Usefulness of a detector inlet overpressure and stream splitting in FIA systems to deal with food sample pre-treatment requirements. Application to wine analysis

José L.F.C. Lima* and António O.S.S. Rangel†

The use of stream splitting to obtain high sampling rate flow injection analysis (FIA) large dispersion manifolds to deal with pre-treatment requirements in the analysis of food components with a high concentration is described. This procedure is illustrated in the FIA determination of calcium using an atomic absorption detector and in the colorimetric determination of phosphate in wines. These manifolds proved to be an advantageous alternative to those including mixing chambers and diluters, as they are simpler and provide higher sampling rates (60–240 samples h^{-1} are achieved). Also described here is the use of an overpressure at the entrance to the atomic absorption nebulizer to minimize matrix physical interferences, by presenting the results obtained for the FIA–atomic absorption copper determination in wines. The results obtained for several wine samples by the developed FIA methodologies were in good agreement with those provided by the reference methods.

Keywords: flow injection analysis; flow splitting; AAS inlet overpressure; copper; calcium; phosphate; wines

INTRODUCTION

In the past few years flow injection analysis (Ruzicka and Hansen, 1988) has been increasingly used in the field of automatic continuous flow analysis mainly because it is simple, inexpensive and provides rapid and precise results. This technique presents a new concept of solution handling, based on the dispersion control of a sample plug introduced in a carrier stream and on the measurement of the analytical signal in non-homogeneous and non-equilibrium conditions. The dispersion control is accomplished by combining sample injection into a carrier stream with detection in rigorous reproducible timing.

Due to its characteristics and performances, this methodology has become an advantageous alternative to the segmented flow systems (SFA) (Skeggs, 1957) in widespread use since the 1960s, with commercially available equipment, mainly dedicated to wine and other food products analysis.

The FIA systems can be used to replace a large number of manual sample pre-treatment procedures that have to be carried out before measurement, which usually determine the analysis time and cost. Actually,

*Physical Chemistry Department, Faculty of Pharmacy of Porto, R. Anibal Cunha, 4000 Porto, Portugal and to whom all correspondence should be addressed
†College of Biotechnology, Portuguese Catholic University, R. Dr. António Bernardino de Almeida, 4200 Porto, Portugal
This paper was presented at the International Symposium on Automatic Control of Food Processes, ACoFoP II, Paris, 14–15 November 1990

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analysis may require extensive sample dilution either because the analyte concentration is much higher than the instrumental linear working range or the matrix composition may in some way interfere in the measurement. The influence of the physical characteristics of the matrix, namely viscosity and superficial tension, on the analytical signal is particularly critical when using atomic absorption or flame emission spectrometry as detection processes, as both the inlet aspiration rate and the nebulization efficiency are affected by these characteristics.

In this situation, it is advantageous to implement high dispersion FIA systems to perform, on-line, the required sample dilution. The development of high dispersion manifolds by using several confluence points, diluters, well-stirred mixing chambers or long tube lengths substantially decreases the sampling rate. This difficulty was overcome by using stream splitting, which provided the required dilution coupled with higher sampling rates.

Additionally, when using an atomic absorption detector an FIA system was used that imposed a flow-rate at the entry of the nebulizer, which was higher than that recommended for conventional solution introduction provided by the instrument. This overpressure was sufficient to minimize the physical interferences of the matrix and also to diminish the analytical signal by reducing the nebulization efficiency, thus requiring smaller on-line dilution.

The advantage of using stream splitting is illustrated in the colorimetric determination of phosphate and by comparing two different manifold performances in the determination of calcium in wines using atomic absorption as the detection system. In both determinations dilution was required because the analyte concentration was too high for direct measurement and because matrix interferences of different sorts were present.

The use of an overpressure at the entry of the atomic absorption nebulizer to minimize the matrix physical interferences is illustrated in the copper determination.

MATERIALS AND METHODS

Instrumentation

The atomic absorption determinations were made with a Pye Unicam Model SP 9 atomic absorption spectrometer. The phosphate spectrophotometric determination was performed with a Bausch & Lomb Model Spectronic 21 spectrophotometer equipped with an Hellma Model 178.713 flow cell. Both instruments were coupled to a Metrohm Model E 586 Labograph chart recorder.

Reagents and solutions

To prepare the solutions, deionized water with a specific conductivity $<0.1\,\mu S\,cm^{-1}$ and analytical-reagent grade chemicals are used. The working copper and calcium standard solutions are prepared by suitable dilution of a stock solution of $1000\,mg\,l^{-1}$ (BDH Chemicals, Poole, UK). For the phosphate determinations, working standard solutions are prepared by dilution of a $10\,000\,mg\,l^{-1}$ stock solution, obtained from careful weighing of di-potassium hydrogenophosphate trihydrate.

In the calcium atomic absorption determinations the lanthanum solutions are 2% in HCl, and 10 000 and $13\,500\,mg\,l^{-1}$ in lanthanum (III): R_1, in *Figure 3a* and R_2 in *Figure 3b*, respectively.

In the phosphate colorimetric determinations, the molybdate solution (R_1 in *Figure 4*) is prepared by dissolving 10.0 g ammonium heptamolybdate tetrahydrate in 0.65 M sulphuric acid and then making up to 1 l with the 0.65 M sulphuric acid. This solution is stable for several months. The reducing solution (R_2 in *Figure 4*) is prepared by dissolving 0.20 g tin (II) chloride dihydrate and 2.0 g hydrazinium sulphate in 0.50 M sulphuric acid and then making up to 1 l with the 0.50 M sulphuric acid. This solution is stable for at least 1 week.

Flow injection manifolds

In the propulsion of the solutions Gilson Model Minipuls 2 peristaltic pumps and pumping tubes of the same brand are used. The injection of the solutions is made with a six port Rheodyne Type 50 injection valve.

The connection between the different components of the manifolds is accomplished by Omnifit Teflon tubing (0.8 mm i.d. for the atomic absorption determinations and 0.5 mm i.d. for the colorimetric determinations) with Gilson end-fittings and connectors, and also home-made Y-joints (Alegret *et al.*, 1987), that could be used as confluence points or stream splitters. To improve mixing and dilution in the calcium determination home-made perspex diluters and a well-stirred mixing chamber similar to those described previously (Valcarcel and Luque de Castro, 1987) were used. The diluters are devices with a flow path in chicane, with an i.d. 1.0 mm and a 17.5 cm length, which produce an increase in radial dispersion. The well-stirred mixing chamber had a conventional configuration, with a 10 mm base diameter and variable height, holding in this case a volume of $\approx 332\,\mu l$. Inside the chamber a magnetic bar rotated at about 320 rotations min^{-1}, activated by an exterior magnetic stirrer.

For the phosphate determination FIA manifold the physical dispersion (dilution) of the sample plug throughout the flow system is presented as Ruzicka's dispersion coefficient (Ruzicka and Hansen, 1988).

In the atomic absorption measurements, as there is an apparent dispersion in the nebulizer that depends on its configuration and flow-rate entry, the dispersion coefficient quantifies the joint effect of the FIA system and the detector as the analytical signal diminishes, and was evaluated as the quotient between the concentration of the species before the introduction in the flow system and the maximum concentration at the moment of the detection (atomizer). Thus, the dispersion coefficients presented for the atomic absorption FIA manifolds represent the overall contribution to the diminishing of the analytical signal.

The values presented for the reproducibility of the FIA methods (precision) (IUPAC, 1976) are expressed as the relative standard deviation of the ion concentration of a wine sample, calculated from 10 repeated injections. The detection limit was calculated as corresponding to three times the standard deviation of the whole assemblage background noise (IUPAC, 1976).

Procedures used to assess the results

In the copper and calcium determinations, analyses were carried out according to the respective Office International de la Vigne et du Vin (OIV) reference method (Bonnemaire and Brun, 1971; OIV, 1986), in which the samples are prepared in volumetric flasks and then introduced in the atomic absorption spectrometer. In the absence of a reference method for the phosphate determination, several recovery tests have been performed by making phosphate standard additions of 100 mg l^{-1}.

RESULTS AND DISCUSSION

In atomic absorption spectrophotometry, as well as in other instrumental methods of analysis, the concentration range in which it is possible to make determinations with a linear response between the physical property measured and the concentration is rather limited, so there are few conventionally performed determinations in which the sample is introduced directly into the detector system. Usually, it is necessary to adjust the analyte sample concentration to the analytical process, thus demanding previous dilution of the sample, which can also be required to reduce matrix physical interferences. In some cases, it is also necessary to add agents to eliminate chemical interferences which occur in the flame. This operation is conventionally carried out simultaneously with dilution in a volumetric flask.

In wine analysis by uv/visible spectrophotometry, alongside the problems of concentration adjustments mentioned previously, it is also necessary to account for the intrinsic light absorption of wines. This latter difficulty, if not eliminated, would demand a blank determination thus reducing the determination sampling rate by half.

To make these pre-treatment procedures with a FIA system, the dilution and reagent addition is done inside the manifold components, thus requiring high dispersion flow injection manifolds.

The advantage of using stream splitting to implement high dispersion manifolds and an overpressure in the atomic absorption nebulizer inlet is shown for copper and calcium atomic absorption determination and for the colorimetric determination of phosphate in wine analysis.

Use of an overpressure in the nebulizer inlet of the atomic absorption detector

As in flame atomic absorption spectrophotometry, the occurrence of spectral interferences is extremely rare, and those of a chemical and ionization nature are easily overcome by the addition of the appropriate reagents. The physical interferences due to matrix viscosity and superficial tension became a major problem that can only be efficiently minimized by sample dilution, by performing a standard addition procedure, or by using standard solutions with a synthetic matrix to match the samples.

This is the current situation in the determination of copper in wine, in which sample dilution is not possible because the sample concentration is close to the method detection limit. Thus a conventional procedure is required, such as a standard addition method (Bonnemaire and Brun, 1971). The usefulness of using a FIA system with an inlet overpressure to overcome this problem is demonstrated here by using a single channel low dispersion manifold (3.0 for the dispersion coefficient) (*Figure 1*).

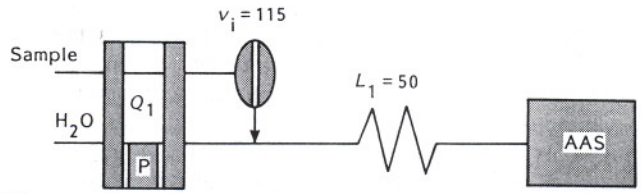

Figure 1 Flow injection manifold for the atomic absorption determination of copper in wines: v_i, injection volume (μl); P, peristaltic pump; L_1, tube length (cm); Q_1, flow-rate (8.0 ml min^{-1}); AAS, atomic absorption spectrophotometer

The sample plug is injected into the water carrier stream, and transported to the detector through L_1 with a flow rate $\approx$ 3 ml min^{-1} higher than the recommended rate for conventional introduction.

The efficiency of using this overpressure is demonstrated by comparing the analytical signal obtained in optimum instrumental conditions for 1 mg l^{-1} copper solutions with an ethanol content varying from 0 to 50%, by conventional nebulizer introduction and with the FIA manifold (*Figure 2*).

From inspection of *Figure 2*, it becomes clear that in conventional solution aspiration the analytical signal is, as expected, strongly influenced by the solution composition, while the measurements performed with the FIA system are virtually independent of the ethanol content.

This can be explained, in the FIA manifold case, by the fact that the introduction flow-rate is only controlled by the peristaltic pump and not by the aspiration rate promoted by the spectrophotometer, which is greatly affected by the physical properties of the matrix. Consequently, wines with very different alcohol contents, such as table wines and ports, can be introduced directly in the flow system without any previous treatment.

To demonstrate that the advantages of this FIA methodology are not incompatible with achieving good quality results, a comparison of the results obtained by

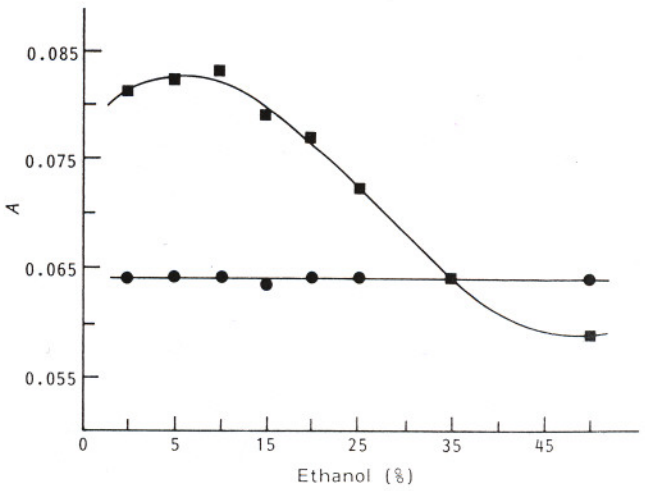

Figure 2 Absorbance (A) variation with the ethanol content of 1 mg l^{-1} copper solutions, in conventional introduction procedures (■) and using the FIA manifold (●)

Table 1 Comparison of the results obtained by FIA and by the reference method for the copper and calcium determination in wines

Copper			Calcium					
			Manifold with diluters and a mixing chamber			Manifold with flow splitting		
FIA ($mg\,l^{-1}$)	Reference method ($mg\,l^{-1}$)	Relative deviation (%)	FIA ($mg\,l^{-1}$)	Reference method ($mg\,l^{-1}$)	Relative deviation (%)	FIA ($mg\,l^{-1}$)	Reference method ($mg\,l^{-1}$)	Relative deviation (%)
1.200	1.100	+9.09	36.5	35.4	+3.11	68.1	68.2	−0.15
0.550	0.560	−1.79	149.2	150.1	−0.60	57.0	55.0	+3.63
0.210	0.230	−8.70	51.5	51.0	+0.97	61.9	60.7	+1.98
0.080	0.070	+14.3	101.6	101.1	+0.49	72.1	70.1	+2.85
0.150	0.140	+7.14	95.1	95.6	−0.53	56.4	56.8	−0.70
0.627	0.536	+17.0	58.2	59.5	−2.18	68.9	69.8	+0.15
0.271	0.280	−3.21	58.2	57.0	+2.11	64.9	66.4	−2.25
0.527	0.520	+1.35	76.0	76.0	0.00	69.8	71.4	−2.24
0.520	0.530	−1.89	109.6	110.8	−1.08	55.8	56.0	−0.36
0.510	0.516	−1.16	86.3	87.3	−1.15	38.6	38.0	+1.58
0.560	0.570	−1.75	84.9	83.5	+1.68	55.2	56.5	−2.30
0.530	0.510	+3.92	87.8	87.3	+0.57	84.9	83.5	+1.68
0.180	0.190	−5.26	62.1	60.0	+3.50	60.7	58.1	+4.48
0.172	0.171	+0.58	78.9	77.0	+2.47	57.1	58.0	−1.55
0.515	0.575	−10.4	101.6	101.1	+0.49	113.5	114.1	−0.53
0.226	0.194	+16.5	47.7	48.5	−1.65	72.6	71.0	+2.25
0.247	0.230	−7.39	109.2	109.4	−0.18	55.3	56.5	−2.12
0.077	0.066	+16.7	113.0	114.1	−0.96	60.7	59.7	+1.68
0.235	0.247	−4.86	121.6	121.3	+0.25	71.7	69.3	+3.46
0.490	0.515	−4.85	121.9	121.3	+0.49	56.2	57.0	−1.40
0.993	1.190	−16.5	132.1	129.6	+1.93	69.8	69.3	+0.72
0.520	0.430	+20.9	122.3	121.3	+0.82	60.7	63.4	−4.26
0.210	0.230	−8.70	124.7	123.6	+0.89	42.5	42.3	+0.47
0.532	0.536	−0.75				106.3	107.3	−0.93
1.020	1.100	−7.27				37.1	38.0	−2.37
0.518	0.509	+1.77				113.0	114.1	−0.96
0.982	1.030	−4.66				76.0	76.0	0.00
0.483	0.462	+4.54				58.2	59.5	−2.18
0.343	0.281	+22.1				36.5	35.4	+3.11
0.490	0.472	+3.81				47.7	48.5	−1.65

FIA (C_f) and by the reference method (C_r) is presented in *Table 1* for 30 samples of different types of Portuguese wines, with varying alcohol contents, ranging from ≈6% for some table wines to >20% for ports. An expression of the type $C_f = C° + S\,C_r$ was established having obtained 0.03 $mg\,l^{-1}$ for $C°$ and 0.93 for S, with a correlation coefficient of 0.98.

With this manifold it is possible to make copper determinations in wine from 0.04 $mg\,l^{-1}$ (detection limit) to 4 $mg\,l^{-1}$, with a reproducibility of 0.82% for a wine with a concentration of 0.92 $mg\,l^{-1}$, and with a sampling rate of 360 samples h^{-1}.

Use of stream splitting in the design of high dispersion flow injection manifolds

The usefulness of incorporating stream splitting in setting-up high dispersion manifolds is demonstrated by comparing two different manifolds for the atomic absorption determination of calcium, and for the colorimetric determination of phosphate.

Calcium determination in wines requires sample dilution before measurement as the content of this cation normally found in wines (Ough and Amerine, 1988) is much higher than the linear response concentration range in atomic absorption spectrophotometry. Additionally, it is necessary to add the modifier, La (III), to suppress chemical interferences that occur in the flame.

In order to develop an appropriate FIA system to provide the sample treatments required, particularly

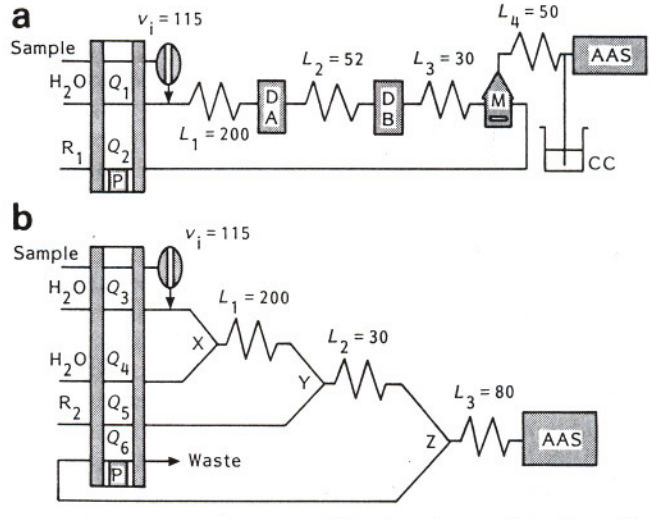

Figure 3 Flow injection manifolds for the atomic absorption determination of calcium in wines incorporating (**a**) a well-stirred mixing chamber and diluters and (**b**) with flow splitting: v_i, injection volume (μl); P, peristaltic pump; L_i, tube length (cm); DA and DB are diluters; Q_i, flow-rate ($ml\,min^{-1}$), $Q_1 = 3.5$, $Q_2 = 1.7$, $Q_3 = 3.5$, $Q_4 = 10.0$, $Q_5 = 8.0$, $Q_6 = 12.5$; M, well-stirred mixing chamber; CC, compensation channel (0.1 $ml\,min^{-1}$); R_1, 10 000 $mg\,l^{-1}$ lanthanum (III) solution; R_2, 13 500 $mg\,l^{-1}$ lanthanum (III) solution; AAS, atomic absorption spectrophotometer

dilution, two approaches have been tested. Either the on-line physical dilution achieved by using long tubes, diluters and mixing-chambers, or the reduction of the analyte quantity in the sample plug, by splitting it in the interior of the flow manifold (*Figure 3*).

The first approach was accomplished with a two channel manifold (*Figure 3a*), in one channel flowed the carrier stream and in the other the lanthanum solution, added to the sample before the detector. To attain the necessary on-line sample dilution, a reduced injection volume was used by directly connecting the original valve tubes, thus setting the volume inserted into the carrier stream to 115 μl. Also a long tube (200 cm) was placed before a Y-shaped confluence point. As the dilution so achieved was not enough, two diluters were intercalated before the Y-shaped confluence point, which was replaced by a well-stirred mixing chamber, to promote a good mixture between the two fluxes, and to significantly increase dispersion. At this point, the carrier and the lanthanum solution were closely mixed, and the sample dispersion continued up to the spectrophotometer and also inside the nebulizer, which acts as a mixing chamber.

Just before the nebulizer entry, a compensation channel was introduced in order to provide a quantity of water that corresponds to the difference between the intrinsic aspiration flow-rate of the atomic absorption and that of the FIA manifold. Finally, the sensitivity of the operational instrument conditions was decreased by shortening the optical path by rotating the burner head about 2.5° relative to the position of maximum sensitivity.

Using this manifold, which has a dispersion coefficient of 13.6, it is possible to execute determinations in a linear response range in wine samples containing calcium up to 200 mg l^{-1} (maximum concentration usually found in wines), with a sampling rate of about 60 determinations h^{-1} and a relative standard deviation of 1.7% for a wine sample containing 131 mg l^{-1} calcium.

The use of this FIA on-line dilution and reagent addition manifold was compatible with attaining good quality results, as demonstrated by comparison with those provided by the reference method for 23 samples of different types of wine (*Table 1*). Using the same comparison approach described previously, a value of 0.6 mg l^{-1} for $C°$ and 0.997 for S was obtained, with a correlation coefficient of 0.9993.

Although the described automatic procedure was much faster ($\approx$10 times) than the conventional manual preparation, in which the sample dilution and reagent addition was executed in volumetric flasks, the sampling rate obtained was not as good as expected for a rapid method as FIA. So an attempt was made to substantially improve it, by using a completely different approach for the reduction of the analytical signal. As stated previously, instead of performing a real on-line dilution, the analyte quantity to be measured was reduced by splitting the sample plug in the manifold interior, and so the intercalation of diluters and mixing chambers would not be required.

The stream splitting was achieved by using a Y-shaped confluence in a non-conventional way. When this device is used as a confluence point, two flowing streams in the same direction are merged. To make it function as a stream splitter, one of the flowing streams is reversed, thus withdrawing part of the solution flowing inside the other. In this way, the sample is sectioned when it reaches this point, a part of the sample flows towards the detector and the other is led to the waste. The sample splitting extension is conditioned by the quotient between the carrier and the withdrawn solution flow-rates. In this process, the sample plug length is shortened, thus more rapid and extensive dilution occurs inside the remaining flow tubes and confluences, and also reduces the quantity of analyte to be measured.

The manifold incorporating the stream splitting (Z) and a channel (Q_5) for lanthanum addition is shown in *Figure 3b*. The sample is intercalated in the water carrier stream, diluted in confluence X (about four times), the lanthanum solution is added at Y, and then stream splitting occurs at Z, where a much reduced length sample plug is sent to the detector through L_3. In this case the burner head was also rotated by 2.5°.

A compensation channel was not used in this manifold, as a slight overpressure was imposed at the entry of the nebulizer which permitted a reduction in the analytical signal by reducing the nebulization efficiency. The matrix physical properties were also minimized, as described previously. In this case the latter observation was not so critical because the sample was already much diluted before reaching the detector.

This manifold had a dispersion coefficient (13.0) which was similar to the manifold with diluters and a mixing chamber, but with a much larger sampling rate (240 versus 60 as previously observed), and allowed calcium determinations to be made in a linear response range between 1.4 (limit of detection) and 200 mg l^{-1}, with a precision of 1.3% (relative standard deviation) for a wine sample containing 70.1 mg l^{-1} calcium. This manifold also presented results for 30 wine samples (*Table 1*) in good agreement with the reference method, obtaining 0.6 mg l^{-1} for $C°$, 0.991 for S and a correlation coefficient of 0.998.

Comparing the performance of this manifold with stream splitting (*Figure 3b*) with the manifold including diluters and mixing chambers (*Figure 3a*), the advantages of the use of stream splitting become clear, especially regarding the much larger sampling rate (four times), as well as simplicity.

An additional advantage presented by manifolds with stream splitting consists in the possibility of directing the sample portion withdrawn to another detector, and so allowing a biparametric analysis to be performed.

The need to perform a dilution and reagent addition before measurement is not only a requirement in atomic absorption, but also in uv-visible spectrophotometry. A high dispersion FIA system with stream splitting has been used for the colorimetric determination of phosphate in wines. The dilution is necessary to adjust the concentration to a linear dependence range and to minimize the intrinsic light absorption of wines.

The colouring reaction used was based on the reaction of phosphate with ammonium molybdate to form heteropolymolybdophosphoric acid, which is subsequently reduced to the molybdenum blue complex by stannous chloride. This reaction, besides being fast and very sensitive, allows the determinations to be done at a wavelength (710 nm) corresponding to the minimum absorption of wine in the visible region, thus permitting large dilutions to be made and, simultaneously, to minimize the original colour effect of the wine.

To implement these on-line operations, a flow injection manifold with stream splitting (*Figure 4*) was

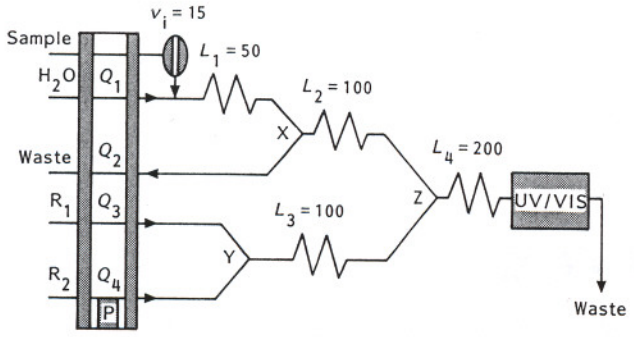

Figure 4 Flow injection manifold for the colorimetric determination of phosphate in wines: v_i, injection volume (μl); P, peristaltic pump; L_i, tube length (cm); Q_i, flow-rate (ml min^{-1}), $Q_1 = 1.6$, $Q_2 = 1.3$, $Q_3 = Q_4 = 0.90$; R_1, ammonium molybdate solution; R_2, tin (II) chloride solution; UV/VIS, u.v./visible spectrophotometer measuring at 710 nm

Table 2 Results obtained in phosphate recovery tests by FIA for 10 wine samples

Wine sample	Concentration (mg l^{-1})	Recovery (%) (addition of 100 mg l^{-1})
1	168	99.0
2	317	103.0
3	319	100.0
4	372	101.0
5	372	99.0
6	304	101.0
7	367	100.0
8	201	101.0
9	258	99.5
10	439	98.5

used. A minimum volume of solution (the valve tubes were changed with a reduction of the injected volume from 115 to 15 μl) was intercalated in the manifold, which was dispersed through L_1. In the stream splitting at X, a portion of the sample plug continues to follow the analytical path while the other part goes to waste through the withdrawn stream, by channel Q_2. The shortening of the sample plug length eases the subsequent sample dilution and contributes to the attainment of a good sampling rate. The colouring reagents, previously mixed at Y and through L_3, are then added to the sample plug at confluence Z.

The use of stream splitting produced a very large dispersion coefficient (160), without the need to use diluters and mixing chambers which significantly decrease the sampling rate. It should be emphasized that it is possible to analyse, in a linear response range, 60 wine samples directly introduced into the manifold per hour, with phosphate concentrations between 9 and 1000 mg l^{-1} with a precision of 0.94% for a wine sample containing 358 mg l^{-1} phosphate. Recovery tests for 10 wine samples (*Table 2*) show that the results obtained were accurate, once again, presenting recoveries between 98.5 and 103%.

CONCLUSIONS

The advantages of using stream splitting to obtain high dispersion flow injection manifolds with a high sampling rate were demonstrated. The sectioning of the sample plug allows a subsequent larger axial dispersion, and a decrease in the quantity of analyte to be measured. These manifolds are an advantageous alternative to manifolds including diluters and mixing chambers as they are much simpler and produce larger sampling rates, as evidenced by comparing two manifold performances for atomic absorption determination of calcium in wine, in which the stream splitting manifold presented a sampling rate four times larger. They are also simpler than some FIA techniques especially designed for dilution such as 'zone sampling' (Ruzicka and Hansen, 1988), which involves the use of two synchronized valves.

An additional advantage is the possibility of performing a biparametric analysis on the same injected sample. In fact, there is a sample portion that is wasted after the flow splitting that could be of use analytically. The solution in this channel could be submitted to an appropriate treatment, led to another detector and so another species could be determined. It should also be highlighted that the use of an overpressure in the atomic absorption nebulizer inlet, imposed by the peristaltic pump to minimize physical interferences, is particularly useful when analysing samples with a complex matrix composition that may influence the analytical signal, as in the case of wines, and thus avoids the standard addition method.

All these FIA procedures present good quality results with high precision. It must be pointed out that they require almost no change in the detector systems to which they are coupled, while the implementation of a segmented flow analysis to automate the determinations using an atomic absorption spectrophotometer proves very difficult.

It should be stressed that the FIA methodologies described in this paper have a general application in food control, as in many cases the sample composition must be adjusted to the measuring system. It may even be applied in the control of bioreactors, as was recently evidenced by Valero *et al.* (1990).

ACKNOWLEDGEMENTS

This work has been supported by NATO project SFS-PO-Food-Chem, PO-Porto Food, SP B.

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