Article

Spectrophotometric Determination of Manganese in Steels by On-Line Electrochemical Oxidation

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É proposto um sistema de análise química por injeção em fluxo para a deteminação espectrofotométrica de manganês em aços baseado no efeito catalítico da Ag(I) na oxidação em linha de Mn(II) a Mn(VII) sobre uma superfície eletródica de platina. Após a injeção simultânea de amostra e eletrólito na célula eletroquímica, a mistura era homogeneizada por bolhas de ar e os íons permanganatos gerados eram monitorados a 545 nm. As alturas dos sinais transientes obtidos refletiam a concentração do manganês na amostra. Foram investigados os principais parâmetros relacionados com os processos coulométricos tais como intensidade de corrente, concentração do mediador, tempo de eletrólise, natureza do eletrólito suporte, bem como aqueles relacionados com a arquitetura do sistema FIA.

O sistema espectrofotométrico proposto possibilitou a determinação de manganês em aços no intervalo de concentrações de 5,00 a 150 mg L^{-1} (r = 0,9998). Com tempos de eletrólise de 60 s, foram possíveis 20 determinações por hora (R.S.D. < 3%). Os resultados da análise aços certificados com o sistema proposto não foram estatisticamente diferentes dos valores certificados e daqueles obtidos pelo método de referência ao nível de 95% de confiabilidade.

The aim of this work is to propose a flow spectrophotometric procedure for manganese determination in steel based on electrochemical oxidation of Mn(II) to Mn(VII) at a Pt electrode surface by means of the catalytic effect of Ag(I).

The on-line oxidation step was obtained by injecting sample and electrolyte solution directly into an electrolytic cell. After electrolysis, the injectate was homogenized by bubbling air. The permanganate ions produced were passed through the spectrophotometer where absorbance was monitored at 545 nm. Effects of direct current, silver concentration, timing, flow rates, concentration and composition of support electrolyte were investigated. Direct current and silver content manifested themselves as the most relevant parameters. For determination of manganese in the 5.00 - 150 mg L^{-1} range (r = 0,9998) and 60 s electrolysis time, the sample throughput was 20 h^{-1}. Accuracy was assessed by analyzing ten steel standard reference materials. Results are precise (R.S.D. < 3%) and in agreement with certified values of reference materials and with standard methods at 95% confidence level.

Introduction

There are several analytical techniques for manganese determination in steel and ferroalloy samples: flame atomic absorption spectrometry (FAAS)[1], electrothermal atomic absorption spectrometry (ETAAS)[2], inductively coupled plasma optical atomic spectrometry (ICP-OES)[3], induc-

tively coupled plasma emission atomic spectrometry (ICP-AES)[4], inductively coupled plasma mass spectrometry (ICP-MS)[5], molecular absorption spectrophotometry (UV-VIS)[6], neutron activation analysis (NAA)[7], X-Ray fluorescence (XRF)[8] and voltametry (ARV)[9]. However, molecular absorption spectrophotometry is a very attractive tool for the analysis of steel samples due to its operational simplicity, low cost, high selectivity and automation potential[10]. Notwithstanding, there are several automated methods for manganese determination based on formation of coloured metallic complexes[11,12] or on catalytic effect of manganese upon several redox systems[13,14]. The classical spectrophotometric method for determining manganese in steel and ferroalloys based on the production of permanganate by using strong oxidizing agents (*e.g.* periodate, persulphate), acidic media and high temperature has proved extremely useful[15]. Additionally, several works have already reported the electrocatalytic effect of silver ion on this oxidation[16-19]. The long warming times and the high strong acid media required for manganese oxidation[14,15] are the Achilles heel of this procedure in flow-injection analysis. This problem can be circumvented by exploiting the approach of coulometric reagent generation. This study reports on a new method for determining manganese in steels and ferroalloy samples by using silver(II) as catalyst for on-line electrochemical generation of permanganate in a flow-injection system.

Experimental

Instrumentation

A B342 II Micronal spectrophotometer provided with flow cell (100 µL inner volume, 10 mm optical path), a RB 101 ECB strip chart recorder, a B-332 Micronal peristaltic pump furnished with Tygon pumping tubes, two home-made injector-commutators, polyethylene tubing (0.7 mm i.d.) and accessories were used. The electrochemical cell was machined in a PMMA acrylic resin (Perspex, ICI). The cell is shown in Fig. 1 and consists of a 1 mL well (24 mm deep, 10 mm i.d.) machined in a resin block. A 2.0 mm hole on the bottom of the well was made for inlet of electrolyte solution and outlet of electrolysis product. A 1.0 mm hole to purge the gases produced in the electrolytical process was located at the top of the cell. The cathode was a platinum helical wire which was separated from the test solution by a glass tube. The contact between the solutions was made by a Vycor seal situated at the bottom of the glass tube. The anode was a platinum cylinder gauze (5 cm[2]) rolled up around the Vycor glass tube. Electric contacts were made by means of platinum wires.

A homemade current source was built to supply current from 20 to 1200 mA. Well defined pulses were assured by using an IC-555 timer[20].
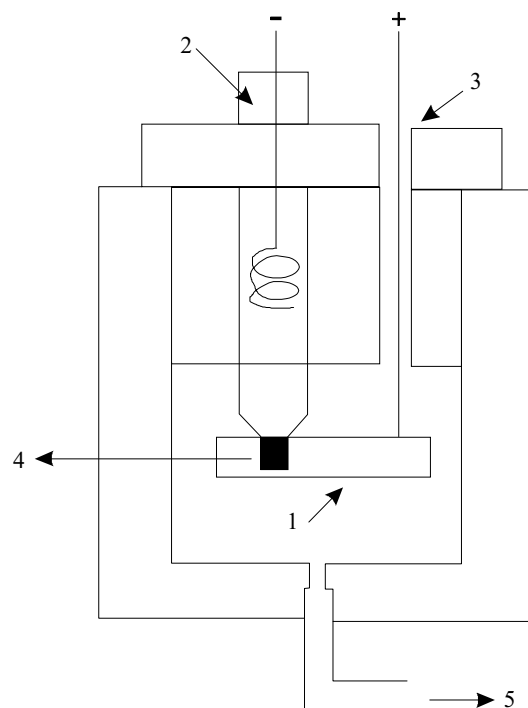
Figure 1. Schematic representation of the electrochemical cell. Main body machined in PMMA resin comprises anode (1), cathode (2), gas outlet (3), ionic contact (4, Vycor seal) and inlet or outlet of solutions (5).

Reagents, standards and samples

All chemicals used were analytical-reagent grade and distilled-deionized (Milli-Q) water. Catholyte was a 20% (v/v) H_2SO_4 solution.

Manganese(II) stock solution was 1000 mg L^{-1} in 0.5 mol L^{-1} HNO_3 (Titrisol, Merck). The analytical solutions (0.00; 50.0; 80.0; 100; 130; 150 mg L^{-1} of Mn) were prepared by dilution of the stock solution. Perchloric acid and iron(III) were added to these solutions in order to match the iron content in the diluted sample digests (10 mg L^{-1}).

The dissolution of the certified steel samples was performed by mixing 1.0000 g of the sample and 20 mL of 50%(v/v) HNO_3 solution and 15 to 30 mL of concentrated $HClO_4$ solution. The mixture was heated up to eliminate nitrous fumes. The final solution was diluted to 100 mL with water.

The 1.0 x 10^{-4} mol L^{-1} $AgNO_3$ electrolyte solution was prepared in 5% (v/v) H_2SO_4 solution.

Procedure

The flow diagram used in this work is shown in Fig. 2. When the injector-commutator IC_1 was in the specified position, L_1 loop (60 cm) and L_2 loop (30 cm) selected the electrolyte, E, and the sample, S, respectively and were mixed with the carries stream C_1 (air, 3.8 mL min^{-1}). The established sample and electrolyte zones were carried to-
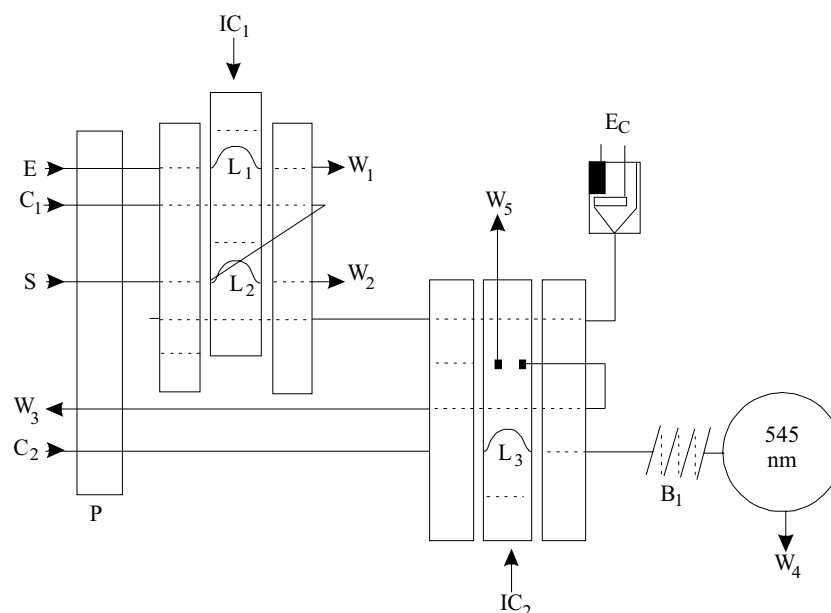
Figure 2. Flow set up. This arrangement was used for characterization of the electrochemical cell and implementation of the method for the manganese determination. IC_1, IC_2: injector-commutators; C_1: carrier stream of electrolyte and sample (air, 3.8 mL in^{-1}); E: electrolyte; S: sample; C_2: analyte carrier stream (water, 3.8 mL in^{-1}); L_1, L_2, L_3: sampling loops (60, 30, 60 cm); B: homogenization coil (50 cm); EC: electrolysis cell; D: detector (545 nm); PP: peristaltic pump; W: waste.

wards the electrochemical cell. To achieve this condition, the injector-commutator IC_2 was operated as shown in Fig. 2. After the sample and electrolyte solutions were delivered into the electrolytic cell, a pulse of electric current of 100 mA during 60 s was applied. This was attained by triggering the timer control of the current source supply. The production of permanganic acid under homogenized conditions by bubbling air takes place inside the cell. Afterwards, the injector-commutator IC_2 was switched to another position and a permanganate volume was selected by the L_3 loop (60 cm) and inserted into the carrier stream C_2 (water, 3.8 mL min^{-1}). During the L_3 sampling, the injector-commutator IC_1 was switched back. Passage of the electrolyzed sample through the flow cell resulted in a transient absorbance monitored at 545 nm and recorded as a peak with height proportional to the manganese content in the sample. After discarding the solution from the electrochemical cell, the injector-commutator IC_2 was switched back to the position specified in Fig. 2, starting another cycle.
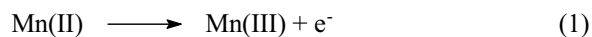
In order to obtain a high permanganate generation, the main parameters related to the efficiency of the electrochemical process such as composition and concentration of acid, silver concentration, electrolyte concentration, current intensity and timing were investigated. Electrolysis was carried out either in perchloric, phosphoric, nitric or sulfuric acid in the 0.5 - 3.0 mol L^{-1} range.

The influence of applied current was studied within a 20 - 160 mA interval with a 100 µg mL^{-1} of Mn.

Optimization of physical, chemical and hydrodynamic parameters involved in the system performance was carried out by the univariate method. Table 1 shows the ranges over which each parameter was investigated.

Results and Discussion

Silver(II) is a very powerful oxidant and undergoes rapid reactions with a wide range of inorganic and organic species[16-19]. At a polarized platinum electrode and in highly acid medium, Ag^+/Ag^{2+} couple is almost reversible and silver(I) can be considered an effective catalyst in the anodic oxidation of manganese(II). Solid particles formation was observed in the absence of Ag^+. According to the Cartwright mechanism[21], manganese dioxide is the main species produced during electrolysis:

$$Mn(II) \longrightarrow Mn(III) + e^- \tag{1}$$

$$Mn(III) + 2H_2O \longrightarrow MnO(OH)_{(s)} + 3H^+ \tag{2}$$

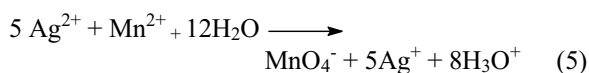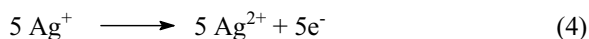$$MnO(OH)_{(s)} \longrightarrow MnO_{2\,(s)} + H^+ + e^- \tag{3}$$

The presence of solid particles in the analytical path caused severe memory effects, drop in sensitivity and occasionally flow-line clogging. With relatively lottle manganese dioxide formation and 60 s electrolysis time, electrical current intensities higher than 100 mA should be applied to guarantee the formation of a small amount of permanganate. These results were in agreement with those commented by Comminellis and co-workers[16-18]. This

Table 1. Optimization of variables.

Type	Variable	Range studied	Selected value
Physical	Temperature/ °C	25	25
	Current / mA	20 - 160	100
FIA	Flow rate/mLmin^{-1}	3,8	3,8
	Reactor length/ cm	20 - 100	50
	Injected volume/ μ L	50 - 150	60
Chemical	Eletrolyte/ mol L^{-1}	0.5 - 3.0	1.0
	Mediador	1×10^{-4} - 1×10^{-2}	1×10^{-4}

drawback was circumvented by adding silver nitrate to the electrolyte (E, Fig. 2). In the presence of 10^{-4} mol L^{-1} AgNO$_3$ a minimum amount of solid and a "pinkish" solution due to permanganate formation were observed. These results show that the presence of silver is a parameter of utmost relevance. When the silver nitrate concentration was varied from 1×10^{-4} to 1×10^{-2} mol L^{-1}, the analytical signals increased proportionally, confirming that silver(I) was a very effective catalyst in the oxidation of manganese(II) to manganese(VII), according to Eqs. 4 and 5:

$$5\,Ag^+ \longrightarrow 5\,Ag^{2+} + 5e^- \qquad (4)$$

$$5\,Ag^{2+} + Mn^{2+} + 12H_2O \longrightarrow$$
$$MnO_4^- + 5Ag^+ + 8H_3O^+ \qquad (5)$$

The divalent silver species oxidized manganese(II) to permanganate in the bulk solution. The reagent was then coulometrically generated at the anode surface according to step (4). Thus, Ag(I) acted as a "current carrier" in the Mn(II) oxidation[22-23]. Since for 1×10^{-4} mol L^{-1} AgNO$_3$ the analytical curve was linear up to 150 mg L^{-1} of Mn, that silver concentration was selected for further experiments.

Concerning acid composition, when the reaction was performed in presence of perchloric or phosphoric acid, lower analytical signals were recorded. In the former case, the reduction in signal was attributed to the oxygen evolution at the anode surface, reducing the current efficiency of the net process. For the later, the signal reduction was attributed to the Mn(II) complexation by phosphate. Higher signals were observed for nitric and sulfuric acid. Since the precision and the sensitivity were better for sulfuric acid, this acid has been chosen for further experiments. Concentrations of H$_2$SO$_4$ were investigated in the range 0.5 to 3.0 mol L^{-1} and showed two distinct behaviors. For acid concentrations < 1.0 mol L^{-1}, the conversion of Mn(II) to permanganate was slow, increasing the sensitivity. The displacement of the chemical equilibrium according (2) and (3) can remove manganese from solution as the oxide, thus reducing sensitivity. The reduction in analytical signal was ascribed to hydrolysis of Mn(III)[16,18]. For a sulfuric acid concentration higher than 2.0 mol L^{-1}, the yield of

permanganate formation was poor. This was attributed to the combined effects of equilibrium displacement towards Mn(II) (Eq. 5) and masking effects of manganese ions due to high sulfate content. These results are in agreement with the literature[16, 18]. It should be commented that the use of highly acidic solutions in flow-spectrophotometry may cause a pronounced Schlieren effect[24] and temperature rise. As the conversion of Mn(II) to MnO$_4^-$ is temperature dependent and as a compromise between system stability, reagent consumption, least temperature variation, and in order to avoid the use of special pumping tubes, a 1×10^{-4} mol L^{-1} AgNO$_3$ plus 1.0 mol L^{-1} H$_2$SO$_4$ solution was selected.

The influence of applied current on the permanganate formation efficiency was evaluated by processing a 100 mg L^{-1} Mn(II) standard solution in the 20 - 160 mA current interval. Analysis of Fig. 3 reveals that the relationship between analytical signal and current intensity was linear. For current intensity greather than 100 mA, powerful gas evolution was observed. As a result, the solution homogenization at the internal cell compartment during the electrolysis was defective. At high current density, side
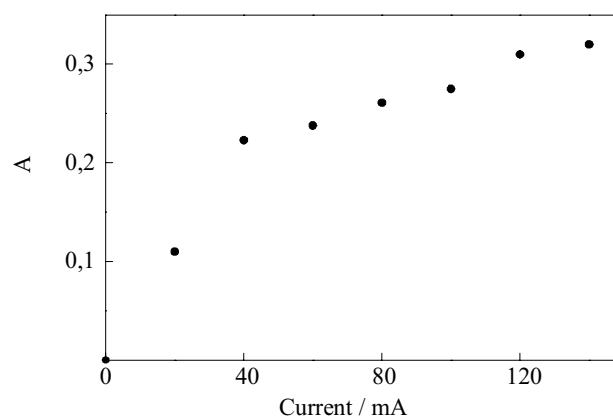
Figure 3. Influence of current intensity. Curve corresponds to electrolysis of 100 mg L^{-1} of Mn at different currents during 60 s. E = 1×10^{-4} mol L^{-1} AgNO$_3$ plus 1 mol L^{-1} H$_2$SO$_4$ plus 10 mg L^{-1} of Fe. A = absorbance (λ = 525 nm).
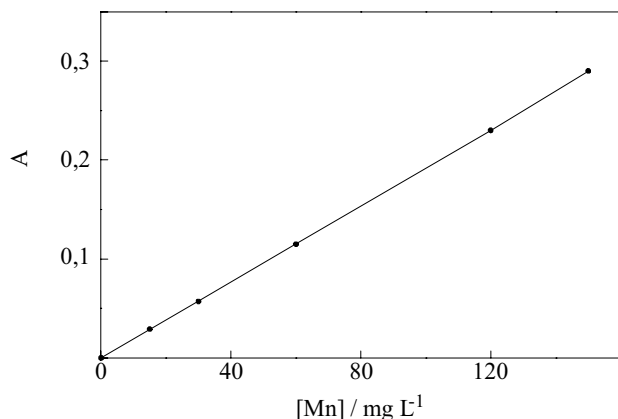
Figure 4. Analytical curve for manganese determination. Curve corresponds to 60-s electrolysis of five analytical solutions (50 - 150 mg L^{-1} of Mn at 100 mA. E = 1 x 10^{-4} mol L^{-1} $AgNO_3$ plus 1 mol L^{-1} H_2SO_4 plus 10 mg L^{-1} of Fe; A = absorbance ($\lambda = 525$ nm). IC_1 in the injection position corresponds to t = 0 s.

reactions due to water electrolysis increase due to anodic deposition of AgO which has high electrocatalylic properties for oxygen evolution. The permanganate formation in this potential region is governed by oxidation in the presence of AgO at the anode surface. With current intensities higher than 100 mA, both the oxygen evolution and anodic AgO deposition were favored. At lower currents the side reactions were minimized. This improved the current efficiency for permanganate formation. A current intensity of 100 mA was fixed for further tests.

Since only large amounts of coloured metal ions (*e.g.* Ni^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}) cause interference, the influence of these elements, commonly present in steel samples, was investigated. Cobalt and copper in up to 200-fold excess and up to 100-fold excess of nickel did not interfere. A

40-fold excess of Cr can be tolerated in samples with < 0.1% of Mn. With regards to chromium(III), its interference was eliminated with a previous oxidation of Cr(III) to Cr(VI) by using perchloric acid during the sample treatment. The residual color of the blank was subtracted from samples. The negative interference due to perchloric acid was eliminated by adding this acid in samples and standard solutions. Matrix interference by iron was minimized by preparing the analytical solutions with iron to match the iron content of the sample solutions [25]. It should be commented that for special sample lots, chorocomplex formation is an effective alternative procedure for previous separation of Mn from Co, Ni, Fe, Cu on anion- and cation-exchange columns.

Features of the method

After system dimensioning, analytical solutions within the 5.00 - 150 mg L^{-1} range (Fig. 4) were injected in triplicate. The linear range was suitable for applying the method to the determination of manganese in steel samples. The precision was studied at the center of the linear range. The relative standard deviations were estimated as 2.12% for 73,6 mg L^{-1} of Mn in the sample digest after ten sequential injections. Accuracy was assessed by analyzing steel reference materials from Villares metallurgical industries (São Carlos, SP, Brazil), IPT (Technological Research Institute, São Paulo, Brazil) and NBS, and the results are shown in Table 2. The results obtained with the proposed procedure were not statistically different from those obtained with the classical method at 95% confidence level (t-test approach). For 5.00 - 150 mg L^{-1} of Mn and 60 s electrolysis time, a throughput of 20 samples per hour was attained, which gives a significant economy in sample and

Table 2. Comparative results. Manganese contents [% (w/w)] in standard reference materials (SRM) determined by the proposed system (A) and by the standard method (B)[1,2]. Uncertainties at the A and B columns are estimates of standard deviations based on triplicate analysis.

SRM	A	B	Certified value
AISI 1040*	0.736 ± 0.012	0.760 ± 0.018	$0.776 \pm 0,003$
EURO 177.1*	0.495 ± 0.005	0.523 ± 0.006	$0.519 \pm 0,002$
EURO 178.1*	0.641 ± 0.011	0.652 ± 0.014	$0.672 \pm 0,003$
IPT 11A**	0.436 ± 0.003	0.435 ± 0.00572	$0.439 \pm 0,003$
IPT 13A**	0.728 ± 0.0114	0.717 ± 0.011	$0.723 \pm 0,005$
IPT 16**	0.791 ± 0.015	0.728 ± 0.009	$0.737 \pm 0,005$
IPT 39**	0.372 ± 0.002	0.337 ± 0.007	$0.340 \pm 0,003$
IPT 43*	1.426 ± 0.083	1.406 ± 0.111	$1.420 \pm 0,006$
IPT 55**	0.836 ± 0.009	0.918 ± 0.015	$0.923 \pm 0,008$
NBS 196	0.569 ± 0.007	0.548 ± 0.010	$0.554 \pm 0,001$

*SRM from Villares metallurgical industries (dilution 1:100).
**SRM from Technological Research Institute.

reagent consumption if compared to other automated or manual procedures for manganese determination.

Conclusions

Permanganate was electrochemically generated by using two polarized platinum electrodes and Ag(II) as catalyst in a flow-injection system. The approach can be efficiently applied to flow spectrophotometric determination of manganese in large scale analysis of steel samples.

Acknowledgments

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