

Article

## Spectrophotometric Determination of Phosphorus in Iron Alloys Employing a Flow Injection System

Ana P. G. Gervasio<sup>a\*</sup>, Carlos E. S. Miranda<sup>b</sup>, Gilmara C. Luca<sup>a</sup>,  
Cristiane A. Tumang<sup>a</sup>, Luis F. P. Campos<sup>b</sup> and Boaventura F. Reis<sup>b</sup>

<sup>a</sup>Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, 13560-970, São Carlos - SP, Brazil

<sup>b</sup>Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, CP 96, 13400-970, Piracicaba - SP, Brazil

Um sistema de análises por injeção em fluxo é proposto para a determinação espectrofotométrica de fósforo em ferro eletrolítico e ferro ligas. O método se baseia na reação com molibdato de amônio após redução com cloreto estanoso em meio ácido. Uma coluna com resina catiônica AG50W-X8A foi acoplada ao sistema para minimizar a interferência causada por Fe(III) e Cr(III). O sistema proposto apresentou uma frequência analítica de 40 determinações por hora para uma faixa de concentração de P de 0,25 a 6,00 mg L<sup>-1</sup> e um baixo consumo de reagentes, 25 mg de molibdato de amônio e 2 mg de cloreto estanoso por determinação. O desvio padrão relativo obtido para uma amostra contendo 2,20 mg L<sup>-1</sup> P foi inferior a 1 % (n=10). Três diferentes tipos de amostras foram empregados para avaliar o desempenho do sistema e a exatidão do procedimento proposto foi avaliada comparando-se os resultados obtidos com os valores dos materiais certificados, não sendo observadas diferenças significativas em nível de confiança de 95%.

A flow-injection procedure for spectrophotometric determination of phosphorus in electrolytic iron and iron alloys is proposed. The method is based on the ammonium molybdate reaction followed by stannous chloride reduction in acidic medium. In order to circumvent the severe interference caused by the major constituents such as Fe(III) and Cr(III), a mini-column packed with AG50W-X8 resin was coupled to the manifold. A sample throughput of 40 determinations per hour, a dynamical range from P 0.25 to 6.00 mg L<sup>-1</sup>, a reagent consumption of 25 mg ammonium molybdate and 2 mg stannous chloride per determination, and a relative standard deviation < 1% (n = 10) for a typical sample with 2.20 mg L<sup>-1</sup> P were achieved. Three different types of samples were used to evaluate system performance. Accuracy was assessed by comparing the results with certified values and no significant difference at 95 % confidence level was observed.

**Keywords:** phosphorus, binary alloys, spectrophotometry

### Introduction

Metals such as chromium and manganese are incorporated into steel in the form of binary alloys such as Fe-Cr and Fe-Mn. These elements are obtained by reduction of ores such as hematite, chromite and manganese oxide, respectively<sup>1</sup>. For manganese and chromium, the region where the ores are extracted should be known since the concentration of phosphorus varies from region to region. As phosphorus is a very important constituent of several steels and its concentration affects the welding conditions, determination and monitoring of phosphorus are mandatory in order to control the characteristics of the final products. Requirements for a rigid quality control in modern metallurgy is then imperative to produce competitive materials. In this context, phosphorus determinations in iron alloys are of relevance.

The often employed spectrophotometric method for the determination of phosphorus is based on an ammonium molybdate reaction, followed by stannous chloride reduction of the complex in acidic medium, which is catalyzed by phosphate ion producing a complex known as molybdenum blue<sup>2</sup>. The method has been carried out in flow injection systems for phosphorus determination in natural waters<sup>3-6</sup>. Additionally, to minimize matrix effects and/or preconcentrate phosphorus for determination in steel by inductively coupled plasma atomic emission spectrometry (ICP-AES), ion exchange<sup>7</sup> as well as solvent extraction<sup>8</sup> have been used. Iron present in the sample solution has been proposed as an efficient chemical modifier for phosphorus determination in steel by use of graphite furnace atomic absorption spectrometry<sup>9</sup> (GFAAS). Otherwise, the official method recommended by ASTM for this determination

comprises several steps, thus requiring a long time and being therefore less suitable for routine analysis in metallurgical laboratories<sup>10</sup>.

In this sense, a fast and automated analytical procedure would be worthwhile especially for the determination of low-concentration elements in alloys to improve the analysis efficiency. In this way, flow injection systems would improve not only the analytical throughput but also the accuracy in the analyses of alloys. The aim of this work was then to design a flow injection procedure using ammonium molybdate for phosphorus determination in electrolytic iron and binary alloys. Phosphorus concentration is however very low when compared to the concentrations of the major constituents such as iron and chromium in the considered matrixes. As interferences of the phosphorus analytical signal caused by these main alloy constituents may manifest themselves, a cationic resin mini-column was coupled to the flow manifold.

## Experimental

### *Chemicals and solutions*

All solutions were prepared with analytical grade reagents and freshly distilled/deionized water.

A 1000 mg L<sup>-1</sup> phosphorus stock solution was prepared by dissolving 2.1965 g KH<sub>2</sub>PO<sub>4</sub> (Merck, Germany) in about 200.0 mL water, adding 2.0 mL conc. nitric acid and making the volume up to 500.0 mL with water. Working reference solutions ranging from 0.25 to 6.00 mg L<sup>-1</sup> P were daily prepared by the appropriate dilutions of the stock solution.

In order to simulate the sample matrix, reference solutions of phosphorus plus iron, chromium and/or manganese in 0.90 mol L<sup>-1</sup> HCl + 0.35 mol L<sup>-1</sup> HNO<sub>3</sub> were prepared with the following composition: 10,000 mg L<sup>-1</sup> Fe; 3,000 mg L<sup>-1</sup> Fe + 7,000 mg L<sup>-1</sup> Cr; 200 mg L<sup>-1</sup> Fe + 800 mg L<sup>-1</sup> Mn.

A 0.40 % (w/v) ammonium molybdate solution was prepared by dissolving 2.0 g of the salt in 250.0 mL of water, adding 5.8 mL conc. sulfuric acid and completing the volume up to 500.0 mL with water.

A 0.20 % (w/v) stannous chloride solution was prepared daily in 0.15 mol L<sup>-1</sup> HCl solution.

A 0.90 mol L<sup>-1</sup> HCl + 0.35 mol L<sup>-1</sup> HNO<sub>3</sub> mixed solution was prepared to be used as carrier and eluent solution.

### *Sample preparation*

The sample fillings (*ca* 0.1g) were accurately weighed and transferred to a 250.0 mL Erlenmeyer flask for the dissolution procedure. Thereafter, 15.0 mL of conc. HCl

plus 5.0 mL of conc. HNO<sub>3</sub> were added and the Erlenmeyer flask was placed on a hot plate and heated (200 °C, 10 min). Under this condition, nitrogen oxides were released from the solution. After cooling to room temperature, the volume was made up to 100.0 mL with water. For the iron-manganese alloy, a 10-mL aliquot of this solution was transferred to a volumetric flask and the volume was made up to 100.0 mL with the carrier solution.

The certified materials IPT-54, IPT-65, and IPT-68 of iron-manganese alloys containing 80.4 % Mn, 15.9 % Fe, 0.22 % P, 1.20 % C (w/w), iron-chromium alloys containing 71.2 % Cr, 17.9 % Fe, 0.006% P, 0.051 % C (w/w) and electrolytic iron containing 0.009 % P, 0.0042 % Mn, 0.0012 % Cr, 0.0071 % C (w/w) were dissolved according to the above described procedure.

The extension of phosphorus losses was evaluated by preparing two solutions with and without iron addition. Two 0.10-mL aliquots of the 1000 mg L<sup>-1</sup> P stock solution were transferred to Erlenmeyer flasks, and 10 g of iron fillings were added to the first one. Afterwards, 15.0 mL of conc. HCl plus 5.0 mL of conc. HNO<sub>3</sub> were added and the flasks heated to 200 °C during 10 min. After cooling, the volume was made up to 100.0 mL with water.

### *Apparatus*

The flow set up comprised a B352 Micronal automatic injector, a model 435 Femto spectrophotometer with a 180 µL inner volume and 13 mm optical path flow cell, an Ismatec IPC-8 peristaltic pump with Tygon pumping tubes, a 486 microcomputer equipped with a PCL-711S (Advantech Co., California, USA) analog/digital interface card and accessories. The analog input of the interface card was connected to the analog output of the spectrophotometer. Software was developed in Quick Basic 4.5 in order to permit data acquisition and storage as ASCII files for further treatment.

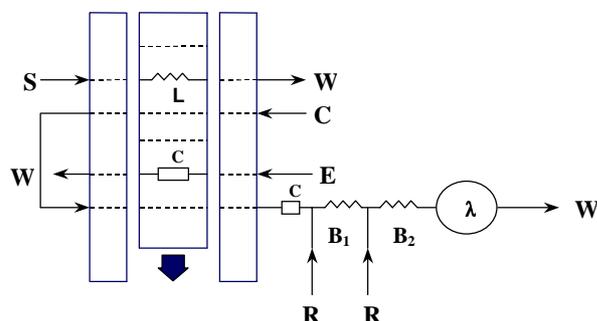
The reaction coils and flow lines were made of 0.8-mm i.d. polyethylene tubing.

Two resin mini-columns (70 mm long and 3 mm i.d., and 1.0 cm long and 3 mm i.d.) were made by filling a Tygon tube with the cationic resin AG50W-X8 (50-100 mesh). Glass wool was placed at the column ends to avoid resin losses during system operation.

### *Procedure*

The flow diagram of the system in the sampling position is shown in Figure 1. The sample solution (S) is aspirated to fill the sampling loop (L) and the excess is wasted (W). Meanwhile, the eluent (E) and carrier (C) streams are pumped through the C<sub>1</sub> and C<sub>2</sub> resin mini-columns towards waste.

In this position, the resin is conditioned to the  $H^+$  form and cleaned from other cations that were retained in the active sites. Afterwards, the injector sliding bar is switched to the alternative position, the sampling loop and  $C_1$  resin column are inserted in the analytical path, and the sample solution is transported by the C carrier stream through the resin columns  $C_1$  and  $C_2$ . As presented in Figure 1, the  $R_1$  and  $R_2$  reagents are added to the sample zone at the  $x$  and  $y$  confluence points. The chemical reactions producing the detectable species occur while the sample zone is transported towards the detector (D) through the  $B_2$  reaction coil. The transient absorbance is recorded at 690 nm as a time function. In the present procedure, peak height constitutes the measurement basis. Displacing back the injector sliding bar to the position specified in Figure 1 initializes the next analytical cycle.



**Figure 1.** Flow diagram. L = sampling loop (200  $\mu\text{L}$ ); C, E = carrier and eluent solutions,  $0.90 \text{ mol L}^{-1} \text{ HCl} + 0.35 \text{ mol L}^{-1} \text{ HNO}_3$  ( $2.5$  and  $2.8 \text{ mL min}^{-1}$ );  $C_1$  and  $C_2$  = resin mini-columns ( $70$  and  $10 \text{ mm}$ );  $R_1$  =  $0.40 \%$  ammonium molybdate ( $2.8 \text{ mL min}^{-1}$ );  $R_2$  =  $0.20 \%$  stannous chloride ( $2.8 \text{ mL min}^{-1}$ );  $B_1$  and  $B_2$  = reaction coils ( $10$  and  $150 \text{ cm}$ );  $\lambda$  = detector ( $690 \text{ nm}$ ); W = waste.

## Results and Discussion

In the proposed system, parameters such as sample residence time, resin selectivity, reagent concentrations, sample volume and mainly matrix effect are among the main parameters that may affect sensitivity. Hence they were investigated thoroughly to establish suitable conditions for the determination of phosphorus.

As the reaction yielding the detectable chemical species occurs slowly, a long mean residence time or a heating step is required for improving sensitivity. The sample residence time could be increased by reducing the overall flow rate, but this decreases the sample throughput. Thus to find the best compromise between sensitivity and sample throughput, experiments were carried out by employing  $B_2$  coil lengths of  $100$ ,  $150$  and  $200 \text{ cm}$  to establish the suitable sample residence time. Signals associated with the  $150\text{-cm}$  reaction coil were  $20 \%$  higher than those related

to the  $100\text{-cm}$  coil. Since no significant increase on the phosphorus signal was observed for a reaction coil longer than  $150 \text{ cm}$ , this figure was selected. The sample residence time corresponding to  $150 \text{ cm}$  reaction coil was about  $24 \text{ s}$ .

Influence of the concentration of ammonium molybdate was verified by using solutions with  $0.40$ ,  $0.60$  and  $0.80 \%$  (w/v) and a  $0.30 \%$  (w/v) stannous chloride solution. Higher analytical signals were obtained by increasing the molybdate concentrations but this concentration could not be increased at will since the signal of the uncatalysed reaction was also increased. Thus, the lowest molybdate concentration investigated ( $0.40 \%$ ) was defined for the following experiments. A similar tendency was observed when the concentration of stannous chloride solution was changed from  $0.20$  to  $0.50 \%$  (w/v). Under these conditions there was an approximately  $25 \%$  increase in the blank signal which could be caused by the uncatalysed reaction. A  $0.20 \%$  (w/v) solution was then selected to minimize this effect.

Increasing the sample volume from  $50$  to  $200 \mu\text{L}$  improved sensitivity by about  $100 \%$  but reduced sampling frequency. As a compromise, a  $40\text{-cm}$  loop that corresponded to  $200 \mu\text{L}$  sample volume was selected for all the experiments.

Heated acid solutions have been commonly used to dissolve several metals and their compounds. This procedure allows quantitative sample dissolution without losses of volatile species. On the other hand, non-metallic elements require special handling to avoid losses due to their high volatility. In this sense, an experiment was carried out to verify the extension of phosphorus losses by heating. Both  $0.1 \text{ mL}$  of  $1000 \text{ mg L}^{-1} \text{ P}$  solution and a  $0.1 \text{ mL}$  of  $1000 \text{ mg L}^{-1} \text{ P}$  solution plus  $10 \text{ g Fe}$  were used as described in the sample preparation item. Afterwards these solutions were analyzed with the proposed system and the results were compared to those obtained with  $1.0 \text{ mg L}^{-1} \text{ P}$  solution which was not dissolved at a high temperature. Considering that the dissolution process was effective and the relative standard deviation obtained by comparing these two situations was  $< 3 \%$ , it is possible to infer that losses of phosphorus are irrelevant.

The phosphorus content in the sample solution was  $1000\text{-fold}$  lower than those of the major elements present in the alloys. In this way, iron, chromium and manganese, could be potential interferants for phosphorus determination in electrolytic iron and binary alloys (Fe-Cr and Fe-Mn). Thus, standard solutions were prepared to simulate the matrices to evaluate the interference extension of such elements on the phosphorus determination.

No interference effects were observed from Fe-Mn alloys on the phosphorus signal for concentrations of up to  $800 \text{ mg L}^{-1}$  Mn. However there was a decrease in analytical signal caused by iron species in concentrations greater than  $2,000 \text{ mg L}^{-1}$  Fe(III) (Figure 2). A decrease in analytical signal was also verified in the presence of Cr(III) at concentrations greater than  $3,000 \text{ mg L}^{-1}$  (Figure 3). These problems were overcome by coupling two cationic resin mini-columns to the manifold (Figure 1). Initially, a 70-mm long resin column was employed to remove iron and chromium cationic species from the sample solution in order to avoid interferences upon the analytical signal. Since this resin mini-column was not long enough to retain

the interferent ions, a longer one was employed. But this attempt failed as well. A second resin column shorter than the first, was coupled to the manifold to retain the cations which were not removed by the first column. Thus the interferent ions were delayed and the analyte was able to freely react with the reagents. As the best results were obtained with two columns, this approach was incorporated. Resins with 50-100 and 200-400 mesh were evaluated to establish which one would be more suitable, and best results were achieved with a resin mesh of 50-100. When a resin with 200-400 mesh was employed there was a decrease in analytical signal probably due to a dispersion process inside the column (Figure 4).

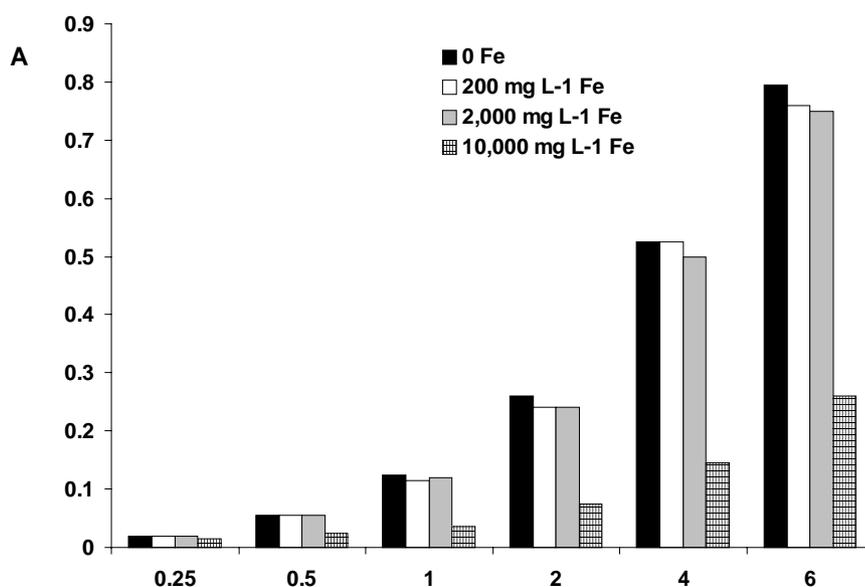


Figure 2. Influence of iron concentration on the phosphorus determination at 690 nm.

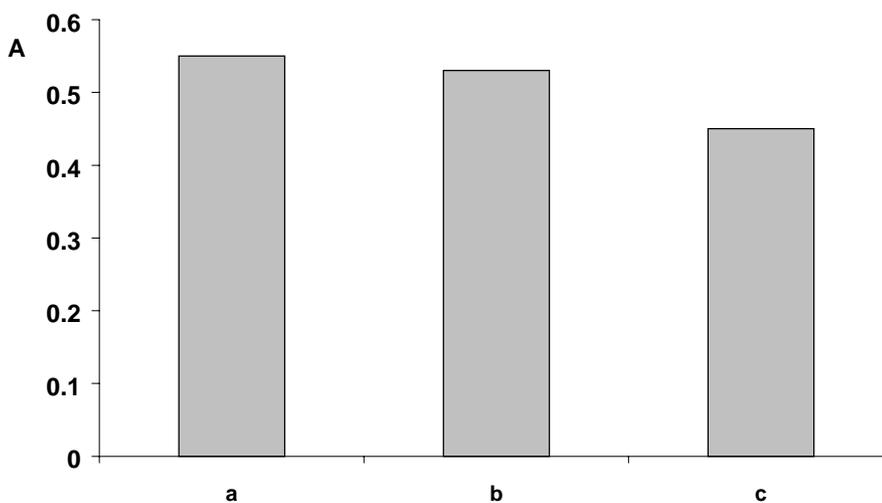
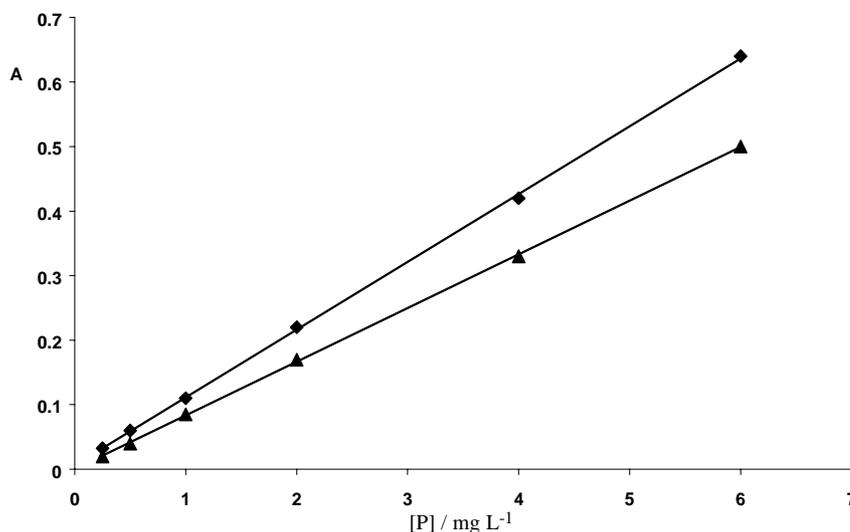


Figure 3. Influence of chromium concentration on the phosphorus determination. a)  $4 \text{ mg L}^{-1}$  P b)  $4 \text{ mg L}^{-1}$  P +  $3,000 \text{ mg L}^{-1}$  Cr(III) P and c)  $4 \text{ mg L}^{-1}$  P +  $7,000 \text{ mg L}^{-1}$  Cr(III).



**Figure 4.** Influence of the resin mesh on the phosphorus determination.  $\blacklozenge$ ) Dowex 50 (50-100 mesh) and  $\blacktriangle$ ) AG50W-X8 (200-400 mesh).

Use of two resin columns led to losses in sensitivity for electrolytic iron. To compensate this drawback all the reference solutions were prepared by simulating the iron matrix with the highest expected iron concentration ( $10,000 \text{ mg L}^{-1}$ ). Even so, sensitivity losses remained, but the matrix matching allowed the monitoring of the extension of iron interference and so to compensate it.

The accuracy of the method was evaluated by analyzing certified samples of Fe, Fe-Cr and Fe-Mn and the results are shown in Table 1. After applying the paired *t*-test, no significant differences at the 95% confidence level between the obtained results and those from the certified samples were found. Other favorable features such as a throughput of 40 determinations per hour, a relative standard deviation of 0.8 % ( $n=10$ ) for an iron manganese sample solution with  $2.20 \text{ mg L}^{-1}$  P, a linear response for  $0.25 - 6.00 \text{ mg L}^{-1}$  P ( $r = 0.999$ ;  $n = 6$ ) and a reagent consumption of 25 mg ammonium molybdate and 2 mg stannous chloride per determination were also achieved.

**Table 1.** Comparative results. Phosphorus concentrations in electrolytic iron, Fe-Cr and Fe-Mn alloys, in % w/w, as determined by proposed system.

Sample	% P (w/w)	
	Certified Value	Proposed procedure
1- Fe-Cr	-	$0.011 \pm 0.009$
2- Fe-Cr	-	$0.025 \pm 0.008$
3- Fe-Cr IPT-65	$0.006 \pm 0.001$	$0.006 \pm 0.001$
4- Fe-Mn	-	$0.11 \pm 0.05$
5- Fe-Mn IPT-54	$0.22 \pm 0.01$	$0.24 \pm 0.06$
6- Fe IPT-68 (electrolytic)	$0.009 \pm 0.001$	$0.010 \pm 0.003$

values are mean  $\pm$  SD,  $n = 3$ .

## Conclusions

The interference of the Fe-Cr matrix on the analytical signal of phosphorus was fully suppressed by coupling two resin mini-columns to the manifold. On the other hand, matrix matching was necessary to minimize the interference caused by electrolytic iron alloy. Three different types of alloys were run by employing the proposed procedure. Despite the pronounced difference among them, just one appropriate analytical curve was used for phosphorus quantification. Since the considered matrixes are complex and phosphorus concentration is low, there was a substantial gain reaching a condition where just one general analytical curve could be employed.

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