

Determination of Iron in Soils by Flow Injection Atomic Absorption Spectrometry

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ABSTRACT

A single-channel flow injection system was optimized for the determination of available iron (Fe) in soil extracts by atomic absorption spectrophotometry. This method of introducing the samples in the spectrophotometer worked particularly well in preventing blockage of the burner head which was observed in the conventional introduction of Fe for its determination by atomic absorption spectrophotometry. The appropriate selection of the manifold parameters, such as injection volume, tube length and flow rate, allowed introduction of any soil extract without requiring any pre-treatment. This system allowed determinations at a detection limit of 0.36 mg L⁻¹ to 5 mg L⁻¹, with an output of 300 determinations per hour. The results obtained for analysis of 15 soil extracts were in good agreement with those provided by the colorimetric method, with average relative deviations of 1.6%. Relative standard deviations of 4.8, 2.5, and 2.3% were obtained for contents of 1.03, 1.85, and 3.99 mg Fe L⁻¹, respectively.

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INTRODUCTION

Analytical determinations by atomic absorption spectrometry (AAS) usually offer a high sample throughput, but in most applications the output rate is not matched by the steps of preparation needed to obtain a solution suitable for analysis. Sample treatments before measurement, which may involve dilution of samples, addition of reagents or even pre-concentration of the analyte, are very time consuming and condition the overall time of analysis. In routine analysis, the concentration of samples in the different analytes is frequently distributed over wide ranges. In the particular analysis by atomic absorption spectrophotometry, the preparation of samples is a determining factor in the analysis time, since the linear working range, either with flame or electrothermal atomization, is very narrow. Therefore, the time of analysis and quality of the results can be improved if these stages of preparation are performed automatically in a flow injection system (Garrido et al., 1996). The potential of replacing the conventional introduction of the sample by flow injection methodologies for use in atomic absorption spectrometry was reported by Tyson (1985). Flow injection analysis manifolds can be designed to automatically carry out large sample dilutions (Lima et al., 1991), pre-concentrate analyte by using in-line ion-exchange resins (Olsen et al., 1983), or to perform liquid-liquid extraction (Kubán, 1991). Besides allowing a higher sample output, these in-line concentration adjustments are much more precise than conventional manual procedures. Reagent addition in flow injection manifolds also yields lower reagent consumption over conventional introduction, especially when the merging zones technique is used (Zagatto et al., 1979). Matrix physical interferences occurring in the aspiration and nebulization process can also be minimized by coupling of a flow injection manifold, that imposes a flow rate higher than the aspiration of the spectrometer. This enables the direct determinations in complex matrices such as wines (Lima and Rangel, 1991). Since only a low sample volume is introduced between the carrier/washing solution, blocking of the burner head is minimized, allowing measurements of samples with high amount of dissolved solids (Mindel and Karlberg, 1981).

This work describes the use of a single-channel flow injection manifold for the determination of available iron in soil extracts by atomic absorption spectrometry as detection process in which, unlike in conventional sample introduction, no burner head blocking was observed. For comparison, similar analysis were conducted by the colorimetric method (Hesse, 1972).

MATERIALS AND METHODS

Reagents and Solutions

All solutions were prepared using deionized water (specific conductivity lower than $0.1 \mu\text{S cm}^{-1}$) and all chemicals were of analytical reagent grade. The solutions used for iron extraction were prepared as described by Hesse (1972):

Ammonium acetate solution, 1M, pH=3. Equal volumes of 2M acetic acid solution and 2M ammonia solution were mixed, and the pH was adjusted to 7 with either one of these solutions. Concentrated hydrochloric acid was finally added to adjust the pH to 3.

Aqua regia was prepared by mixing hydrochloric acid and nitric acid in proportions of 1:4 (v/v).

For the analytical determinations, the following reagents were used:

Hydroxylamine hydrochloride 10% w/v was prepared by dissolving 10 g of hydroxylamine hydrochloride in water, and the volume was made up to 100 mL. This reducing solution was prepared daily.

The 1,10-phenanthroline solution was prepared by dissolving 1.5 g in ethanol and made up to 100 mL with ethanol.

Iron (II) stock solution (200 mg L^{-1}) was prepared by dissolving 1.404 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a mixture of 20 mL of sulphuric acid and 50 mL of deionized water, and this mixture was made up to 1 L with water. The standards used for establishing calibration curves, both for the FIA (1.0 to 5.0 mg L^{-1}) and the colorimetric method (0.4 to 1.6 mg L^{-1}) were prepared by dilutions of the iron (II) stock solution in water.

Instrumentation and Flow Injection Manifold

The colorimetric determination of iron was carried out with a Unicam 8625 UV-visible light spectrophotometer.

The FIA determinations were performed with a GBC 902 atomic absorption spectrophotometer with an air-acetylene flame. The detector was connected to a Kipp & Zonnen BD 111 chart recorder. The solutions were propelled by a Gilson Minipuls 2 peristaltic pump in Gilson propulsion tubes. Standards and soil extracts were injected with a Rheodyne Type 50 injection valve. The connections between the different components of the manifolds were made with 0.8 mm (i.d.) Omnifit PTFE tubes and Gilson end-fittings.

The flow injection system for the determination of available iron in soil was a single-line manifold (Figure 1). The extracts from 15 soil samples were injected directly in the FIA system without any previous treatment, and the concentration of iron was calculated by interpolation on the calibration curves established between 1 and 5 mg L^{-1} .

Sample Preparation and Colorimetric Method

For the extraction procedure, reference is made to Hesse (1972). The soil samples were air dried, and ground, and passed through a 1-mm sieve. Twenty-five g of soil were shaken for 30 seconds with 250 mL of 1M ammonium acetate solution (pH=3) and then vacuum filtered through a Whatman-3 filter paper. The soil was leached through the filter three times with 50 mL of the ammonium acetate solution.

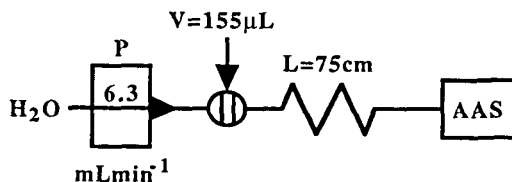


FIGURE 1. Flow injection manifold for the determination of available iron in soil extracts by atomic absorption spectrophotometry: P=peristaltic pump; V=injection volume; L=tube length; AAS=atomic absorption spectrophotometer.

The filtrate was evaporated in a boiling water bath after which it was digested with 10 mL of *aqua regia* until dryness, for removal of traces of organic matter. The residue was taken up with 1 mL of 1M hydrochloric acid and transferred into a 100 mL volumetric flask, and the volume was made up to the mark with deionized water. This final extract was then used for both colorimetric and FIA determinations.

The calibration curve for the colorimetric method was made with standards in the range of 0.4 to 1.6 mg L⁻¹ in 25 mL volumetric flasks. After dilution with 5 mL of deionized water, the pH was adjusted to 1.5-2.7 with dilute hydrochloric acid or ammonia, after which 2 mL of 10% hydroxylamine hydrochloride solution, followed by 1 mL of 1.5% 1,10-phenanthroline solution, were added and the volume made up with deionized water. The same procedure was applied to duplicate soil extracts. The optical density was read at 508 nm.

RESULTS AND DISCUSSION

The manifold parameters (injection volume, tube length and flow rate) were optimized to assure the necessary concentration adjustment of the solutions and their introduction in the atomic absorption spectrophotometer, without the blocking effects observed in the direct aspiration of the samples. The optimization procedure is subsequently described.

Samples and standards were injected in a water stream propelled by a peristaltic pump that guarantees a constant flow rate at the nebulizer entry. The normal aspiration rate of the spectrophotometer was 5.8 mL min⁻¹, and the flow rate imposed by the FIA system at the nebulizer entry was 6.3 mL min⁻¹. The use of a flow rate higher than the intrinsic aspiration of the spectrophotometer resulted in better reproducibility as this overpressure imposed by the FIA system minimizes the influence of the aspiration rate variations on the analytical signal. This effect was previously reported by Brown and Ruzicka (1984) who emphasized that to

achieve optimum performance it is essential to maintain a forced rather than an aspirated flow into the nebulizer. This overpressure also contributes to minimize the influence of physical characteristics of the samples (Lima and Rangel, 1991).

The effect of changing the injection volume has mainly been investigated for its effect on the dispersion in the manifold (Tyson et al., 1985) but in this work, the selection of the injection volume was not only a function of the dispersion demanded for this particular matrix, but it should also be the smallest possible to avoid the blocking of the burner head. In fact, when the soil extracts were introduced in a conventional way in the atomic absorption spectrophotometer (Soil and Plant Analysis Council, 1992) problems with the blocking of the burner head were observed, probably due to the high level of dissolved solids. The introduction of the sample extracts resorting to the flow system could solve this problem not only because the sample is not continuously aspirated to the nebulizer, but also the burner head is cleaned by the continuous flow of water between consecutive injections. Volumes of 130, 155, 180, and 205 μL were tested. The injection loop volumes were determined by making ten injections of a 0.100M HCl solution in a water stream. The collected solution was then titrated with a 0.105M NaOH solution previously standardized; the injection volume was calculated from the average of three assays. The selected volume was 155 μL as lower volumes increased too much the dispersion of the system resulting in a poor sensitivity. Larger volumes did not allow linearity up to 5 mg L^{-1} (maximum concentration found in the analyzed extracts) and contributed to the gradual blocking of the burner head, as observed in conventional aspiration.

The dispersion of the plug took place in a 75-cm tube before reaching the nebulizer. Other lengths (75, 100, 150, and 225 cm) were tried and it was found that a tube longer than 75 cm significantly decreased the sensitivity.

Using the system with the previously optimized conditions, the methodology presents a detection limit of 0.36 mg L^{-1} , calculated as three times the standard deviation of the system background noise (IUPAC, 1976).

The precision of the system was evaluated from ten consecutive injections of three soil extracts with concentrations of 1.03, 1.85 and 3.99 mg L^{-1} , and the relative standard deviations obtained were 4.8, 2.5, and 2.3%, respectively. These results also show that the system is free from blockage effects on the burner head.

The system output is of 300 samples per hour which is significantly higher than that of the manual colorimetric method. An output of about ten samples per hour is usually common in the colorimetric method as for each different sample it is necessary to adjust the pH of each extract before adding the reducing and color development reagents. In addition each extract has to go through a multi-step dilution process to adjust it to the linear working range of the UV/Vis spectrophotometer.

In order to assess the accuracy of the FIA methodology (mg Fe L^{-1} of extract), analysis of extracts of 15 soil samples using the flow injection manifold (C_f) and the colorimetric method (C_c) were carried out and the results are shown in Table

TABLE 1. Results obtained for the determination of iron in soil extracts by the FIA system, and the colorimetric method and the corresponding relative deviations.

Soil	FIA (mg L ⁻¹)	Colorimetric method (mg L ⁻¹)	Relative deviations (%)
1	1.87	1.85	+ 1.08
2	3.54	3.53	+ 0.28
3	1.47	1.47	0.00
4	2.94	2.85	+ 3.16
5	2.30	2.30	0.00
6	2.13	2.23	- 4.48
7	4.12	3.98	+ 3.52
8	2.81	2.94	- 4.42
9	1.61	1.60	+ 0.63
10	4.75	4.80	+ 1.04
11	1.53	1.53	0.00
12	1.43	1.44	- 0.69
13	1.46	1.46	0.00
14	3.17	3.12	+ 1.60
15	4.30	4.44	- 3.15

1. Relative deviations between the two methodologies with an average value of 1.6% were obtained, indicating that the results are comparable. Additionally, the regression equation $C_f = C_0 + s C_r$ parameters were $C_0 = 0.012 (\pm 0.093)$ mg L⁻¹, $s = 0.993 (\pm 0.033)$, and a correlation coefficient of 0.998, and they are evidence for a good agreement with the colorimetric method. The confidence limits (in parenthesis) of the intercept and slope, were obtained with a 90% confidence level for 13 degrees of freedom ($t = 1.77$) (Miller and Miller, 1993).

CONCLUSIONS

A simple single-line FIA manifold was found suitable for the determination of iron, and a very high output was obtained. The small volume of injected extract together with an overpressure at the nebulizer entry prevented blockage of the burner head which was a problem with the conventional nebulization process. This method has improved this process of preparing and introducing the extract at an even higher sample output than ordinary AAS methods. Compared with the colorimetric method, this method was considerably faster, and yielded results of

similar or better quality. This FIA system requires no operations for preparation of extracts before measurement, and implementation for routine analysis is easier.

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REFERENCES

- Brown, M.W. and J. Ruzicka. 1984. Parameters affecting sensitivity and precision in the combination of flow injection analysis with flame atomic-absorption spectrophotometry. *Analyst* 109:1091-1094.
- Garrido, J.M.P.J., R.A.S. Lapa, J.L.F.C. Lima, C. Delerue-Matos, and J.L.M. Santos. 1996. FIA automatic dilution system for the determination of metallic cations in waters by atomic absorption and flame emission spectrometry. *J. Autom. Chem.* 18:17-21.
- Hesse, P.R. 1972. *A Textbook of Soil Chemical Analysis*. Chemical Publishing, New York, NY.
- IUPAC. 1976. International Union of Pure and Applied Chemistry. *Anal. Chem.* 48:2294.
- Kubán, V. 1991. Liquid-liquid extraction flow injection analysis. *Crit. Rev. Anal. Chem.* 22:477-557.
- Lima, J.L.F.C. and A.O.S.S. Rangel. 1991. Usefulness of a detector inlet overpressure and a stream splitting in FIA systems to deal with food sample pre-treatment requirements. Application to wine analysis. *Food Control* 146-151.
- Lima, J.L.F.C., A.O.S.S. Rangel, and M.M.S. Roque da Silva. 1991. Determination of Ca, Mg, Na, and K in wines by atomic absorption and flame emission spectrometry using a flow injection manifold with a dialysis unit. *Atomic Spectro.* 12:204-206.
- Miller J.C. and J.N. Miller. 1993. *Statistics for Analytical Chemistry*. 3rd ed. Ellis Horwood, Chichester, United Kingdom.
- Mindel, B.D. and B. Karlberg. 1981. A sample pretreatment system for atomic absorption using flow injection analysis. *Lab. Pract.* 719-723.
- Olsen, S., L.C.R. Pessenda, J. Ruzicka, and E.H. Hansen. 1983. Combination of flow injection analysis with flame atomic-absorption spectrophotometry: Determination of trace amounts of heavy metals in polluted seawater. *Analyst* 108:905-917.
- Soil and Plant Analysis Council. 1992. *Handbook on Reference Methods for Soil Analysis*. Soil and Plant Analysis Council, Athens, GA.

- Tyson, J.F. 1985. Flow injection analysis techniques for atomic-absorption spectrometry. A review. *Analyst* 110:419-429.
- Tyson, J.F., C.E. Adeeyinwo, J.M.H. Appleton, S.R. Bysouth, A.B. Idris, and L.L. Sarkissian. 1985. Flow injection techniques of method development for flame atomic-absorption spectrometry. *Analyst* 110:487-492.
- Zagatto, E.A.G., F.J. Krug, H. Bergamin, S.S. Jorgensen, and B.F. Reis. 1979. Merging zones in flow injection analysis. Part 2. Determination of calcium, magnesium and potassium in plant material by continuous flow injection atomic absorption and flame emission spectrometry. *Anal. Chim. Acta* 104:279-284.