

## Turbidimetric determination of sulphate employing gravity flow-based systems

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### Abstract

A gravity flow-based manifold to perform turbidimetric determination of sulphate, comparing different approaches, such as sequential injection analysis (SIA), FIA with multicommutation and binary sampling (FIA-MBS), FIA with sandwich sampling (FIA-SS) and monosegmented flow analysis (MSFA) is described. Solutions of 5.0% barium chloride, 0.25 mol l<sup>-1</sup> perchloric acid and 0.3% EDTA in 0.2 mol l<sup>-1</sup> NaOH were used as precipitating agent, carrier fluid and cleaning solution, respectively. After optimisation, SIA, FIA-MBS and FIA-SS approaches showed linear response ranges from 40 to 200 mg l<sup>-1</sup>, while for MSFA the range was from 20 to 125 mg l<sup>-1</sup>. In the SIA system, a sampling frequency of 30 samples per hour was obtained, while a value of 40 samples per hour was obtained when FIA-MSB, FIA-SS and MSFA approaches were employed. The flow manifold was evaluated by determining sulphate in plant, bovine liver and blood serum digests. The SIA, FIA-SS, FIA-MBS and MSFA systems showed a R.S.D. of 3.2, 2.7, 2.0 and 1.0%, respectively, expressed as the relative standard deviation of the signal intensities of six measurements of a 120 mg l<sup>-1</sup> SO<sub>4</sub><sup>2-</sup> solution. When the results were compared with those obtained by conventional FIA, no significant differences were observed for FIA-MSB, FIA-SS and MSFA at a confidence level of 95%, while for SIA the results were similar at a level of 97.5%. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* MSFA; SIA; Multicommutation; Binary sampling; Flow analysis; Turbidimetry

### 1. Introduction

Fluid movement in flow systems can be implemented either at a constant flow, usually by employing a peristaltic pump or at a constant pressure, by means of gas pressure [1] or the action of gravity [2,3]. A serious drawback arises when the pressure is utilised to impel fluids in flow systems, since the hydrodynamic pressures of two different channels can be different. As a result, it is very difficult to properly mix two reagent

solutions through a confluence point, because the flow rates are dependent on the solution viscosity, and the length and internal diameter of the tubing, which directly affect the precision of the measurements. Therefore, when the fluid movement is achieved by means of constant pressure, either a single line manifold should be employed or only one solution should be delivered at a time, which is difficult to be surmounted when there need to be confluence points in the flow manifold. In this aspect, the use of solenoid valves has been proposed to control solution delivery in systems based on gas pressure [1] and gravitational force [3]. The use of solenoid valves permits sequential insertion of sample and reagent solutions into the

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analytical path, maintaining the flow rate in a reproducible pattern, even if there are some small fluctuations due to pressure differences at the confluence points.

Turbidimetric methods have usually been implemented in flow analysis for the determination of chloride [4], sulphate [5–13] and aminoacids [14–16]. As far as the sulphate determination is concerned, different approaches have been proposed, employing either barium chloride [5–8,11–13] or lead nitrate [9,10] as the precipitating agent. In 1972, Basson and Böhmer [5] proposed a continuous flow analysis (CFA) system for sulphate determination, based on its precipitation with barium chloride. Krug et al. [6], in 1977, were the first to adapt this methodology to a FIA system for the determination of sulphate in plant digests. Later, methodologies which employ lead nitrate as precipitating agent were also described for the determination of sulphate in natural waters [9] and total sulphur in plants [10]. As new flow assemblies were developed, the turbidimetric determinations of sulphate were also performed by employing FIA with multicommutation and binary sampling [12] and SIA [11] systems.

Some drawbacks must be overcome in order to improve the analytical performance of a turbidimetric sulphate determination. First, a stable suspension of barium (or lead) sulphate should be attainable, as a means of obtaining reproducible results. In this aspect, poly(vinyl alcohol) [6,8,9], Tween 80 [12] and gelatine [5,11] have frequently been employed as stabilisers. Other approaches have also been described, aimed at improving both the detection limit of sulphate and the linear response range. Ethanol (up to 50% v/v aqueous solution) has frequently been used to decrease the solubility of barium and lead sulphate precipitates [9,10], improving the limit of detection. The linear response range has been enlarged by adding, through a confluence point, a diluted solution of sulphate, which enhances the nucleation step [8,10]. Furthermore, when the sulphate determination is carried out with barium chloride, the precipitate formed can adhere to the walls of the reaction coil and even to those of the flow cell, imposing difficulties for cleaning the system. This trouble has been circumvented with a cleaning step employing an alkaline EDTA solution, which complexes the barium, dissolving the remaining precipitate [5,11,12].

Finally, a pulsed flow pattern, provided by the peristaltic pump, can also deteriorate the reproducibility of the measurements, since pulsation can affect the pattern of light scattering caused by the suspension [10].

As discussed above, several methods for determination of sulphate by flow analysis and turbidimetry have been proposed, which show satisfactory analytical performance, concerning detectability, linearity and sample throughput. Monosegmented Flow Analysis (MSFA), since it was introduced in 1985 [17], has been increasingly applied to perform different analytical procedures, such as extraction [18], dilution [19], titration [20] and gas diffusion [21]. This work is aimed at comparing the performance of MSFA [17], SIA [22], FIA with multicommutation and binary sampling (FIA-MBS) [23] and FIA with sandwich sampling (FIA-SS) [24] systems for the turbidimetric determination of sulphate. A microcomputer-controlled flow system based on a 6-way solenoid valve and gravity-pumped solutions has been proposed and the determination of sulphate was taken as a model in order to achieve the above mentioned objective.

## 2. Experimental

### 2.1. Reagents and solutions

All solutions were prepared with distilled and deionised water. All chemicals employed in this work were of analytical grade.

A 1000 mg l<sup>-1</sup> sulphate stock solution was prepared by dissolving 1.376 g of ammonium sulphate in 1000 ml of water. A 0.3% (m/v) EDTA in 0.20 mol l<sup>-1</sup> NaOH solution was employed as cleaning solution. A 5.0% (m/v) BaCl<sub>2</sub> solution was used as precipitating agent, containing 0.1% Tween 80 as stabilising agent. A 0.25 mol l<sup>-1</sup> HClO<sub>4</sub> solution was employed as carrier fluid. Sulphate reference solutions, in 0.25 mol l<sup>-1</sup> HClO<sub>4</sub>, were prepared by proper dilution of the stock solution. Sample solutions were obtained after nitric-perchloric acid digestion of plant, bovine liver and blood serum materials [6].

### 2.2. Apparatus

The flow manifold, shown in Fig. 1, was implemented by employing a 6-way solenoid valve

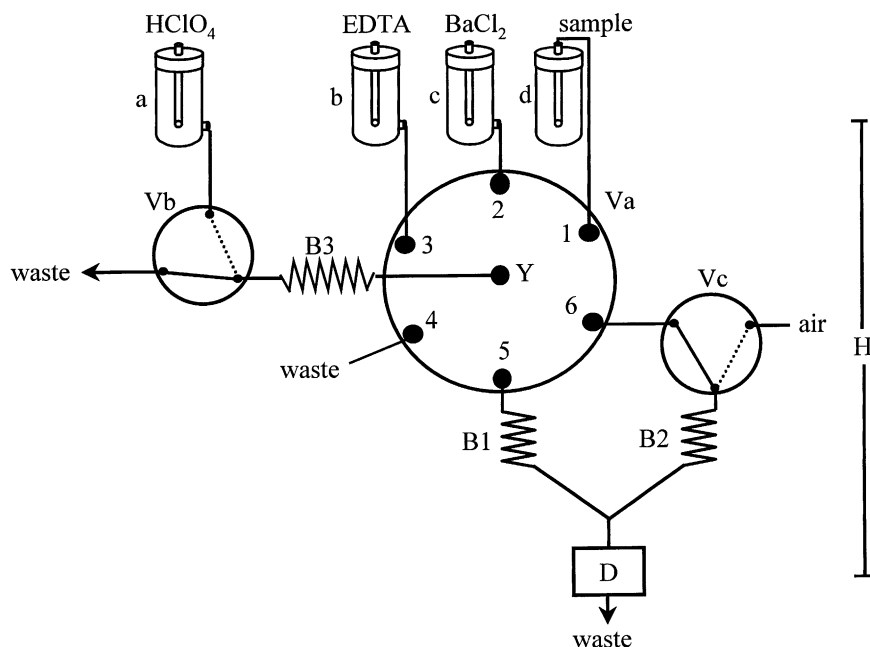


Fig. 1. Schematic diagram of the flow manifold — Va: 6-way solenoid valve; Vb and Vc: 3-way solenoid valves; Y: central channel of Va; a, b and c: Mariotte flasks; d: sample recipient; B1: 0.8 mm i.d., 150 cm long reaction coil for SIA, FIA-MBS and FIA-SS approaches; B2: 1.6 mm i.d., 130 cm long reaction coil for MSFA; B3: 0.8 mm i.d., 150 cm long holding coil; D: spectrophotometer (410 nm); H: 100 cm height difference between Mariotte flasks and detector.

(NResearch 225T091) in conjunction with two 3-way solenoid valves (NResearch 225T031). PTFE reaction coils of 0.8 mm  $\times$  1.6 mm i.d. were employed. A Femto model 432 spectrophotometer (São Paulo, Brazil) with a flow cell (180  $\mu$ l inner volume and 13 mm optical path) was employed as detector. A 100 MHz Pentium Microcomputer, furnished with a PCL-711 Advantech parallel interface card was utilised to control the system, using software written in Visual Basic 3.0, which also allowed the acquisition and treatment of data. Mariotte flasks were employed to maintain the pressure constant in the system, providing constant and reproducible flow rates.

### 2.3. Procedure

Fig. 1 shows the flow manifold employed to implement the SIA, FIA-SS, FIA-MBS and MSFA processes. The flow rate was maintained at 2.2 ml min<sup>-1</sup> by placing the Mariotte flasks 100 cm above the detector. The measurements were carried out at

410 nm. Each solution is sequentially inserted into the system during the sampling step, as follows.

#### 2.3.1. SIA procedure

The valve Vb is initially switched to waste, halting the delivering of the carrier fluid. Then, channels 2 and 1 of the valve Va are sequentially switched on in order to insert barium chloride and sample solutions, respectively, into the holding coil B3. Finally, valve Vb and channel 5 of valve Va are simultaneously switched on, delivering the carrier fluid through reaction coil B1 and on to the detector. After processing each sample, the system is cleaned with EDTA solution. When the SIA procedure is performed, an aliquot of the solution is inserted into the holding coil B3 and then delivered through the reaction coil B1. After cleaning, valve Vb is opened to remove the cleaning solution and fill the line with carrier fluid.

In each of the following procedures, the channel of the valve Vb used to deliver solution to waste is

maintained closed with a polypropylene threaded plug. When the valve is switched off, the channel used to deliver perchloric acid solution is closed, allowing the insertion of sample, reagent or washing solutions into the flow system.

### 2.3.2. FIA-MBS procedure

Channel 5 is permanently on, while channels 2 and 1 are sequentially switched on/off in order to insert small aliquots of reagent and sample, respectively, into reaction coil B1. The number of reagent/sample cycles to make the string is initially defined by the operator. Finally, valve Vb is switched on, permitting the carrier fluid to impel the sample zone through B1 towards the detector. In this case, the EDTA cleaning solution is delivered through reaction coil B1.

### 2.3.3. FIA-SS procedure

Channel 5 is switched on, as describe in the FIA-MBS procedure. Channels 2 and 1 are alternately switched on, inserting aliquots of reagent, sample and reagent, in this sequence. Afterwards, valve Vb is switched on, delivering the mixture through reaction coil B1 to the detector. Cleaning with the EDTA solution is also through coil B1.

### 2.3.4. MSFA procedure

Channel 6 is permanently switched on, with channel 5 off, selecting reaction coil B2 to perform the analysis. First, valve Vc and channels 2 and 1 of valve Va are alternately switched on, introducing into the reactor small aliquots of air, reagent, sample and air, in this sequence. Then, valve Vb is switched on, impelling the monosegment in direction of the detector. After, a small aliquot of the EDTA solution is delivered through coil B2.

For all sampling procedures, the volume of the aliquot of solution introduced into the system is determined by the interval of time in which the respective valve or channel is switched on, as the flow rate is constant at each confluence point due to the Mariotte flasks. The system is fully controlled by the computer; the operator introduces the values of the variables necessary to perform each task at the beginning of the analysis, such as system to be used, switching time for the valves, number of replicates and, in the case of FIA-MBS procedure, the number of cycles employed to produce a string of reagent and sample

in the FIA-MBS procedure. Finally, the data obtained are saved in a file for posterior treatment.

## 3. Results and discussion

### 3.1. Optimisation of the flow system

The proposed system works at constant pressure, employing gravity action, thus flow rate was determined by the height difference between the recipients containing the solutions (Mariotte flasks) and the detector. When the Mariotte flasks were placed on a shelf, 100 cm above the detector, a constant flow rate equal to  $2.2 \text{ ml min}^{-1}$  was obtained. Furthermore, each solution was inserted into the flow system separately and sequentially during the sampling step, in order to guarantee the reproducibility of the measurements.

In a turbidimetric determination, it is necessary to maintain the suspension of the precipitate as homogeneous as possible, in order to improve the precision of the measurements. In this work, a 0.1% Tween 80 solution was employed to stabilise the suspension, as it has been successfully employed before [12].

As pointed out earlier, a barium sulphate precipitate can continuously adhere to the walls of the reaction coil and flow cell and could clog the system in an extreme situation. The precipitate adhering onto the walls of the system cannot be easily removed by the carrier fluid, as its solubility is relatively low in a perchloric acid solution. Therefore, to overcome this trouble, a cleaning step was always performed between determinations, employing  $200 \mu\text{l}$  of a 0.3% EDTA alkaline solution, subsequently returning to carrier before the next determination.

#### 3.1.1. Effect of the length of the reactor

Initially, the influence of the reactor length on the analytical signal was investigated. Fig. 2 shows the results obtained employing  $100 \mu\text{l}$  of 5.0%  $\text{BaCl}_2$  reagent solution and  $200 \mu\text{l}$  of  $\text{SO}_4^{2-}$  reference solution, whose concentration was 120 and  $160 \text{ mg l}^{-1}$  for monosegmented and non-segmented systems, respectively. As can be noted, a 150-cm reaction coil is long enough to achieve highest signals. For MSFA approach, the reactor length shows a slight influence on the signal intensity, since the mixing of the solutions is improved due to the air bubbles, which also avoid

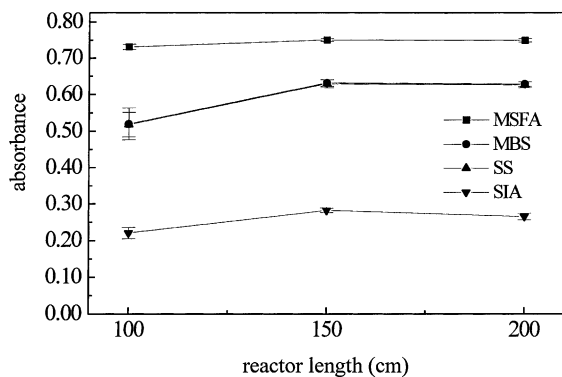


Fig. 2. Effect of the length of reaction coil on the signal intensity (see text for details, error bars represent the standard deviation of three measurements).

sample dispersion. For the FIA-SS, FIA-MSB and SIA systems, the maximum signal is obtained with a 150-cm long reaction coil, indicating that reaction cannot be completed for shorter reaction coils.

### 3.1.2. Effect of the reagent and sample volume ratio

The ratio between sample and reagent volumes inserted in a flow system is essential to determine the analytical performance of a methodology. In this aspect, signal magnitudes as a function of the ratio between sample and reagent volumes were initially evaluated by employing a 150  $\mu\text{l}$  aliquot of a 75  $\text{mg l}^{-1}$  sulphate reference solution and different volumes of reagent. Fig. 3 shows the effect of the injected volume

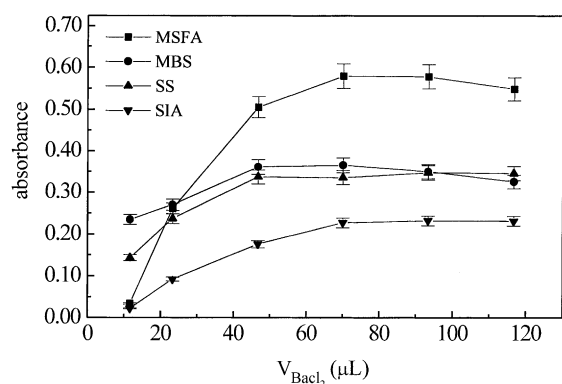


Fig. 3. Effect of the volume of 5.0%  $\text{BaCl}_2$  solution (150  $\mu\text{l}$  of a 75  $\text{mg l}^{-1}$   $\text{SO}_4^{2-}$  reference solution, error bars represent the standard deviation of three measurements).

of a 5.0% barium chloride solution on the analytical signal. It can be verified that signal intensities increase as the volume of the reagent is increased reaching maximum values for all approaches when 70  $\mu\text{l}$  of reagent solution was employed. These behaviours arise from the fact that there is a lack of reagent when volumes smaller than 70  $\mu\text{l}$  were employed. The curves concerning the FIA-SS and FIA-MBS approaches presented similar profiles, while SIA showed the worst sensitivity, probably due to the poor mixing between sample and reagent and also to higher sample dispersion. The MSFA system showed the highest signals, as a consequence of the low dispersion in the sample zone. It is worth noting that in the MSFA response, the signal suffered a small decrease when the reagent volume was higher than 70  $\mu\text{l}$ , because an excessive volume of reagent was added, causing sample dilution in the monosegment. This result is in accordance with those described elsewhere [25], confirming that the sensitivity of a MSFA methodology can be improved by employing small volumes of a concentrated reagent [19]. In spite of this evidence, 150 and 75  $\mu\text{l}$  of sample and reagent were employed in the following experiments, in order to compare these approaches, considering that the total volume of reagent should be divided into small aliquots in order to implement the FIA-MBS approach.

### 3.1.3. Effect of the concentration of $\text{BaCl}_2$

The concentration of the  $\text{BaCl}_2$  reagent was also studied, maintaining the above mentioned volume ratio. As can be seen in Fig. 4, signal intensities decreased as the concentration of the reagent was decreased because insufficient reagent was added. A 5.0%  $\text{BaCl}_2$  solution was used as precipitating agent, since this solution provided higher signals for SIA system.

## 3.2. Figures of merit of the flow systems

Table 1 summarises the figures of merit presented by each flow approaches studied in the present work.

The repeatability of each methodology was evaluated by processing a 120  $\text{mg l}^{-1}$   $\text{SO}_4^{2-}$  reference solution. SIA, FIA-SS, FIA-MBS and MSFA systems showed a R.S.D. of 3.2, 2.7, 2.0 and 1.0%, respectively (average of six measurements). The MSFA system presents the best precision, which can be

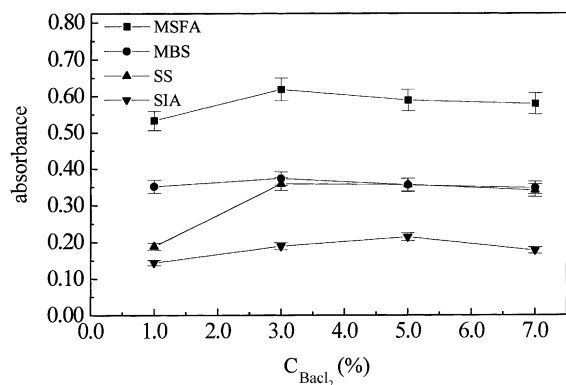


Fig. 4. Effect of the  $BaCl_2$  solution concentration ( $150 \mu l$  of a  $75 mg l^{-1} SO_4^{2-}$  reference solution,  $75 \mu l$  of  $BaCl_2$  reagent solution, error bars represent the standard deviation of three measurements).

explained based on the homogeneity of the precipitate suspension. The air bubbles of the monosegment, that confine the sample and avoids its contact with the carrier fluid, induces a more efficient convection movement, such as those described in the “bolus flow” model [26], improving the homogeneity of the sample zone. The precision shown by FIA-SS, FIA-MBS and SIA are in agreement with those currently described in [8,9,11,12]. Besides presenting better precision, the MSFA system also shows better sensitivity, as confirmed by Fig. 5. MSFA provide better sensitivity and, as a consequence, presented a narrower linear response range, up to  $120 mg l^{-1}$ , while the FIA and SIA systems showed a linear range up to  $200 mg l^{-1}$ . In addition, a non-linear response was not as prominent at the beginning of the analytical curves, mainly for MSFA, as is usually noted in the methodologies described in [8–10]. Therefore, it can be affirmed that the nucleation process, necessary for the formation of the precipitate, is occurring more properly under the experimental conditions chosen to carry out this work.

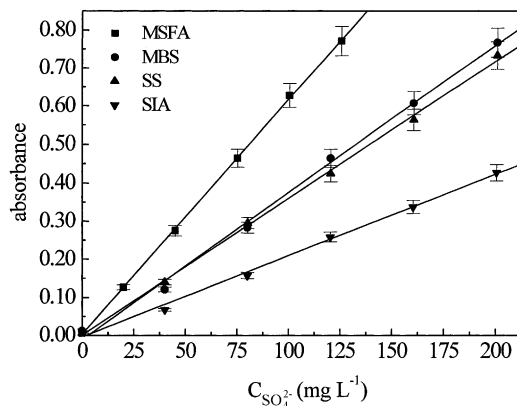


Fig. 5. Analytical curves obtained with different flow approaches ( $150 \mu l$  of sample,  $75 \mu l$  of  $BaCl_2$  reagent solution, error bars represent the standard deviation of three measurements).

The sampling frequencies were also calculated for the proposed systems, as also shown in the Table 1. A value of 30 samples per hour was obtained for the SIA system as a consequence of the two-step procedure (sampling into a holding coil and delivering towards the reaction coil) necessary in this flow methodology.

### 3.3. Determination of sulphate in samples

Application of the flow manifolds were evaluated by determining the amount of sulphate in 12 samples of plants (3 samples), bovine liver (4 samples) and blood serum (5 samples), previously mineralised by means of a nitric-perchloric acid digestion [6] and with sulphur content in the range from 0.09 to 0.210%. Results were compared with those obtained with the conventional FIA methodology [6], which is employed for routine analysis at CENA laboratory (Piracicaba). By applying paired *t*-test, no significant differences were found at a 95% confidence level for MSFA, FIA-SS

Table 1  
Figures of merit for MSFA, FIA-MBS, FIA-SS and SIA systems

	MSFA	FIA-MBS	FIA-SS	SIA
Repeatability <sup>a</sup>	$0.720 \pm 0.007$	$0.643 \pm 0.013$	$0.628 \pm 0.017$	$0.476 \pm 0.015$
Sampling rate ( $h^{-1}$ )	40	40	40	30
Linear range ( $mg l^{-1}$ )	20–125	40–200	40–200	40–200
Detection limit ( $mg l^{-1}$ )	15	30	29	33

<sup>a</sup> Average of six measurements of a  $120 mg l^{-1} SO_4^{2-}$  solution.

and FIA-MBS approaches, while for SIA system, the results were similar at a confidence level of 97.5%.

#### 4. Conclusions

The proposed manifold, based on gravitational force to impel the fluids, showed good performance for determining sulphate by turbidimetry. Four different flow approaches, MSFA, SIA, FIA-SS and FIA-MBS, can be easily implemented, without any change in the manifold, since it is fully controlled by a microcomputer. The MSFA system showed, in this particular application and flow set up, the best analytical performance, regarding precision and sensitivity, while the SIA system provided the poorest results, corroborating results described previously for the determination of Fe(III) in natural waters [25]. However, the difference in sensitivity provided by these flow systems makes the flow manifold more versatile, since the appropriate methodology can be chosen according to the concentrations of the samples being analysed.

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