

# A versatile set up for implementing different flow analysis approaches Spectrophotometric determination of nickel in steel alloys

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## Abstract

An arrangement capable of implementing the four principal types of flow analysis processes, monosegmented flow analysis (MSFA), flow injection analysis with multicommutation and binary sampling (FIA-MBS), flow injection analysis with sandwich sampling (FIA-SS) and sequential injection analysis (SIA) is described. The core of the flow manifold is a six-way solenoid valve that is assembled together with three three-way solenoid valves in order to provide a versatile flow network. Software was written in VisualBasic 3.0 to give a friendly working structure allowing the user to easily choose the flow variables and the kind of flow system. The reliability of the flow set up for implementation of the four flow analysis systems was evaluated by means of the spectrophotometric determination of nickel in steel alloys, based on the formation of a colored complex with dimethylglyoxime (DMG). The performances of the four different flow methodologies were compared. The reagent consumptions per determination were 4.0 mg of triethanolamine, 6.0 mg of potassium persulfate and 0.6 mg of DMG. When the flow set up was instructed through the software to implement MSFA, FIA-MBS, and FIA-SS approaches, a sampling frequency of 40 samples/h was obtained, while 30 samples could be processed per hour in the SIA mode. The precisions, evaluated as the relative standard deviation of ten determinations were 0.7%, 1.6%, 1.8% and 3.1% for the MSFA, FIA-MBS, FIA-SS and SIA systems, respectively. The results for determination of nickel in steel alloys presented good agreement with the reference method (ICP OES), showing no significant difference at a confidence level of 95%. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Flow analysis; MSFA; SIA; Multicommutation; Binary sampling; Nickel; Steel alloys

## 1. Introduction

Analytical chemists are focused on the development of precise and accurate analytical procedures, which, in addition, may present simplicity, high sample throughput, low reagent/sample consumption and robustness. Considering these aspects, analytical procedures based on flow analysis processes fulfill all these requirements. Although the flow analysis process was first proposed in 1957 by Skeggs [1], who developed continuous flow methodologies (CFA) based on multi-segmentation of the sample, this research area underwent its greatest development after the introduction of the Flow Injection Analysis (FIA) process in 1975 [2]. The use of a non-segmented carrier stream was one of the main reasons for the

popularization of flow injection systems, as they permit the implementation of simpler flow manifolds without moving parts. Flow injection has attracted the attention of many researchers throughout the world, allowing implementation of virtually all kinds of analytical procedures, such as titration [3], gas phase separation [4], liquid–liquid extraction [5], ion-exchange pre-concentration [6], and standard addition determinations [7].

An intrinsic characteristic of FIA systems is the dispersion of the sample in the carrier fluid, which depends on the sample volume, length and diameter of the reaction coil and flow rate. Although many advantages can be obtained from dispersion, it presents some drawbacks when the concentration of the analyte in the sample is low, reducing detectability. In order to overcome this drawback, monosegmented flow analysis (MSFA) was proposed in 1985 by Pasquini and Oliveira [8], merging the simplicity of FIA and the detectability of CFA

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systems. In the MSFA systems, sample plus reagents are inserted into the flow path between two air bubbles, which avoid sample dispersion in the carrier fluid, as a consequence increasing the detectability of the method. Furthermore, longer sample residence times permit longer reaction times without sacrificing sample throughput.

In spite of their recognized simplicity, many FIA systems need a more elaborated flow set up, in order to implement a given analytical procedure. As a consequence, many flow lines are necessary, leading to the known “spaghetti-like” manifold. In addition, the flow set up often must be changed (sample volume, length of the reaction coil, flow rate) before using a defined system for the determination of a different analyte. In 1990, Ruzicka and Marshall proposed sequential injection analysis [9], in which the flow system is based on a rotary valve, allowing the implementation of different analytical methodologies with the use of a single line manifold. Along the same lines, in 1994, Reis et al. [10] proposed the concept of multicommutation and binary sampling (FIA-MBS), by employing three-way solenoid valves to assemble the flow system manifold. In SIA systems, an analytical determination is carried out by aspirating sample and reagent solutions into a holding coil; the zone comprising sample and reagent solution aliquots is subsequently pumped towards the detector by reversing the flow direction. On the other hand, in the FIA-MBS systems small slugs of sample and reagents are alternately aspirated into the analytical path towards the detector. In both cases, the flow systems run under the control of a microcomputer, which allows modification of the operational variables without changing their physical configurations.

In 1999, Cerdá et al. [11] developed a multi-syringe flow analysis system, which combines some characteristics of both SIA and FIA, avoiding the use of a peristaltic pump to impel the solutions and improving the robustness of the system. Solenoid valves were used by these authors, as a means of improving the capability of the system, by allowing the combination of different flow techniques (FIA-SIA, SIA-multi-syringe). Nevertheless, the use of several syringes to manage the solutions should be considered as a disadvantage inherent to this technique.

Araújo et al. have proposed a flow-batch system, which employs several solenoid valves, allowing the use of a single standard solution to perform determinations based on titration [12] and the standard addition method [13]. This system combines the advantages of batch methods with the sample throughput of flow systems.

Obviously, many analytical methods have been described in the literature employing one of the flow systems mentioned above, as a tool to manage the sample, standard and reagent solutions. However, most of them are developed for dedicated systems, based on a single flow approach that restricts their application to different matrices, in which different analytes can be found at different concentrations, diluted or concentrated.

This work describes a multipurpose flow analysis system, which permits implementation of analytical procedures based on the MSFA, FIA-MBS, FIA-SS and SIA approaches. The flow set up was assembled employing one 6-way and three 3-

way solenoid valves, which were arranged to provide enough versatility to implement all the above mentioned approaches. A spectrophotometric method for determination of nickel in steel alloys based on the reaction of this metal ion with dimethylglyoxime to form a colored complex was selected as a model to demonstrate the reliability of the proposed flow system.

## 2. Experimental

### 2.1. Apparatus

The equipment set up consisted of an IPC-4 Ismatec peristaltic pump furnished with Tygon pumping tubes; transmission lines and helical reactors of 0.8 mm i.d. and 1.6 mm i.d. PTFE tubing; a 432 Femto spectrophotometer with flow cell (10 mm optical path and 180  $\mu\text{L}$  inner volume); three 3-way solenoid valves (NResearch 225TO3 1); a 6-way solenoid valve (NResearch 225T091); a microcomputer furnished with an electronic interface PCL-711 (Advantech), running software written in VisualBasic 3.0; and a home-made electronic interface to match the control signals coming from the PCL-7 11 interface card to the 12 V required to drive the solenoid valves.

### 2.2. Reagents and solutions

Analytical grade reagents and distilled/deionized water were employed to prepare all solutions. A 0.25 mol  $\text{L}^{-1}$  NaOH solution was used as carrier fluid. The determination of nickel was performed by using a 6.0 % (v/v) triethanolamine (TEA) solution in 1.0 mol  $\text{L}^{-1}$  NaOH; a 5.0% (w/v) potassium persulfate (PER) solution and a 1.0% dimethylglyoxime (DMG) solution in 0.25 mol  $\text{L}^{-1}$  NaOH. A 1.000 mg  $\text{L}^{-1}$  nickel stock solution was prepared by dissolving 1.000 g of the metal in 14 mL of concentrated  $\text{HNO}_3$ , made up to 1000 mL with water. Ni(II) reference solutions ranging from 0.0 to 120.0 mg  $\text{L}^{-1}$  were prepared in 0.1 mol  $\text{L}^{-1}$  nitric acid by proper dilution of the stock solution. All reference solutions contained 200 mg  $\text{L}^{-1}$  Fe(III).

### 2.3. Software

The software to control the flow system and for data acquisition was written in Microsoft VisualBasic 3.0. When the program is run, the user is asked about the variables of the flow system, such as type of flow set up (FIA-MBS, FIA-SS, SIA or MSFA), time interval to turn on each valve, sampling cycles (for FIA-MBS system) and number of replicates. After this information is inserted into the program, the system is able to perform all steps concerning the analytical procedure, comprising sample and reagent solution management and signal measurement as well as plotting the absorbance as a function of time on the screen, saving the data for further calculations.

### 2.4. Flow manifold

The flow system designed to implement the flow analysis approaches (MSFA, FIA-MBS, FIA-SS and SAL) is depicted

in Fig. 1. The core of the manifold is the device Va, constituted of six lateral ports (1–6), which communicate with the central port (Y) through six solenoid valves (not shown in the diagram). The solenoid valves are normally closed, thus no solution flows through the inner channels when the valves are switched off. The working conditions to emulate the four flow analysis modes are described below.

The sequential injection analysis (SIA) system was implemented by employing the holding coil B3, which was selected by turning on valve Vc. After selecting coil B3, the peristaltic pump was rotated backwards in order to aspirate sample, TEA, PER and DMG solutions into the coil (in this sequence). The sampling step was carried out by the microcomputer, which sent control signals through the digital outputs of the PCL711 interface card to sequentially turn on the solenoid valves related to the inner channels of ports 1, 2, 3 and 4. While this step was being performed, valve Vd was maintained on to avoid the reflux of waste solution into the system. After sampling, valve Vd was turned off, the rotation of the pump was reversed and the sampling zone was impelled towards the detector through reaction coil B2 (port 6). The pump rotation was constant while the sampling step was performed, thus the volume of each solution was determined by the time interval that each respective solenoid valve of Va was turned on.

Different from SIA, other flow systems were implemented by maintaining valve Vd turned off, as waste solution was not pumped back to the detector in these manifolds.

The flow injection with sandwich sampling (FIA-SS) procedure was performed by selecting reaction coil B2 (port 6). First, valve Vc was turned off in order to allow the carrier solution to be pumped back to its flask. Afterwards, a sample aliquot was inserted into coil B2, sandwiched between two portions of reagents by sequentially aspirating DMG, PER, TEA, sample, TEA, PER and DMG. The respective ports were turned on for a given interval of time to permit the solutions to flow through the inner channels of Va, as mentioned above. After sampling, valve Vc was turned on, allowing the carrier

fluid to be pumped through the system, impelling the sampling zone towards the detector through reaction coil B2.

Flow injection with multicommutation and binary sampling (FIA-MBS) was implemented by employing basically the same strategy as FIA-SS. However, the sampling cycle was repeated several times, as defined by the user at the beginning of the program.

The monosegmented flow (MSFA) approach was accomplished by selecting channel 5 instead of channel 1. First, valve Vc was turned off and valve Vb was turned on for a pre-set time interval and an air bubble was aspirated into reaction coil B1. Afterwards, aliquots of sample, TEA, PER and DMG solutions were inserted into coil B1 by aspirating through their respective ports, which were turned on by switching the respective solenoid valves. After this step, a second air bubble was introduced in the flow path by turning on valve Vb. Afterwards, valve Vc was turned on and carrier solution flowed through coil B1, displacing the sample zone towards the detector between two air bubbles.

### 3. Results and discussion

The reaction of nickel ion with dimethylglyoxime requires the addition of TEA, PER and DMG solutions in this sequence, which act as complexing agent for Fe(III) ions, oxidizing agent and chromogenic reagent, respectively. Therefore, this sequence was always obeyed in the four approaches implemented with the flow set up. Flow rates of 0.30 and 0.50 mL min<sup>-1</sup> were employed for sampling and measurement, respectively, for all methods.

The flow system variables, such as concentrations of the reagents, volumes of reagent and sample solutions were optimized employing the FIA-SS approach, as it can be considered an intermediate system between the SIA and FIA-MBS systems. As a consequence, by employing the same conditions, the performance of the MSFA approach can be straightforwardly compared.

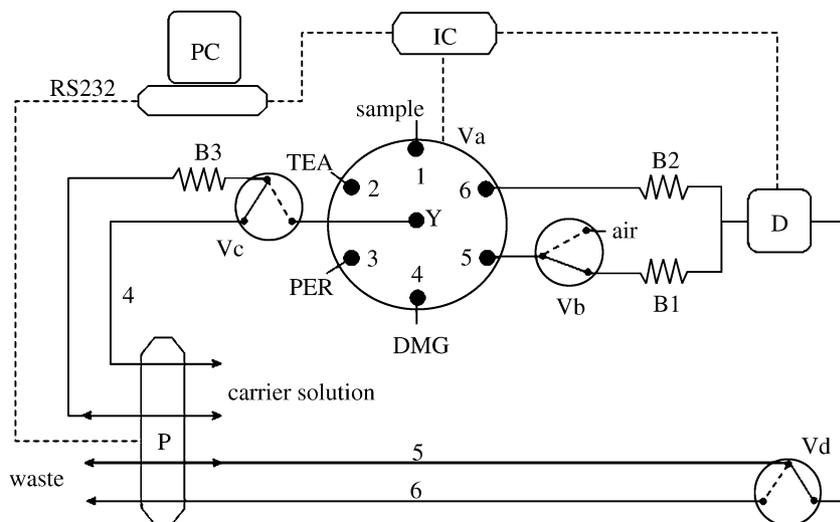


Fig. 1. Flow manifold employed to implement MSFA, FIA-MBS, FIA-SS and SIA systems. PC, microcomputer; IC, interface card; Va, 6-way solenoid valve; Vb, Vc and Vd, 3-way solenoid valves; Y, central port of the 6-way solenoid valve; P, peristaltic pump; D, spectrophotometer; B1, 1.6 mm i.d. PTFE reaction coil; B2, 0.8 mm i.d. PTFE reaction coil; B3, 0.8 mm i.d. PTFE holding coil. Solid lines shown in valves Vb, Vc and Vd indicate the open channel when the valves are turned off.

### 3.1. Concentration and volume of the DMG reagent solution

The optimization of these variables was performed using 30  $\mu\text{L}$  of  $120 \text{ mg L}^{-1}$  Ni(II) solution, 60  $\mu\text{L}$  of 6.0% TEA solution and 120  $\mu\text{L}$  of 5.0% (w/v) PER solution. With the use of 60  $\mu\text{L}$  of solution, the concentration of the DMG was varied from 0.5% to 2.0% (w/v), providing analytical signals of similar intensities. In order to guarantee an excess of reagent, a 1.0% DMG solution was used. Afterwards, the effect of the volume of this solution was studied. No improvement in the analytical signal was obtained for aliquots larger than 15  $\mu\text{L}$ , so this value was used in the measurements.

### 3.2. Volume of the 5.0% (w/v) potassium persulfate solution

The kinetics of the reaction between Ni(II) and DMG is principally affected by the concentration of persulfate ion [14,15]. Considering that the maximum concentration of this ion in an aqueous solution is ca. 5.0% (w/v) at 25 °C, the effect of the volume on the analytical signal was studied by using a solution with this concentration. Aliquots from 90 to 150  $\mu\text{L}$  provided similar detectability, while smaller aliquots resulted in lower signals due to a deficiency of reagent and larger volumes contributed to sample dispersion, also leading to lower signals. Therefore, a volume of 120  $\mu\text{L}$  was chosen for the subsequent determinations.

### 3.3. Interference of the Fe(III) ion

Iron is the major component of the steel samples employed in this work and Fe(III) ion also reacts with DMG, forming a complex that presents an absorption band coincident with the Ni(II) complex. In order to minimize this interference, triethanolamine was employed to complex Fe(III) ions. By employing a 6.0% (w/v) TEA solution, the analytical signals provided by 30  $\mu\text{L}$  of  $20 \text{ mg L}^{-1}$  Ni(II) solution without and with  $600 \text{ mg L}^{-1}$  of Fe(III) were compared as a function of the volume of TEA solution. Fig. 2 shows the results obtained, demonstrating that 60  $\mu\text{L}$  of TEA solution are enough to minimize Fe(III) interference.

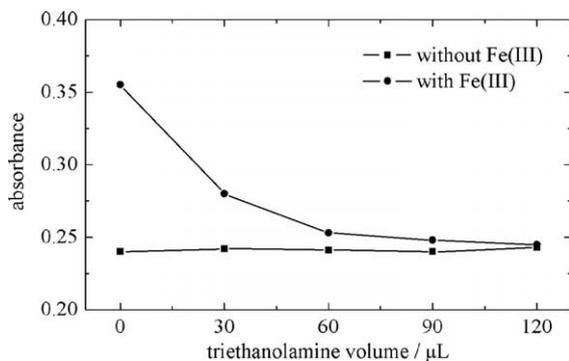


Fig. 2. Effect of the volume of a 6.0 % TEA solution on the analytical signal without and with  $600 \text{ mg L}^{-1}$  Fe(III). Conditions: 30  $\mu\text{L}$   $20 \text{ mg L}^{-1}$  Ni(II) standard solution; 120  $\mu\text{L}$  5.0 % persulfate solution; 60  $\mu\text{L}$  1.0% DMG solution.

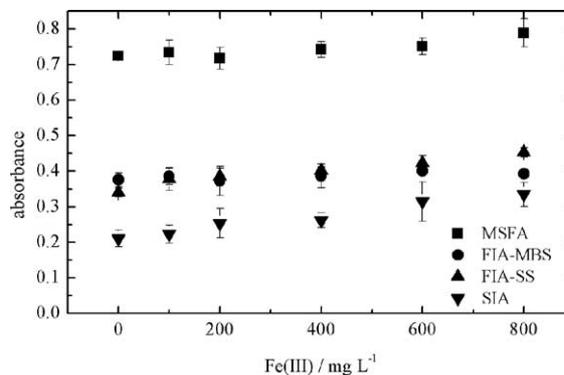


Fig. 3. Effect of Fe(III) concentration on the absorbance signal for the reaction of  $40 \text{ mg L}^{-1}$  Ni(II) with DMG, in the presence of 6.0% TEA (error bars represent the standard deviations of three determinations).

In order to compare the efficiency of the four flow approaches for minimizing Fe(III) interference, a series of measurements was performed using a  $40 \text{ mg L}^{-1}$  Ni(II) standard solution, containing Fe(III) from 0 to  $800 \text{ mg L}^{-1}$ . When the FIA-MSB approach was employed, the total volume of the solutions was inserted into the flow path in five sampling cycles, as described elsewhere [10]. Fig. 3 depicts the signal intensities obtained for these measurements, as well as the standard deviations (3 determinations). Errors can be estimated from the signals obtained with the solutions without Fe(III) ions as reference. As can be noted, the worst performance was obtained with the SIA system, which can be explained considering the low efficiency of mixing with this flow approach. In addition, the signals provided by the MSFA system are higher than those obtained with the other flow systems, indicating its higher detectability, as discussed in the next section.

### 3.4. Performances of the systems

After optimizing the conditions of analysis, a set of Ni(II) reference solutions was processed employing the four flow approaches. Table 1 lists the analytical curves obtained in these measurements, demonstrating that the highest sensitivity is provided by the MSFA approach, as a consequence of the low dispersion of the sample in this system. On the other hand, the SIA system provided the lowest sensitivity (78% lower than MSFA), as a consequence of its poor capacity to mix reagent and sample solutions and high sample dispersion. The FIA-

Table 1

Calibration lines for Ni(II) (conditions: 30  $\mu\text{L}$  Ni(II) standard solution, 60  $\mu\text{L}$  6.0 % TEA solution, 120  $\mu\text{L}$  5.0 % persulfate solution; 60  $\mu\text{L}$  1.0% DMG solution) and some figures of merit for the flow systems (relative standard deviation evaluated as the average of 10 replicates of a  $40 \text{ mg L}^{-1}$  Ni(II) solution)

Flow system	Calibration line	sample frequency (sample $\text{h}^{-1}$ )	RSD (%)	LOD ( $\text{mg L}^{-1}$ )
	$a + b [\text{Ni}] (r^2)$			
MSFA	$0.030 + 0.020 [\text{Ni}] (0.997)$	40	0.70	1.0
FIA-MBS	$0.010 + 0.0068 [\text{Ni}] (0.999)$	40	1.60	2.5
FIA-SS	$0.028 + 0.0056 [\text{Ni}] (0.999)$	40	1.80	2.7
SIA	$0.028 + 0.0043 [\text{Ni}] (0.996)$	30	3.05	3.3

Table 2

Results obtained in the determination of Ni(II) in steel alloys by ICP OES and the proposed methods (results expressed as average of 3 determinations  $\pm$  standard deviation)

Sample	ICP OES	MSFA	FIA-MBS	FIA-SS	SIA
1	5.09 $\pm$ 0.03	5.12 $\pm$ 0.12	5.18 $\pm$ 0.13	5.24 $\pm$ 0.15	5.41 $\pm$ 0.14
2	4.83 $\pm$ 0.07	4.44 $\pm$ 0.19	4.23 $\pm$ 0.05	5.22 $\pm$ 0.12	4.93 $\pm$ 0.24
3	7.15 $\pm$ 0.08	7.44 $\pm$ 0.12	6.90 $\pm$ 0.12	6.90 $\pm$ 0.19	7.48 $\pm$ 0.14
4	6.24 $\pm$ 0.10	6.69 $\pm$ 0.23	6.47 $\pm$ 0.15	6.83 $\pm$ 0.13	5.73 $\pm$ 0.46
5	8.36 $\pm$ 0.06	8.27 $\pm$ 0.20	8.59 $\pm$ 0.18	8.53 $\pm$ 0.08	7.35 $\pm$ 0.21
6	9.12 $\pm$ 0.08	9.39 $\pm$ 0.20	9.07 $\pm$ 0.21	9.99 $\pm$ 0.28	8.55 $\pm$ 0.34
7	7.03 $\pm$ 0.21	6.90 $\pm$ 0.69	7.15 $\pm$ 0.23	6.93 $\pm$ 0.29	7.37 $\pm$ 0.51
8	5.86 $\pm$ 0.22	6.18 $\pm$ 0.45	6.43 $\pm$ 0.47	5.63 $\pm$ 0.17	5.75 $\pm$ 0.42
9	4.80 $\pm$ 0.04	4.62 $\pm$ 0.10	4.55 $\pm$ 0.10	4.52 $\pm$ 0.09	3.59 $\pm$ 0.32
10	10.71 $\pm$ 0.08	9.84 $\pm$ 0.29	10.02 $\pm$ 0.23	9.72 $\pm$ 0.36	8.85 $\pm$ 0.33
11	5.76 $\pm$ 0.18	5.46 $\pm$ 0.31	5.85 $\pm$ 0.27	5.63 $\pm$ 0.46	5.78 $\pm$ 0.39
12	4.69 $\pm$ 0.03	4.85 $\pm$ 0.13	4.83 $\pm$ 0.13	4.80 $\pm$ 0.22	5.46 $\pm$ 0.44

MBS and FIA-SS systems showed intermediate performances, with the former approach providing a sensitivity slightly better than the latter, because it provides better conditions for mixing the reagent and sample solutions, as they are inserted in the flow path in five cycles. Table 1 also lists the figures of merit of the several flow systems, which again show that better performance is obtained with the MSFA approach. The lowest sampling frequency obtained with the SIA system is a natural consequence of its sampling step, which is not performed while the sample is pumped towards the detector. In addition, the relative standard deviation is higher for the SIA approach, as a consequence of the difficulty of mixing solutions in this system. Finally, the best limit of detection was obtained with the MSFA approach, as sample dispersion is lowest.

The nickel content of steel samples was determined by employing these flow systems and the results were compared with those obtained with an ICP OES reference method. Table 2 lists the results obtained, which agree at a confidence level of 95%.

#### 4. Conclusions

The proposed flow set up allowed easy implementation of several of the most employed flow approaches (MSFA, FIA-MBS, FIA-SS and SIA), without changing the configuration of the system. The different sensitivities provided by these flow systems, evaluated by means of the spectrophotometric determination of nickel in steel alloys, demonstrated that the system can be applied to different matrices, according to the concentration of the analyte in the sample.

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