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Sampling strategies in sequential injection analysis: Exploiting the monosegmented-flow approach

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Abstract

An evaluation of different sampling techniques employing sequential injection analysis (SIA) is described. The reaction between Fe(II) and 1,10-phenanthroline, which needs a pH adjustment with acetate buffer and a prior reduction with hydroxylamine solution, was employed. As a general rule, sensitivity, compared to that of the usual SIA technique, can be enhanced with binary sampling, sandwich sampling and monosegmented flow, in that order. Under the employed conditions, signals 13, 31 and 58% higher than those provided by conventional SIA can be obtained with the binary, sandwich and monosegmented sampling, respectively. The monosegmented-flow approach was applied in determining iron in natural waters and results do not differ significantly from those obtained by ICP/AES at the 95% confidence level. The precision was 1.1%, expressed as relative standard deviation obtained by the measurement of nine replicates of 1.0 mg l^{-1} Fe(III) reference solution. © 1998 Elsevier Science B.V.

Keywords: Sampling techniques; Monosegmented flow; Sequential injection; Binary sampling

1. Introduction

Nowadays, flow analysis is a widespread technique employed in many branches of chemistry. Since the original paper published by Skeggs [1] on multisegmented continuous flow analysis (CFA), many improvements and even simplifications have been made. Flow injection analysis (FIA), introduced by Ruzicka and Hansen [2] is a very important one and due to its simplicity, versatility and low cost has achieved great acceptance. CFA differs conceptually from FIA because, in the first technique, measurements can be made under conditions of chemical equilibrium, steady state and with minimized sample dispersion. In fact, the segmentation of the sample by air is used to provide these facilities. On the other hand, with FIA, which does not employ air segmentation, measurements can be performed without attaining chemical equilibrium and, therefore, simpler manifolds can be designed, enabling higher sampling frequency with lower reagent and sample consumption. In 1985, Pasquini and Oliveira [3] proposed

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monosegmented-flow analysis (MSFA), which embodies advantageous features of both FIA and CFA. In MSFA, sample and reagents are injected into a reaction coil between two air bubbles, providing facilities to maintain various sample zones in the analytical path, with insignificant carry over. Under these conditions, long residence times (up to 10–15 min) can be achieved, with minimal sample dispersion and high sampling frequency.

High sampling frequency and low reagent consumption were among the main objectives to be attained by flow analysis, from the mid-70s to the end of 80s. During these 15 years, thousands of papers were published and more complex manifolds were employed to perform extraction [4], pre-concentration [5,6], gas diffusion [7,8], dilution [9], etc. As an evolution of the flow analysis process, Ruzicka and Marshall [10] introduced a new concept, called sequential injection analysis (SIA) [10]. In this system, sample and reagent solutions are aspirated into a holding coil, after which the flow is reversed in order to propel the solutions towards the detector. Robustness, versatility and simplicity are the main features of SIA, as pointed out by the authors. The systems are microcomputer controlled, allowing to perform determinations of different analytes, employing a single channel manifold with minor modifications. However, the sampling frequency is lower than that of the usual flow systems. Recently, Reis et al. [11] introduced multicommutation and binary sampling in flow analysis using three-way solenoid valves. The concept of binary sampling refers to the insertion in the reaction coil of strings formed by aliquots of sample in tandem with aliquots of reagent solutions. Flow analysis systems with multicommutation have the same characteristics as SIA, but allow sampling frequencies as high as those of FIA and MSFA.

The basic difference among MSFA, SIA and FIA with multicommutation–binary sampling lies fundamentally in the way the sample is introduced into the reaction coil. While MSFA employs a sampling loop to select the sample aliquot, in the other two techniques the aliquots of sample and reagents are directly aspirated into the analytical path. Also, binary and sandwich sampling produce sample zone patterns different from those obtained in ordinary SIA. Furthermore, as a consequence of air segmentation and flow inversion, there are significant differences in the sample zone profile obtained by these three techniques, which directly influence the analytical sensitivity.

When three or more reagent solutions are necessary, it is difficult to attain a good mixture with SIA systems [10,12]. On the other hand, sampling in SIA can be easily carried out by employing binary and sandwich techniques, which can be implemented with a non-segmented or a monosegmented-flow approach.

This work aimed to evaluate these sampling techniques, employing the reaction of Fe(II) with 1,10-phenanthroline as a model, whose analytical steps require pH adjustment with an acetate buffer solution and prior reduction of Fe(III) to Fe(II) with hydroxylamine solution. Finally, the determination of iron in natural waters was carried out, employing the SIA system with monosegmented-flow approach.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with distilled and deionized water. Aliquots of 3.0 and 8.0 mg l^{-1} Fe(II) reference solutions, in 0.05 mol l^{-1} sulfuric acid, made from ferrous ammonium sulfate (Merck) were prepared. For the determination of iron in natural waters, Fe (III) reference solutions, in 0.05 mol l^{-1} sulfuric acid, were prepared by proper dilution of a 1000 mg l^{-1} Fe(III) stock solution, made from ferric ammonium sulfate (Merck). A 1.0 mol l^{-1} sodium acetate (Merck), 5.0% (w/v) hydroxylamine hydrochloride (NH_2OH; Merck) and 0.5% (w/v) 1,10-phenanthroline (*o*-phen; Merck) solutions were used. A 0.05 mol l^{-1} sulfuric acid solution was used as carrier fluid.

2.2. Apparatus and manifold

The diagram of the flow system is shown in Fig. 1. An eight port valve (Valco, model E8) was employed to insert sample and reagent solutions into the system. A peristaltic pump (Ismatec, model IPC8), equipped with tygon tubing, was employed to aspirate solutions into the holding coil (0.8 mm i.d., 1.5 m long polyethylene tube) and impel them towards the reaction coil. A PC-AT 386 microcomputer, furnished with an interface card (Advantech, model PCL-711S) controls the valve and the peristaltic pump, employing a soft-

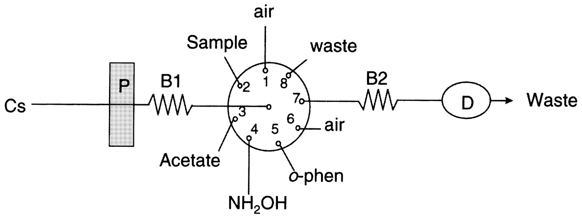

Fig. 1. Schematic diagram of the flow system. Cs=Carrier; B1=Holding coil; B2=Reaction coil; D=Detector; P=Peristaltic pump.

ware written in Microsoft QuickBasic 4.5. Absorbance measurements were made at 510 nm, employing a spectrophotometer (Femto, model 432) with a flow cell with an optical path of 10 mm. A PTFE tube (0.5 mm i.d. and 540 mm long) was used as the reaction coil in the experiments without air segmentation. For the monosegmented-flow approach, PTFE tubes with 1.6 mm i.d. and 300 mm in length were employed.

2.3. Procedure

The solutions were aspirated into the holding coil at a flow rate of 0.8 ml min^{-1}. Afterwards, the flow was reversed in order to propel sample and reagents towards the detector at a flow rate of 2.6 ml min^{-1}. The usual SIA sampling was performed by sequentially aspirating sample, buffer, reductor and chromogenic reagent solutions. To perform binary sampling, the volumes of the solutions were halved and the sampling pattern was repeated twice. In the sandwich approach, sampling was implemented by aspirating chromogenic reagent, reductor, buffer, sample, buffer, reductor and chromogenic reagent solutions, in this order. To do this, the volume of the reagent solutions were halved. In the monosegmented-flow procedure, an air bubble of 60 µl was inserted in the holding coil, followed by aliquots of reagents and sample, and another air bubble identical to the first. This was done in order to avoid direct contact of the sample with the carrier solution.

3. Results and discussion

Sensitivity in SIA depends greatly on the mutual penetration of reagents and sample, due to controlled dispersion [10,12] and, therefore, sampling techniques could affect the analytical signal magnitude. To ascertain this effect on the proposed system, experiments employing sandwich sampling were carried out by aspirating 1,10-phenanthroline, Fe(II) and 1,10-phenanthroline solutions, in that sequence, where Fe(II) sample solution volume was varied. As can be seen in Fig. 2, large sample volumes produce two peaks (peak profile a), presumably caused by a reagent deficiency in the central zone of the sample. This situation simulates the usual SIA, if one looks only at the first peak. On decreasing the sample volume, an overlap of the two peaks occurs, and the sensitivity is improved. This improved sensitivity increases up to a maximum

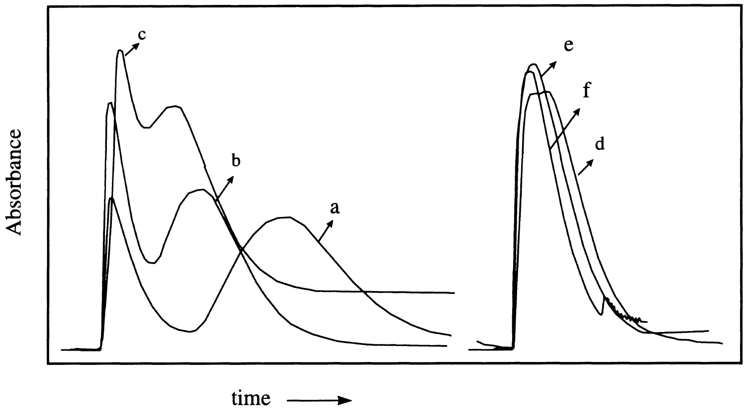

Fig. 2. Signal profiles obtained for different sample volumes for sandwich sampling, employing a 3.0 mg l^{-1} Fe(II) reference solution and a total reagent volume of 210 µl. Sample volumes: 1200 µl (a); 600 µl (b); 400 µl (c); 267 µl (d); 200 µl (e) and 133 µl (f).

value, which represents the optimized condition (peak profile f). As the sample aliquot was sandwiched by reagents, there were two interfaces between sample and reagents, resulting in a more effective mixture. On using the same quantities of reagent, sandwich sampling produced signals that were ca. 25 and 35% higher than those obtained by the usual SIA technique. The magnitude of the signals obtained by SIA is affected by the sample and reagent aspiration order [12]. Therefore, in addition to the higher sensitivity observed, sandwich sampling presents a reagent consumption smaller than or equal to that of conventional SIA sampling.

Different sampling strategies were employed and the results obtained are shown in Fig. 3. As can be noted, with the monosegmented approach, the signal was not affected when sampled volumes increased from 85 to 170 µl, maintaining the aliquot ratios. In this case, as pointed out elsewhere [13], there is no concentration gradient in the sample bulk, thus minimizing dispersion. In the conditions employed, binary sampling presented a sensitivity similar to the usual SIA. This fact can be explained considering that the volume of the sample aliquots were halved, increasing the dispersion effect. Under these conditions, if the binary sampling pattern was repeated more than twice, one would expect an increased signal. The sandwich sampling always showed a sensitivity higher than the usual SIA while the height of the signal increased with sample volume. Nevertheless, the sample volume could not be increased at will considering the difficulty of reagent distribution throughout the sample zone, resulting in signal profiles with shoulders or double peaks, as shown in Fig. 2.

Better conditions for the monosegmented sampling was achieved as shown in Fig. 4. A significant increase in the analytical signal for 1,10-phenanthroline volumes from 13 to 53 µl was observed. For curves a, b, c and d, presumably there was not enough reagent to attain reaction stoichiometry. For the monosegmented approach, the best conditions occurred with a 1,10-phenanthroline volume of 27 µl, indicating more efficient mixing. The decreases in signal, observed from 53 µl, could be attributed to the dispersion effect which was minimized with sandwich sampling.

As pointed out earlier, when the monosegmented system is employed, zone samples with a minimum concentration gradient are achieved [13]. Considering this fact, experiments were performed for sandwich sampling, binary sampling and usual SIA sampling with the monosegmented approach. Its beneficial

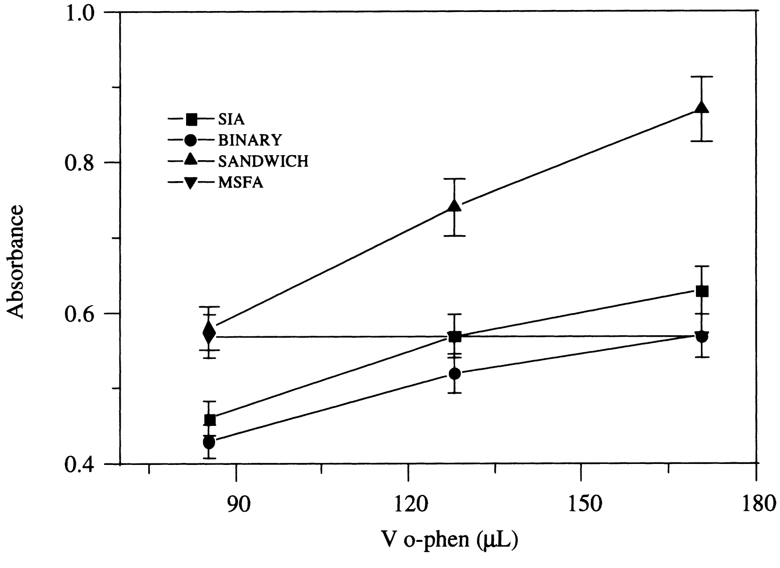

Fig. 3. Results obtained with different sampling strategies of an 8.0 mg l^{-1} Fe(II) reference solution, where the volume ratios of the solutions were constant, as follows: sample: 85, 128, 170; NH_2OH: 21, 32, 43; acetate: 107, 160, 213, *o*-phen: 107, 160, 213.

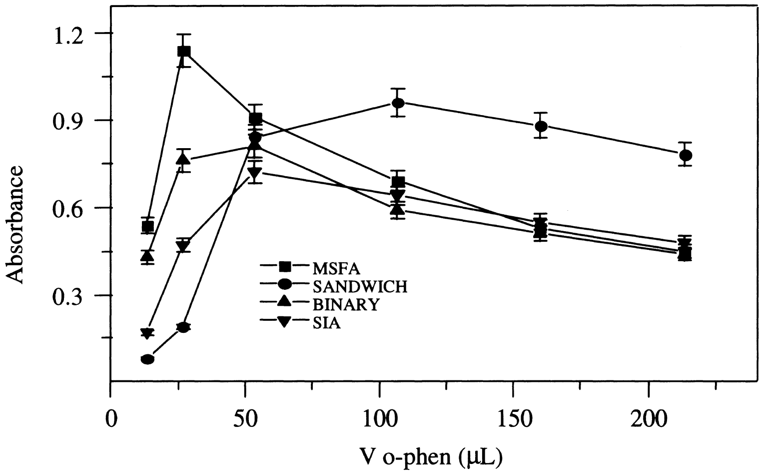

Fig. 4. Results obtained with different sampling strategies, using 170 μl of an 8.0 mg l^{-1} Fe(II) reference solution and the following volumes (μl) of reagent solutions: NH_2OH: 3, 5, 11, 21, 32, 43; acetate: 13, 27, 53, 107, 160, 213; *o*-phen: 13, 27, 53, 107, 160, 213.

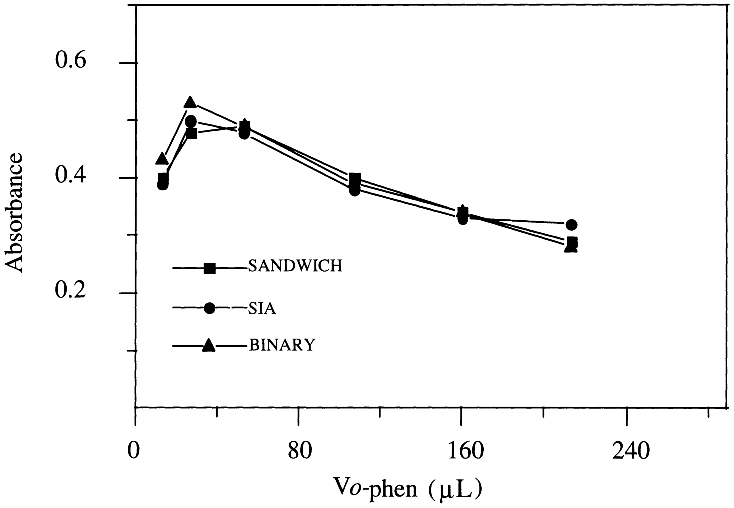

Fig. 5. Results obtained with the three sampling strategies implemented with the monosegmented-flow approach. Solution volumes were the same as described in Fig. 4 (error bars were omitted for clarity).

effect can be observed in Fig. 5 where, despite its different features, identical results were obtained.

These studies indicated the potential of monosegmented sampling. To ascertain its feasibility as an analytical procedure, total iron in natural waters was determined. The precision of the method, evaluated as the relative standard deviation of nine replicates of a 1.0 mg l^{-1} Fe(III) reference solution, was 1.1%, with a reagent consumption of 0.15 mg 1,10-phenanthroline and 0.45 mg hydroxylamine. Table 1 shows the results obtained with the monosegmented–SIA system and those obtained by ICP/AES, showing no significant difference at a 95% confidence level.

4. Conclusions

Different sampling approaches were performed without modifications in the flow network, indicating the versatility and robustness of the SIA technique.

Table 1
Determination of iron in natural waters by SIA–MSFA and ICP–AES

Sample	SIA–MSFA (mg l^{-1})	ICP–AES (mg l^{-1})
1	0.125±0.018	0.156±0.002
2	0.710±0.017	0.867±0.001
3	0.101±0.018	0.132±0.001
4	0.664±0.012	0.715±0.002
5	1.649±0.016	1.714±0.001
6	1.649±0.017	1.714±0.001
7	0.107±0.035	0.111±0.006

Sensitivity can be improved by employing binary sampling, sandwich sampling and monosegmented flow. These results show that SIA with a monosegmented approach can be an important tool in flow analysis.

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