SAMPLE ZONE CUTTING BY RELOCATION OF A COILED REACTOR:

AN ALTERNATIVE TO INCREASE MANIFOLD VERSATILITY

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Abstract

The versatility of flow systems can be extended by relocating manifold components, such as resin columns, flow cells, and coiled reactors. The feasibility of the relocation of a coiled reactor was investigated. This approach was applied to reduce the washing time, to adjust the sample concentration range, and to decrease the amount of sample introduced in the nebulization chamber of a flame atomic absorption spectrophotometer (FAAS). Relocation of the coiled reactor allowed cutting the rear of the sample zone and different strategies were implemented employing the same flow system. In nitrite determination using the Griess's reaction, sampling rates were 212 h^{-1} and 327 h^{-1} without and with a 200-cm relocating reactor, respectively. The adjustment of the sample concentration to the linear response range of the detector was achieved by changing the delay time for relocating the coiled reactor. Relocation of a coiled reactor also made feasible the direct determination of calcium in milk by FAAS, decreasing by 62% the volume of the milk suspension introduced in the nebulization chamber, which is useful to avoid clogging. The accuracy of this procedure was checked using two kinds of whole milk powders standard reference

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materials (NIST-8435 and IAEA-153) and the results obtained agreed with the certified values at a 95% confidence level.

1. Introduction

One of the trends in flow injection is to increase the versatility of manifolds. In the 80's versatility was attained by adopting ingenious systems such as zone sampling [1], zone trapping [2], intermittent [3] or alternating [4] flows, and associating gradient techniques with stopped flow [5]. In this decade new approaches were proposed, e.g. sandwich techniques [6-8], trial measurements [9], and relocation of manifold components [10-15].

Sandwich techniques [6] were used for redox speciation of iron [7] and to adjust the chromium concentration range in a spectrophotometric procedure [8]. The adjustment of concentration range was also performed employing the trial measurements procedure [9]. In this case, sample zones with different degrees of dispersion flowed towards the detector and after attaining an established threshold signal the remaining sample zone was diverted to waste.

The most classical use of relocation of manifold components is to put a resin column in the position of a sample loop [10]. The proposal of relocation of flow cells is more recent and was applied for parallel monitoring of aluminum and iron [11], serial iron redox speciation [11], determination of glycerol and sucrose [13], and

determination of calcium and magnesium [14]. This approach was also used for air bubble removal in a monosegmented flow system proposed for boron determination [12]. Additionally, filter relocation was recommended for avoiding clogging caused by continuous accumulation of precipitate [15] and kinetic discriminations were implemented using relocatable reactors [16].

Relocatable reactors can be employed to cut the rear of the sample zone. This approach could be adopted to increase the sampling rate; to decrease the volume of aggressive samples introduced in the detector; to avoid saturation and memory effects of the detector caused by concentrated solutions; and also to remove air bubbles in monosegmented systems.

In this work was evaluated the relocation of a coiled reactor to reduce the washing time, and consequently to increase the sampling rate. This procedure was implemented by using a non-temporized commutator to cut the rear of the sample zone after the maximum signal. This allows a reduction of the washing time without affecting the residence time. A flow system was designed for spectrophotometric measurement of nitrite based on Griess's reaction. For comparison, measurements were carried out by employing a manifold with an intermittent flow to accelerate the sample zone removal after the maximum signal [3].

A relocatable reactor was also used to adjust the concentration range and to decrease the amount of a potentially clogging sample introduced into the nebulizer in a flame atomic absorption spectrophotometric procedure for direct calcium determination in milk.

2. Experimental

2.1. Apparatus

The flow manifold was assembled by using a sliding bar commutator and polyethylene tubes (0.8 mm i.d.). An Ismatec IPC-8 peristaltic pump with Tygon tubes (Technicon) of different diameters was employed for fluid propulsion. Molecular absorption measurements were carried out with a 432 Femto spectrophotometer (Brazil), using flow cells with 10 mm optical path and volumes of 53, 80, or 200 μl. A flame atomic absorption spectrophotometer (Varian) and an electronically temporized sliding bar commutator (Micronal, Brazil) were employed in the direct determination of calcium in whole milk. A strip-chart recorder (Cole Parmer) was used to register the transient signals.

2.2. Solutions

All solutions were prepared with analytical grade reagents and distilled deionized water. The Griess's reagent was a mixture of 2% (w/v) sulfanilamide, 0.1% (w/v) N-1-naphthylethylenediamine dihydrochloride, and 3.0% (v/v) phosphoric acid prepared in aqueous medium. A 1.0 mg l^{-1} nitrite solution was prepared by dilution of 1000 mg l^{-1} stock solution prepared from sodium nitrite. Calcium reference solutions containing 20.0, 40.0, 80.0, 100 and 200 mg l^{-1} were prepared by proper dilution of a 2000 mg l^{-1} stock solution prepared from $CaCO_3$.

In the milk experiment, a 2.0% (v/v) water soluble tertiary amines solution (Spectrasol, USA) was used as carrier. This solution improves the nebulization of the milk suspension [17]. A mass of 0.1 g of milk powder standard reference

materials (NIST-8435 and IAEA-153) was dissolved in 10 or 25 ml of 5% (v/v) amines solution, respectively.

2.3. Flow diagram and procedure

The flow manifold employed in all experiments involving relocation of the coiled reactor is shown in Fig. 1. Experiments to demonstrate the feasibility to reduce washing time by sample zone cutting were carried out with a molecular absorption spectrophotometer. The Griess's solution was employed as chromogenic reagent (R). Measurements were done at 535 nm. Sample loops (L) of 100 or 200 cm were employed to introduce 500 or 1000 μl sample volumes. A 200-cm relocatable reactor was used. After the maximum absorbance signal, the central bar of the commutator was slid, to remove the rear of the sample zone, which was directed by the washing flow (S_w) towards waste (W). Simultaneously, the sample loop was filled with other sample (S), allowing to start a new measurement cycle. For comparison, a system with an intermittent stream at 3.0, 4.5, or 6.2 ml min^{-1} was used.

The feasibility to match sample concentrations with the linear response range of the detector and to decrease the amount of a potentially clogging matrix introduced in the nebulization chamber were demonstrated through the direct determination of calcium in whole milk by flame atomic absorption spectrophotometry. Measurements were carried out at 422.7 nm, by employing a stoichiometric air/acetylene flame and an aspiration rate of 9 ml min^{-1}. The flow system shown in Fig. 1 was employed without reagent addition by confluence. When a suitable signal was achieved, the commutator was moved, to allow diverting the remaining portion of the sample zone towards waste.
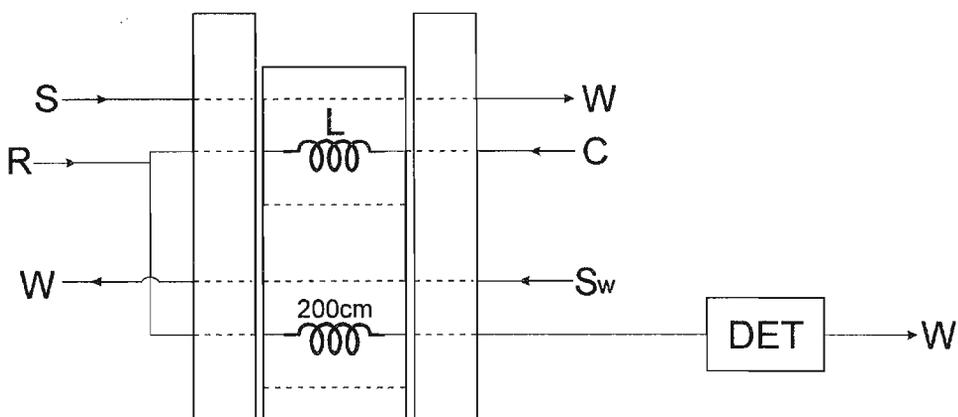
Fig. 1. Flow diagram of the system employed in all experiments. S = sample solution at 3.9 ml min^{-1}. C = Carrier stream. S_w = Water washing stream, at 7.2 ml min^{-1}. L = sample loop. W = waste. Det = detector. In the molecular absorption measurements, carrier stream = water at 3.9 ml min^{-1} and L = 100 or 200 cm, R = Griess's reagent solution flowing at 1.0 ml min^{-1}. In the flame atomic absorption spectrophotometric determination of calcium in milk powder, carrier = 2% (v/v) amines solution at 10 ml min^{-1}, L = 20 cm. Water carrier stream at 4.2 ml min^{-1} and a sample loop of 20 cm were used to demonstrate the feasibility to adjust the sample concentration to the linear response of the detector. For more details, see text.

3. Results and Discussion

The decrease of washing time by sample zone cutting was demonstrated with a system for nitrite determination. The results obtained with a relocatable coiled reactor were compared to those attained with an intermittent washing flow [3]. Figure 2 shows the transient signals obtained with this system and with that shown in Fig.1 with or without relocating the reactor. For a 500-μl sample loop and a 200-μl flow cell, the sampling rates were 212 h^{-1} and 327 h^{-1} without and with relocation of a 200-cm reactor, respectively. Sampling rates were 240, 257, and 267 h^{-1} when intermittent flow rates of

3.0, 4.5, or 6.2 ml min^{-1} were introduced after the signal maximum. It can be concluded that the relocation of the coiled reactor is more effective than the use of an intermittent washing flow for the fast removal of the rear of the sample zone. Additionally, systems with intermittent flows cause a variation of the composition of the solution flowing through the flow cell, which can affect the baseline stability. With regard to electroanalytical detectors, the variation of the flow rate can affect the response even when the composition is not significantly altered.
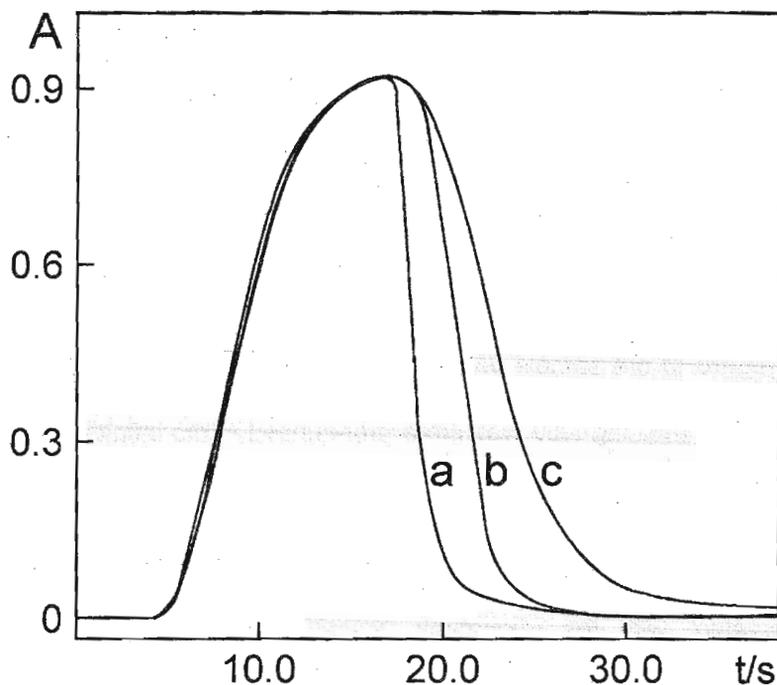

Fig. 2. Transient signals for 1.0 mg L^{-1} nitrite: (a) by relocating the coiled reactor after signal maximum; (b) with an intermittent flow rate of 6.2 ml min^{-1} introduced immediately before the flow cell, after attaining the maximum signal; and (c) with the system shown in Fig. 1, without relocating the coiled reactor. Results for a 200-μl flow cell and 200-cm sample loop.

The effect of flow cell volume on the washing time was evaluated (see Table 1). The reduction of the washing time was more pronounced when measurements were done with a 53-μl flow cell. This effect can be explained considering the dispersion caused by the dead volume of the flow cell. When employing a 100-cm (500 μl) sample loop, the washing times were reduced by 50%; 83%, and 125% as the flow cell volume was decreased (Table 1). Thus, the sample throughput could be proportionally reduced but this is also dependent on the sampling time.

Table 1 - Influence of the flow cell volume on washing time (100 cm sample loop)

Flow cell volume / μl	Washing time / s	
	Without relocation	With relocation
53	9	4
80	11	6
200	12	8

With regard to the sample volume it was observed that the effect of relocating the reactor on the washing time was more pronounced in the infinite volume condition. Using sample loops of 500 μl and 1000 μl, sampling rates were increased in 90% and 129%, respectively, when comparing systems with and without relocation.

The system with the relocatable reactor was used to match the sample concentration and the linear response range for calcium in flame atomic absorption spectrophotometry. This was attained by relocating the reactor after attaining an instrumental response in the linear range. Figure 3 shows that different absorbance signals can be obtained by relocating the coiled reactor at different times after sample injection. The sample dispersion could be increased by using an additional reactor

before the nebulizer, permitting to implement a procedure similar to the zone sampling approach [1].
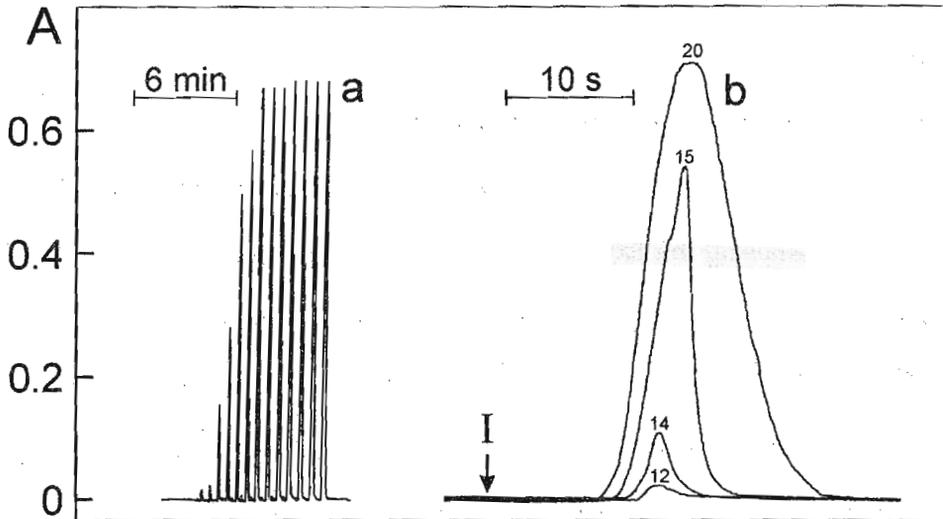

Fig. 3. Transient signals for calcium by flame atomic absorption spectrophotometry. (a) results obtained by relocating the coiled reactor at different times after sample injection (time intervals varied from 11 to 23 s in 1s increments). (b) Overlaid signals obtained by relocating the coiled reactor at 12, 14, 15 or 20 s after injection (I).

The relocating approach was also applied for direct calcium determination in milk by flame atomic absorption spectrophotometry. The direct analysis of milk can be troublesome with techniques involving a nebulization chamber as the sample introduction system. Experiments with an inductively coupled plasma atomic emission spectrometry (ICP-AES) showed deceptive results, and these were related to nebulization and atomization problems [18]. These results can be understood considering that milk is a complex suspension and its direct aspiration in a pneumatic nebulizer causes clogging of the system. This problem can be circumvented by

employing a flow injection system for the continuous washing of the nebulizer tip and chamber. The performance of the system is improved if the amount of the sample introduced is reduced, and the relocation of the reactor is a practical alternative to implement it.

This was experimentally demonstrated for the determination of calcium in two certified milk reference materials. As shown in Figure 4, there was a reduction of the sample volume attaining the flame when the coiled reactor was relocated. The signal without sample zone cutting is shown for comparison. The baseline-to-baseline times were 7.9 s and 3.0 s for the system without and with relocation, respectively. Thus the sample volume introduced in the nebulization chamber and in the burner was reduced by 62%. In long-time run experiments, this reduction will have a pronounced effect on the instrument performance. This approach is also potentially applicable to decrease the volume of aggressive samples in contact with instrument components, such as alkaline or hydrofluoric acid solutions in quartz torchs in ICP's.
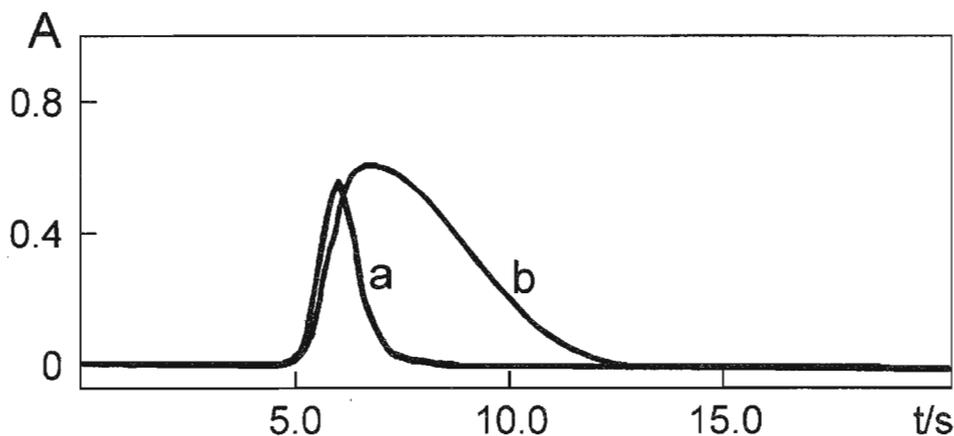

Fig. 4. Transient signals obtained for whole milk powder suspensions: (a) by relocating the coiled reactor after signal maximum and (b) without relocation.

The results obtained for two kinds of whole milk powders standard reference materials were (12.5 ± 0.3) mg/g for the IAEA-153 and (11.6 ± 0.1) mg/g for the NIST-8435, both calculated at a 95% confidence interval. The certified values for these materials are (12.87 ± 0.31) mg/g and (9.22 ± 0.49) mg/g, respectively. Certified and found results were in agreement at a 95% confidence level.

These experiments demonstrated the potential of the reactor relocation procedure to increase the versatility of flow systems. Using only one manifold it was possible to increase the sampling rate, to adjust the sample concentration range, and to decrease the volume of complex samples introduced in the instrument. On the other hand, the technique here reported does not affect the analytical sensitivity or the precision, since the residence time is not changed and the signal maximum is measured in usual conditions. It should be noted that for spectrophotometric systems the relocation of the coiled reactor could cause a slight variation in the baseline stability, but this is not detrimental because it occurs after signal measurement.

Acknowledgments

References

[1] B.F. Reis, A.O. Jacintho, J. Mortatti, F.J. Krug, E.A.G. Zagatto, H. Bergamin Fº and L.C.R. Pessenda, *Anal. Chim. Acta*, (1981) 221.

[2] F.J. Krug, B.F. Reis, M.F. Gine, E.A.G. Zagatto, J.R. Ferreira and A.O. Jacintho, *Anal. Chim. Acta*, **151** (1983) 39.

[3] E.A.G. Zagatto, A.O. Jacintho, J. Mortatti and H. Bergamin Fº, *Anal. Chim. Acta*, **120** (1980) 399.

[4] F.J. Krug, E.A.G. Zagatto, B.F. Reis, O. Bahia Fº, A.O. Jacintho and S.S. Jorgensen, *Anal. Chim. Acta*, **145** (1983) 179.

[5] S. Olsen, J. Ruzicka, and E.H. Hansen, *Anal. Chim. Acta*, **136** (1982) 101.

[6] J. Alonso, J. Bartrolí, M. del Valle, M. Escalada and R. Barber, *Anal. Chim. Acta*, **199** (1987) 191.

[7] J. Alonso, J. Bartrolí, M. del Valle and R. Barber, *Anal. Chim. Acta*, **219** (1989) 345.

[8] J. Alonso, J. Bartrolí and R. Barber, *Anal. Chim. Acta*, **261** (1992) 219.

[9] B.F. Reis, E.A.G. Zagatto, P.B. Martelli and S.M.B. Brienza, *Analyst*, **118** (1993) 719.

[10] H. Bergamin Fº, B.F. Reis, A.O. Jacintho and E.A.G. Zagatto, *Anal. Chim. Acta*, **117** (1980) 81.

[11] E.A.G. Zagatto, H. Bergamin Fº, S.M.B. Brienza, M.A.Z. Arruda, A.R.A. Nogueira and J.L.F.C. Lima, *Anal. Chim. Acta*, **261** (1992) 59.

[12] A.R.A. Nogueira, S.M.B. Brienza, E.A.G. Zagatto, J.L.F.C. Lima and A.N. Araújo, *Anal. Chim. Acta*, **276** (1993) 121.

[13] J.A. Gomes Neto, A.R.A. Nogueira, H. Bergamin Fº, E.A.G. Zagatto, J.L.F.C. Lima and M.C.B.S.M. Montenegro, *Anal. Chim. Acta*, **285** (1994) 293.

[14] A.R.A. Nogueira, S.M.B. Brienza, E.A.G. Zagatto, J.L.F.C. Lima and A.N. Araújo, *J. Agric. Food Chem.*, **44** (1996) 165.

[15] O. Fatibello Fº, J.A. Nóbrega and A.J.M.G. Santos, *Talanta*, **41** (1994) 731.

[16] M.A.Z. Arruda, E.A.G. Zagatto and N. Maniasso, *Anal. Chim. Acta*, **283** (1993) 476

[17] J.A. Nóbrega, Y. Gélinas, A. Krushevska and R.M. Barnes, *J. Anal. At. Spectrom.*, **12** (1997) 1243.

[18] E. Coni, A. Stacchini, S. Caroli and P. Falconieri, *J. Anal. At. Spectrom.*, **5** (1990) 581.