

Autocatalysis in the Spectrophotometric Flow-Injection Determination of Manganese as Permanganate. Soil, Plant and Rock Analysis

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Received: August 8, 1989, October 30, 1989

Um procedimento empregando sistema de injeção em fluxo, baseado na formação do íon permanganato, é proposto para a determinação espectrofotométrica de manganês em solos, plantas e rochas. A oxidação pelo periodato é conduzida sob condições ácidas a aproximadamente 95°C. A velocidade desta reação é incrementada explorando-se o efeito autocatalítico pronunciado, pela adição de um fluxo confluyente de permanganato. Concentrações dos reagentes, nível de adição de permanganato, acidez, vazões, estabilidade da cor e efeitos dos interferentes são estudados. Oxidação quantitativa é conseguida e ácido clorídrico nas amostras é tolerado até 0.5 M. O limite de detecção é de aproximadamente 0,3 mg Mn/l. O sistema processa aproximadamente 60 amostras por hora, fornecendo resultados precisos (d.p.r. < 1%) e concordantes com espectrometria de emissão atômica.

A flow-injection procedure based on permanganate formation is proposed for spectrophotometric determination of manganese in soils, plants and rocks. The oxidation by periodate is carried out under acidic conditions at about 95°C. The rate of this reaction is accelerated by exploiting the autocatalytic effect which is enhanced with the addition of a permanganate confluent stream. Reagent concentrations, permanganate addition level, acidity, flow rates, colour stability and interference effects are studied. Quantitative oxidation is attained and hydrochloric acid in the samples is tolerated up to 0.5 M. The detection limit is about 0.3 mg Mn/l. The system can handle about 60 samples per hour, yielding precise results (r.s.d. < 1%) in agreement with atomic emission spectrometry.

Key words: *autocatalysis; flow-injection; manganese.*

Introduction

Oxidation of manganous ions to permanganate constitutes the basis of a classical spectrophotometric method for manganese determination in soil, plant and rock samples¹. In spite of its inherent selectivity, the applicability of this method to routine analysis is limited because the oxidation reaction is relatively slow requiring high acidity, heating and catalysis^{2,3}. In addition, sensitivity is low and some reducing agents, e.g. hydrochloric acid, should be avoided.

Although this method has been adapted to air-segmented continuous flow analysis⁴, its incorporation into a flow-injection system^{5,6} is better accomplished after optimization of the oxidation process which should be as fast as possible and carried out under low acidity in order to avoid the use of concentrated acid solutions which may impair the pumping process.

Faster oxidation is attained when periodate is used as oxidant and the reaction proceeds in nitric-phosphoric medium at about⁷ 90 °C. Also, the induction period is greatly reduced when manganese dioxide is added under

high acidity³. The solubility of this compound, however, impairs its application in flow-injection analysis. Preliminary experiments indicated that, by adding a permanganate confluent stream to promote autocatalysis, quantitative oxidation by periodate could be attained in a flow-injection system under low acidity at about 95 °C.

In this work, the feasibility of this catalytic approach was investigated in order to develop a spectrophotometric flow-injection procedure for manganese in soils, plants and rocks.

Materials and Methods

For preparation of soil and rock extracts^{8,9}, 0.500 g powdered samples (100 – 200 mesh) plus 5 ml aqua regia (3HCl:1HNO₃ v/v) were placed in PTFE bombs left open overnight. Then, 5.0 ml HF were added and the bombs closed and heated at 140 °C for at least two hours. Thereafter, the bombs were removed, cooled in running water and opened. After addition of 2.0 ml HClO₄, the open bombs heated at 210 °C until dryness. If silica was

not completely eliminated, 5.0 ml HF were added and the open bombs were heated again until dryness. The residue was dissolved in 10 ml of a warm (ca 60 °C) 0.5 M HCl solution. After filtration through a Whatman #1 filter paper, the volume was completed to 25ml with water.

The mineralization of plant samples was carried out similarly as in earlier work¹⁰: 1.000 g oven-dried powdered samples (60 °C to constant weight) were ashed in silica crucibles for 3-4 hours at 550 °C. The ashes were moistened with 1 ml water, mixed with 5.0 ml of a 4.0 M HNO₃ solution, dried at 60 °C and mixed thoroughly with 10 ml of a 1.0 % v/v HNO₃ solution. The solutions were filtered (Whatman #1) and the procedure was repeated until 50-ml filtrates were obtained.

All chemicals were of analytical-reagent grade and distilled-deionized water was used throughout.

The manganese stock standard solution, 1000 mg Mn/l was prepared by dissolving 2.0300g MnSO₄·4H₂O in water, adding 50ml of a 10% v/v HNO₃ solution and completing the volume to 500 ml with water. This stock solution was standardized by using EDTA. Working standards within the 0 - 15 mg Mn/l range were also 0.2 M HCl (soil and rock samples) or 1.0% v/v HNO₃ (plant samples).

The permanganate stock solution, 1000 mg MnO₄/l, was prepared by dissolving 0.332 g potassium permanganate in water, adding 25 ml of a 10 % v/v H₃PO₄ solution and completing the volume to 250 ml with water. The solution was kept in a dark bottle.

The sample carrier stream (C - Fig. 1B) was either 0.2 M HCl (soils and rocks) or 1.0 % HNO₃ (plants) solutions.

The oxidant catalyst reagent (R - Fig. 1B) was 4.0 M H₃PO₄ 0.7 % w/v NaIO₄ and 30.0 mg/l MnO₄ solution.

A Technicon AAI or a mp3 GJ4 Ismatec peristaltic pump with color-coded pumping tubes of tygon, and a manually operated injector-commutator¹¹ were used. The spectrophotometer was a Beckman 24/25 ACC model provided with a Hellma 178 OS flow-cell (80μl inner volume, 10 mm optical path) and connected to a REC-61 Radiometer recorder. Polyethylene tubes (0.8 mm i.d.) were used to construct the sampling loops and transmission lines. PTFE tubes (0.3 mm i.d., wall thickness < 0.2 mm) were used in the analytical path because of their inert chemical characteristics and tolerance towards heating. Heat transfer is more efficient with a thinner wall. The B1 coiled reactor (Fig. 1) was immersed in boiling water under reflux, using a heating mantle with a 1l round-bottom flask and a 50 cm reflux condenser. To avoid heating of the flow-cell, the T-shaped D debubbler¹² and the B2 reactor were immersed in a current water bath.

The conditions for automated manganese oxidation were investigated with the flow-injection system outlined in Fig. 1A. The system was designed with low confluent flow rates and large injected volume in order to preserve the sample volumetric fraction¹³. The required reagents were added separately. Thus the preparation of an excessive number of solutions was avoided.

In Fig. 1A, the samples (S) and a solution with a potential interfering species (I) converged with identical flow rates before reaching the sampling loop (L). The concentrations of the convergent streams were then halved. When selectivity was not being investigated, a blank solution was placed as I.

When the injector-commutator was switched to the injection position, the sample selected volume was placed in the carrier stream. The acid (R1), catalyst (R2) and oxidant (R3) reagents were added by confluence, allowing manganese oxidation inside the following B1 heated coil. The mechanism of this oxidation has been discussed elsewhere^{1-3,14}. Cooling was attained inside the following coil. When passing through the debubbler (D) a fraction of the sample zone was aspirated together with eventual air bubbles towards waste (W). The remainder of the processed zone reached the detector set at 548 nm. The transient absorbance was recorded as a peak, proportional to the manganese content of the sample.

The system shown in Fig. 1B, a simplified version for routine analysis, was similarly operated.

System 1A with a 100 cm sampling loop (about 500 μl) was employed to define optimum conditions for the flow-injection manganese oxidation. Standard solutions within the 0.0 - 180.0 mg Mn/l range were used as S and a blank solution (1.0 % v/v HNO₃) as I. The sample carrier stream (C) and the standard solutions were also 1.0 % v/v HNO₃. The influence of acidity was investigated by using different solutions (0.0 - 3.0 M H₃PO₄ plus 0.0 - 6.0 M HNO₃ plus 0.0 - 3.0 M H₂SO₄) as R1 reagent. The catalyst and oxidant reagents were 30.0 mg MnO₄/l plus 1.0 % w/v HNO₃ (R2) and 1.0 % NaIO₄ (R3) solutions, respectively. The influence of permanganate addition under different acidities (R1 = 0.0 - 3.0 M H₃PO₄) was investigated by placing 0.0 - 60.0 mg MnO₄/l solutions as R2. With a permanganate concentration of 45.0 mg/l the effect of the periodate concentration in the oxidant reagent was studied within the 0.5 - 3.0 % w/v NaIO₄ range. Whenever necessary, the percentage of oxidation was evaluated by placing a 60.0 mg Mn/l standard solution in the infinite volume situation¹¹: after attainment of steady state, the peristaltic pump was stopped for three minutes and the additional peaked signal obtained after flow rate restoration was considered.

After the above experiments, the R1 stream removed and the R2 and R3 reagents were fixed as 1.0 % w/v NaIO₄ and 45.0 mg MnO₄/l (both 2 M in H₃PO₄). With this simplified system, the flow rate of the sample carrier stream was changed within the 0.8 - 2.5 ml/min range. For each flow rate, R2 and R3 reagents were selected in order to maintain the concentrations inside the reaction coils. With 1.6 ml/min flow rate, the length of the sampling loop was changed from 50 to 200 cm and the possibility of reducing the B2 coil was investigated. With a 150 cm loop, the influence 0.5, 1.0 and 2.0 M perchloric, hydrochloric and hydrofluoric acids in the sample was checked by placing successively the acid solutions as I and 0.0 - 30.0 mg Mn/l standard solutions as S (Fig. 1A). Effects of potential interfering ions were similarly investigated. In this experiment, V (as ammonium vanadate), Mg, Cu, Co and Ni (as sulphates), Fe, Pb, Sr and Ba (as nitrates), Cr (as potassium bichromate or chromic nitrate) and Ti (as oxide) standard solutions were used. Thereafter, the system was simplified to that shown in Fig. 1B.

Results and Discussion

Quantitative manganese oxidation by periodate was better attained when phosphoric was the only acid in the R1 reagent and autocatalysis was employed (Figs 2 and 3). Without permanganate addition, the percentage of oxi-

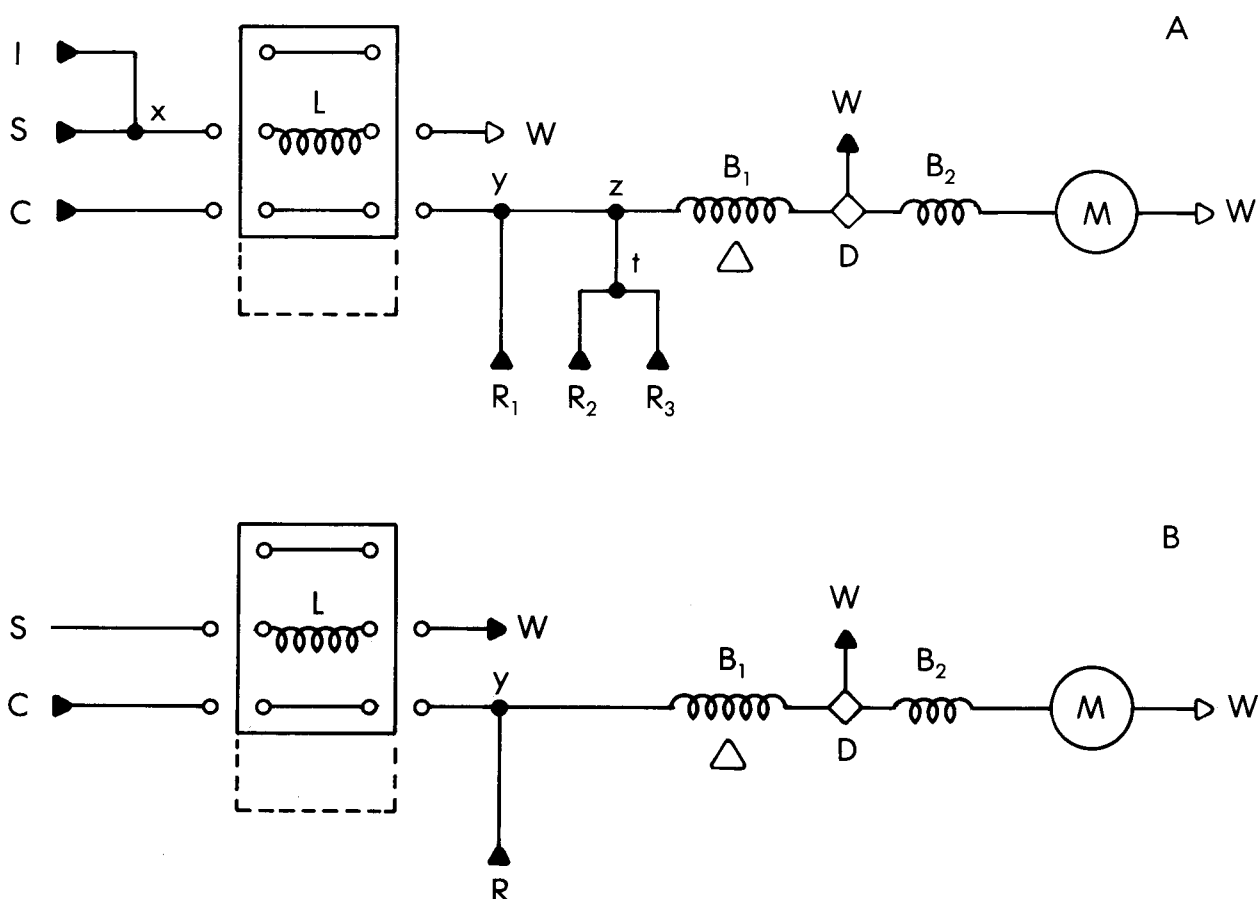


Figure 1. Flow diagrams

A: used to investigate manganese oxidation. *S* - sample (2.0 ml/min); *I* - solution with a potential interferent (2.0 ml/min); *L* - sampling loop; *C* - carrier stream (0.80 ml/min); *R*₁, *R*₂ and *R*₃ - acid, catalyst and oxidant reagents (0.80, 0.42 and 0.42 ml/min); *B*₁ and *B*₂ - 400 and 200 cm teflon coils immersed in boiling and running water, respectively; *D* - debubbler with a 0.42 ml/min outlet towards waste; *M* - detector at 548 nm; *x*, *y*, *z*, *t* - confluence points; *W* - waste.

B: proposed for soil, plant and rock analysis. *S* - sample aspirated at 3.9 ml/min; *L* - 150-cm loop; *C* - carrier stream (1.6 ml/min); *R* - oxidant/catalyst reagent (0.6 ml/min); *B*₁ and *B*₂ - 400 and 50 cm teflon coils. Other symbols as in Fig. 1A.

duction for the lowest standard solution was only about 30 % (curve c, Fig 2A) because the induction period was too long. The oxidation rate increased with the added permanganate amount, improving sensitivity and linearity of the calibration curve (Fig. 2). Even under the permanganate catalytic effect, sample residence time could not be decreased indefinitely. After doubling the peristaltic pump speed, the sensitivity and the linearity of the calibration curve deteriorated (Fig. 2B). Therefore, improvement in sampling frequency by increasing flow rates was limited by reaction kinetics. The permanganate concentration in the *R*₂ reagent could not be increased at will in order to avoid an excessive baseline absorbance with an attendant drop in sensitivity. As no significant variations were observed when concentration was changed from 45.0 to 60.0 mg MnO₄/l the former value was selected. This means a baseline of 0.16 A and is equivalent to 30.0 mg MnO₄/l in the proposed system (Fig. 1B).

Sulfuric, nitric and phosphoric acid mixtures have been

recommended in batch analysis^{1,2,7}. However, the presence of sulfuric acid in the *R*₁ reagent induced precipitation with an attendant drop in sensitivity and reproducibility.

Although the manganese oxidation rate under nitric-phosphoric medium is quite fast for classical procedures⁷, it was not enough for the flow-injection system being proposed, especially under higher nitric acid concentrations. (Figs 3A and 4A). When nitric acid was added, the analytical signals decreased and the linearity of the calibration curve deteriorated; the effects became less pronounced under higher phosphoric acid concentrations (Fig. 3). However, there was a pronounced reduction in the analytical signals when 3.0 M HNO₃ was added, even with 3.0 M H₃PO₄ in the *R*₁ reagent of the 1A flow-injection system. In this situation, the procedure became more susceptible to flow rate variations (Fig. 4), indicating only partial manganese oxidation. Although a flow-injection procedure with incomplete reaction de-

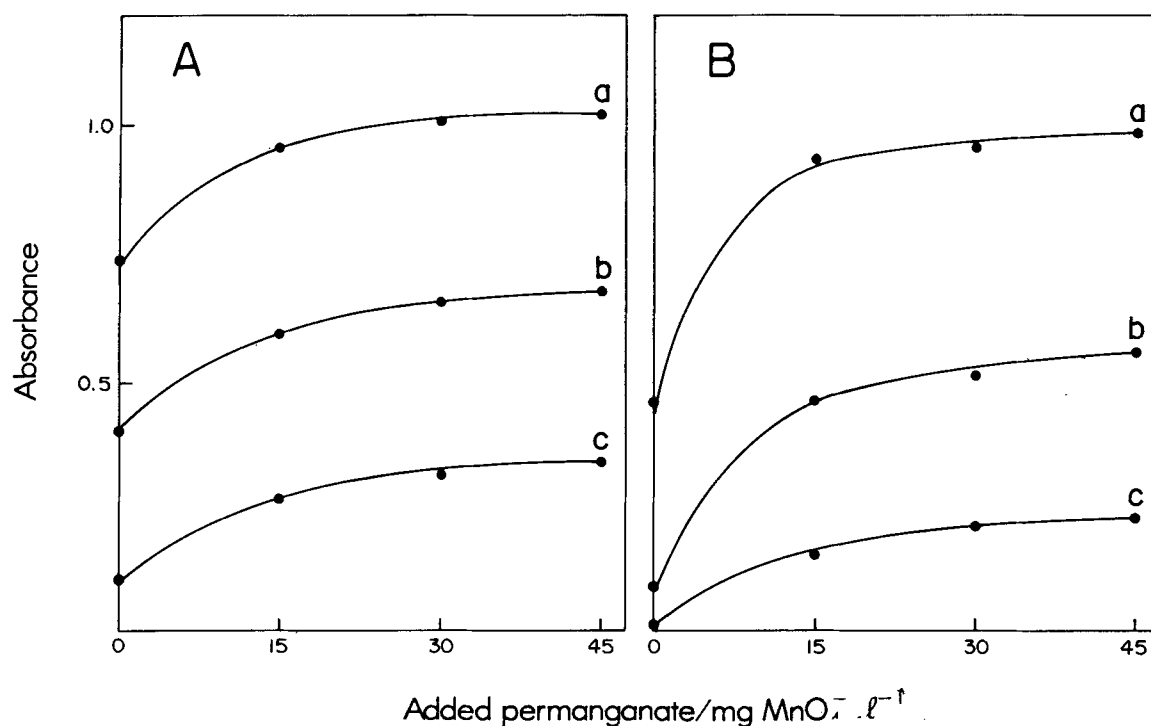


Figure 2. Influence of permanganate addition. Figure refers to the 1A system with $R1 = 3.0 M H_3PO_4$, $R3 = 1.0\%$ w/v $NaIO_4$, $I = 1.0\%$ v/v HNO_3 and $S = 180.0$ (a), 120.0 (b) or 60.0 (c) mg Mn/l standard solutions. Abscisses correspond to $R2$ concentrations (mg MnO_4/l), and ordinate to peak heights (absorbance units). The 2A portion refers to flow rates indicated in Fig. 1, and the 2B to doubled flow rates.

velopment is feasible⁵, quantitative oxidation was the goal in the present work because sensitivity was critical. It should be stressed that, after a 3 min stop period, the final absorbance almost reached the value obtained when phosphoric was the only acid in the R1 reagent, thus confirming that the oxidation rate decreased in the presence of nitric acid (see also Fig. 4). To a lesser extent, the above effects were also observed when lower nitric acid concentrations were used. Therefore, although tolerated in lower concentrations in the presence of concentrated phosphoric acid (Fig. 3A), nitric acid should be avoided in the R1 reagent.

With an insufficient phosphoric acid concentration, Beer's law was not followed, the completion of oxidation was more pronounced for manganese standards of higher concentrations. When this concentration was 3.0 M, linearity of the calibration curve was attained, quantitative manganese oxidation observed, and the drawbacks inherent to the presence of nitric acid were minimized. This concentration was selected for the R1 reagent, which corresponds to 3.7 M in the oxidant/catalyst in the proposed system (Fig. 1B). Considering the beneficial effects of the phosphoric acid, its concentration in the oxidant/catalyst reagent was fixed as 4.0 M. In this situation, the presence of 1.0 % v/v nitric acid in the samples and sample carrier stream (inherent to sample preparation) was tolerated.

The periodate concentration was not an important parameter. Quantitative oxidation had already been attained when this concentration was 1.0 % w/v. However, a higher value was selected (0.7 % w/v in the 1B system)

to avoid interference effects, as discussed later. Other oxidation procedures involving ammonium persulphate (5 - 20 % w/v) in the R2 reagent were tried without success, even after addition of silver nitrate or cobalt sulphate as catalyst^{1,7}.

The flow rate of the sample carrier stream had a marked effect on the proposed procedure. When it was increased, the sample dilution at the confluent points became less pronounced, the mean available time for oxidation decreased and the heating conditions became worse, as the stream through B1 coil could be regarded as a cooling stream. With a 0.80 ml/min flow rate, good linearity of the calibration curve was attained but the slope was about 80% of that observed for the 1.6 ml/min flow rate. When the carrier stream flowed at 2.5 ml/min, the linearity deteriorated because, with too short time available for oxidation development, the induction period became also a limiting factor. As a compromise between sensitivity, sampling rate and linearity of the calibration curve, 1.6 ml/min was selected as the flow rate for the sample carrier stream. This corresponds to about 8 s inside the B1 heating coil.

The B2 coil length was not an important parameter within the 50 - 200 cm range because its inner volume was much lower than the analytical path dead volume; it was fixed as 100 cm (about 500 μl inner volume). It should be mentioned that permanganate color fading was observed when polyethylene was employed to build up the B2 coil.

The length of the sampling loop was chosen as 150 cm in order to obtain peak height absorbances of about 90%

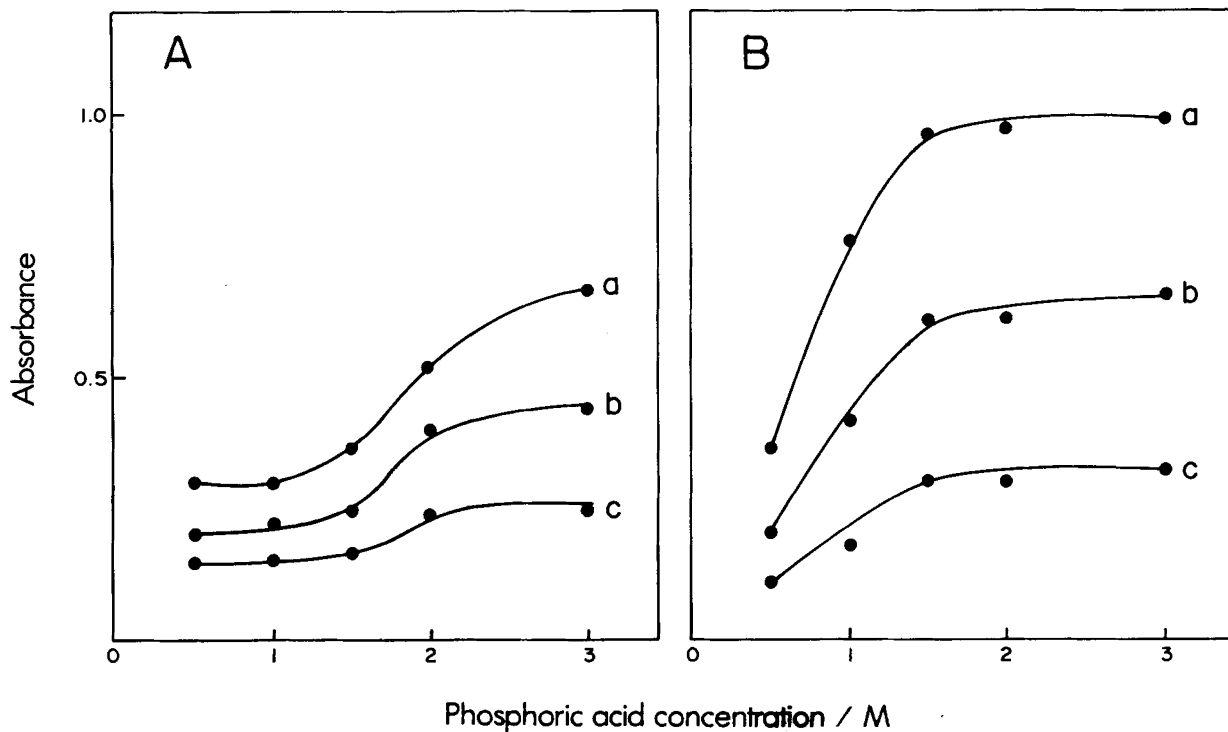


Figure 3. Influence of nitric and phosphoric acid concentrations. Figure refers to the 1A system with $R1 = H_3PO_4$ plus $3.0 M HNO_3$ (A) or H_3PO_4 (B), $R2 = 45.0 mg MnO_4/l$, $R3 = 1.0\% w/v NaIO_4$, $I = 1.0\% v/v HNO_3$ and $S = 180.0$ (a), 120.0 (b) or 60.0 (c) $mg Mn/l$ standard solutions. Abscisses correspond to phosphoric acid concentrations in R1 and ordinate, to peak heights (absorbance units).

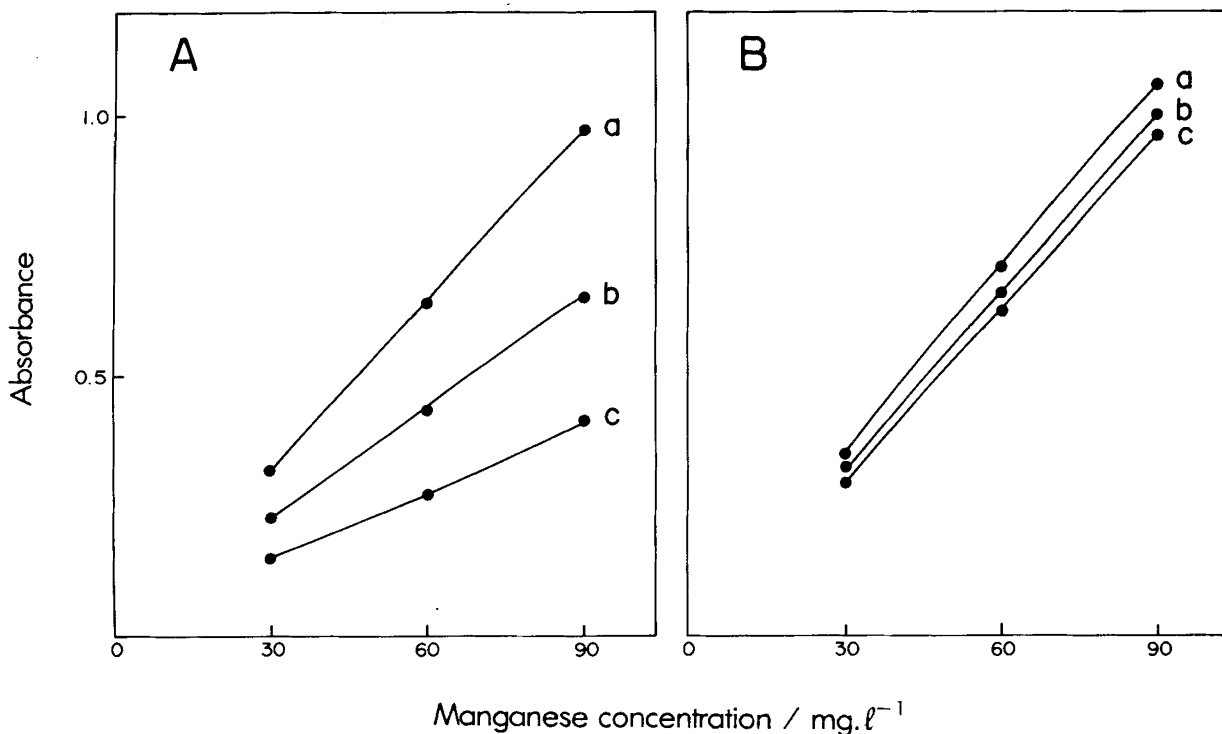


Figure 4. Influence of total flow rate. Figure refers to the 1A system with $R1 = 3.0 M H_3PO_4$ plus $1.5 M HNO_3$ (A) or $3.0 M H_3PO_4$ (B). Other conditions as in Fig. 3. Abscisses correspond to actual manganese concentrations inside the sampling loop (mg/l), and ordinate to peak heights (absorbance units). Flow rates associated to curves, a, b and c correspond to 100, 200 and 300% of those specified in Fig. 1.

of those related to the infinite volume situation¹¹.

Although with a sensitivity reduction of about 10% relatively to 526 nm, the wavelength was set at 548 nm to diminish interference effects⁷.

The proposed procedure is very selective to manganese. No measurable interference was found when Ba, Sr, Ni (50 mg/l), V, Pb or Cu (5.0 mg/l) were added to 5.00 and 10.00 mg Mn standard solutions. The Fe, Mg and Ti interferences were negligible (Fig. 5) and the Co and Cr (VI) interferences, mainly due to the colors of the involved aquo-complexes themselves, were perfectly tolerated in view of the contents of these ions in the samples. It is interesting to mention that, when the periodate concentration was lower than 1.0% w/v, a negative Mg interference of about 15% was verified. This interference, probably due to ionic strength effects, disappeared when the periodate concentration was increased to 1.5% w/v (0.7% w/v in the 1B system).

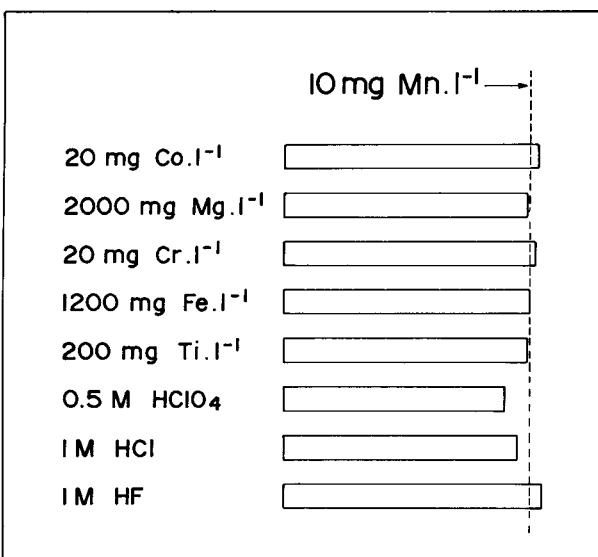


Figure 5. Interferent effects. Figure refers to the 1A system. The dashed line corresponds to the peak height recorded for 10.00 mg Mn/l standard solution (0.11 A). Bars correspond to peak heights recorded for this standard in the presence of interferents. Numbers indicate actual concentrations inside the sampling loop.

As the sample acidity was an important parameter and perchloric and hydrofluoric acids induced significant interferences (Fig. 5), care should be taken in order to eliminate them during sample preparation. In contrast with the batch procedures which usually cannot be carried out in the presence of hydrochloric acid, the interference of this acid in the flow-injection system (Fig. 5) was not observed for concentration below 0.5 M. Therefore, sample solubilization in hydrochloric acid solution is feasible. In the present work, the soil and rock digest were 0.2 M HCl. Alternatively, plant ashes could also be dissolved in 0.2 M HCl.

Conclusions

The proposed system is remarkably stable. During an 8h working period, only slight variations of the coefficients of the calibration equation (usually < 5%) were observed. Beer's law is precisely followed, the regression coefficient for the calibration equation is often higher than 0.9999 (N = 4).

Precise results are obtained; relative standard deviations of results for typical samples (digests with 2 - 15 mg Mn/l) are below 0.5%. The detection limit was 0.3 mg Mn/l at a signal-to-noise ratio of two.

Accuracy can be assessed from Tab. 1. No statistical differences between methods at the 99% confidence level were found.

With a sampling rate of about 60 measurements per hour, the reagent consumption is only 600 μ l per sample. Sampling rate, heating conditions and consumption of reagents can be improved with monosegmentation¹⁵ without the problems associated with air removal, as the debubbler is already present in the analytical path. Studies focusing this matter are presently in progress in our laboratory.

Acknowledgments

Partial support from FAPESP (Fundação de Amparo à Pesquisa do Estado de S. Paulo), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FINEP (Financiadora de Estudos e Projetos) is greatly appreciated. Mrs. D. Athie is thanked for linguistic improvement.

Table 1. Manganese contents in soils, plants and rocks as determined by the proposed system (FIA) and by atomic emission spectrometry (ICP-AES). Results in μ g Mn/g (dry basis).

Plants	FIA	ICP-AES	Soils and rocks	FIA	ICP-AES
Rubber-plant	80	78	Soil 1	144	144
Pinus	143	146	Soil 2	1280	1292
Soybean	253	245	Soil 3	752	747
Sugarcane	296	301	Lake sediment	1460	1432
CENA 1*	295	291	Rock 1	97	96
Rice	411	398	Rock 2	219	225
Coffee	302	307	Rock 3	427	452

* Plant sample for analytical quality control.

References

1. M. D. Cooper and P. K. Winter, in: I. M. Kohltoff and P. J. Elving, Eds, *Treatise on Analytical Chemistry. Part II. Analytical Chemistry of the Elements*. Vol. 7. (Interscience Pub., N. York, 1962) p. 427.
2. Z. Marczenko, *Separation and Spectrophotometric Determination of Elements* (Ellis Horwood Limited, Chischester, UK, 1988) p. 360.
3. J.D.H. Strickland and G. Spicer, *Anal. Chim. Acta* **3**, 517 (1949)
4. P.H. Scholes and C. Thulbourne, *Analyst* **88**, 466 (1963).
5. J. Ruzicka and E. H. Hansen, *Flow Injection Analysis*, 2nd Edn (Wiley-Interscience, N. York, 1988).
6. M. Valcárcel and M.D. Luque de Castro, *Análisis por Inyección en Flujo* (Imprenta S. Pablo, Cordoba, Spain, 1984).
7. I. M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein, *Quantitative Chemical Analysis* (The Macmillan Co., N. York, 1969), p. 1122.
8. A. O. Jacintho, B. R. Figueiredo, B. F. Reis, E. A. G. Zagatto, F. J. Krug, M. F. R. Gine, M. C. U. Araujo, N. N. Pereira and R. E. Bruns, *Análise Química de Rochas por ICP-AES* (Editora UNICAMP, Campinas SP, 1985).
9. C. H. Lim and M. L. Jackson, in: A.L. Page, Ed., *Methods of Soil Analysis. Part 2* (American Society of Agronomy Inc., Soil Science Society of America Inc. Publisher, Madison, Wisconsin, 1982), p. 1.
10. L. C. R. Pessenda, A. O. Jacintho and E. A. G. Zagatto, *Anal. Chim. Acta* **214**, 239 (1988).
11. F. J. Krug, H. Bergamin F^o and E. A. G. Zagatto, *Anal. Chim. Acta* **179**, 103 (1986).
12. I. L. Mattos, E. A. G. Zagatto and A. O. Jacintho, *Anal. Chim. Acta* **214**, 247 (1988).
13. E.A.G. Zagatto, H. Bergamin F^o and B. F. Reis, *Anal. Chim. Acta*, in press.
14. H. H. Willard and L. H. Greathouse *J. Am. Chem. Soc.* **39**, 2366 (1917).
15. C. Pasquini and W. A. Oliveira, *Anal. Chem.* **57**, 2575 (1985).