4} absorbance units and the detection limit is 0.02 $\mu g \cdot mL^{-1}$ at the 99.7% confidence level. The standard deviation from six measurements of standard solutions of phosphorus of 1 and 4 $\mu g \cdot mL^{-1}$ is ±0.01 $\mu g \cdot mL^{-1}$. The sampling rate is 120 samples per hour with negligible carry-over, as observed in Figure 5B. The MCFA procedure allows a sensitivity 65% higher than that reported by Ruzicka and Hansen (*12*) for the FIA procedure employing the same reagents, detection wavelength (660 nm), and similar sample volume (320 μL for FIA and 300 μL for MCFA). The sampling rate is about 50% higher with the MCFA system and, in addition, no thermostatic bath needs to be employed to accelerate color development.

Table III. Results for the Determination of Ammonia in Natural Water

sample	C_{NH_3}, $ng \cdot mL^{-1}$ proposed method	C_{NH_3}, $ng \cdot mL^{-1}$ ref method[b]
1[a]	629	620
2	168	192
3	238	238
4	108	118
5	281	292
6	179	180
7	35	27
8	157	139

[a] Sample analyzed after 2-fold dilution. [b] From ref 11.

Determination of Chromium(VI). The reaction between Cr(VI) and 1,5-diphenylcarbazide is frequently used for determination of this toxic metallic species, due to high selectivity and sensitivity (*13*). Under suitable conditions of acidity, color develops rapidly. Preliminary experiments stopping the carrier stream revealed that the reaction is completed within 10 s. The residence time in the present work was fixed at 30 s and the determination was carried out by use of the MCFA system shown in Figure 3C.

Linearity of response was observed in the range 0–0.7 $\mu g \cdot mL^{-1}$ in which the absorbance value A is related to the Cr(VI) concentration C_{Cr} by the equation $A = -(3.5 \times 10^{-3}) + 0.6684C_{Cr}$ with correlation coefficient of 0.9999. The standard deviation of ten blanks is 5×10^{-4} absorbance units allowing a detection limit of 3 $ng \cdot mL^{-1}$ with a confidence level of 99.7%. The precision of the measurements is ±2 ng·mL for ten replicates of signals obtained for standard solution with 0.025, 0.1, and 0.5 $\mu g \cdot mL^{-1}$ of Cr(VI). A sampling rate of 210 samples per hour was observed with negligible carry-over. Figure 5A shows a calibration run for Cr(VI) determination.

A recent reported FIA procedure for Cr(VI) determination (*14*) based on the same chemistry is more than 3 times less sensitive and has a sampling rate about 75% lower than that obtained with the MCFA system. Sensitivity for the FIA

procedure can be increased if the single-line system used (*14*) is changed to one with confluence. If this is done, however, the sampling rate is diminished.

Comparison of the MCFA with SCFA and FIA. The MCFA system utilizes air segmentation in order to avoid large dispersion values. Models developed to estimate the extension of dispersion in SCFA (*15*) show that the frequency of sample and carrier segmentation has an optimum value for a given flow rate. Thus, a procedure that distributes the sample as a single segment leads to larger dispersion coefficients. However, the MCFA system proposed here allows residence times as large as 5 min, with acceptable dispersion coefficients and negligible carry-over, even at sampling rates of 120 samples per hour.

The advantages of the MCFA in comparison with SCFA seem to be its simplicity and the possibility of working with smaller sample volumes and larger sampling rates. The MCFA does not require an automated sampler with wash cycle and its segmentation is generated in a reproducible way by an inexpensive valve, eliminating the air-bar timed at roller liftoff of the peristaltic pump. The presence of only a few air bubbles in the MCFA system contributes to timing reproducibility. The manifold is simpler than that in SCFA, because the air segmentation is created and eliminated without additional pumping tubes. The start up time for the MCFA varies with the residence time from 30 s to 5 min. In the present system, small sample volumes, such as 100 μL, can be introduced by the valve with a reproducibility better than 1%. Total sample consumption can be minimized by decreasing the volume of the sampling tube (S, Figure 3) and the aspiration flow rate. If smaller flow cells (e.g., 2 μL) are available for detection, sample volumes can be reduced. In addition, the perfect timing between the air bubbles can facilitate the detection, with the bubbles passing through the flow cell. The MCFA yielded a sampling rate 2 times higher than that for typical SCFA (60 samples/h) for slow reactions (as in ammonia determination) and this value can be increased for fast reactions (as in Cr(VI) determination).

The principal advantage of the MCFA over FIA is that the first system allows long residence times. When a slow reaction is employed in FIA there is an interdependence between sampling rate and sensitivity. Then, when sensitivity is an important factor, all the attempts to improve it have caused a decrease in sampling rate (e.g., stop flow and zone trapping techniques (*10*)). On the other hand, if a fast reaction is employed, the intrinsic capacity of the MCFA to keep dispersion low allows the system to operate with small sample volumes, resulting in higher sampling rates and reaching at least the same sensitivity of FIA (as demonstrated in the determination of Cr(VI)). If sensitivity is necessary, the MCFA manifold is as simple as those for FIA. However, for analytical procedures where sensitivity is not essential, FIA manifolds can be simpler and can give higher sampling rates.

Reagent consumption in the present work was decreased because the sampling rate was increased for all determinations. Nevertheless, additional reagent economy could have been obtained by using a lower flow rate for the sample and reagent streams than that used for the carrier stream (keeping the necessary sample to reagent ratio). This is possible because in the MCFA system the reagents are introduced into the sample stream before its insertion into the carrier stream (see Figure 3) and also because the insertion valve remains in the sampling position most of the analytical cycle. A limit on reagent economy is imposed by the volume needed to wash the feed line, and for this reason this line is made as short as possible. In the present work, reagent consumption was not diminished to lower levels because only a few Tygon pumping tubes were available.

Manual operation of the sampling valve is possible with the MCFA. For operation of the valve in this mode, some marks are made on the incubation coil which indicate the time to change the valve position, after the passage of the first or second bubble of a previously introduced sample.

The results obtained with the proposed system and its favorable characteristics seem to permit the conclusion that MCFA can advantageously substitute SCFA and FIA systems in determinations that can be done by using continuous flow analysis. Further studies will be necessary to investigate in detail the behavior of dispersion in MCFA systems and to study the possibilities of miniaturization.

Registry No. NH_3, 7664-41-7; H_2O, 7732-18-5; Cr, 7440-47-3; P, 7723-14-0.

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