Determination of Manganese (II) using Flow Injection Analysis with Chemiluminescence detection

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Abstract

The determination of manganese (II) using flow injection analysis with chemiluminescence detection was investigated. Mn^{2+} in sample solutions injected into a carrier stream of sodium bismuthate ($NaBiO_3$) were oxidised to form MnO_4^- ions which were capable of producing luminescence after reaction with luminol/KOH in a flow cell. The linear range of the system is from 20 to 80 mg/L with a detection limit 8 mg/L. The proposed system is suitable for determination of Mn^{2+} in steel alloys after dissolution, filtration and dilution at a rate of approximately 60 samples per hour with a relative standard deviation (RSD)1.2%. Statistical comparison between the proposed system and standard spectrophotometric method revealed that there is no significant difference between the two methods.
Keyword: Manganese, Flow injection analysis, Chemiluminescence

Introduction

Flow injection analysis has proved to be a very fast technique for the determination of small amounts of ions and was enabled in some cases, picomolar concentration of some analyte to be detected(1). Different methods were reported for the determination of manganese by flow injection with spectrophotometric detection(2),IR laser ablation inductively coupled plasma atomic emission spectrometry(3), atomic absorption spectrometry(4),flame electrothermal and flow injection(5,6), ... etc. There are different methods for determination of manganese in steel , metals and metal alloys(7-11).even if problems arise due to sever interferences caused by major ions originating from the steel matrix (Fe, Cr, Ni and Mo) and also from the acids used for wet-digestion(HCl, HNO_3 and HF)(12). In the present work. sodium Bismuthate $NaBiO_3$ was used as oxidizing agent to convert Mn^{2+} to MnO_4^- , in which can later produce chemiluminescence after reaction with Luminol/KOH mixture(13).

Experimental

Reagents

Luminol Solution (0.1M)1.7717g of solid luminol (Fluka) is dissolved in 100ml of 0.1M sodium carbonate solution and completed to 1L in a volumetric flask with the same solution. Other concentrations were prepared by serial dilutions of the stock solution with 0.1M sodium carbonate. KOH (1M) Standardized against standard HCl. The serial solutions were prepared from the stock solution . Na_2CO_3 solution (0.1M) 10.599 gm of solid Na_2CO_3 (BDH) dissolved in a liter distilled water adjusting the pH of the solution to 10.5 using 0.1M HNO_3. Sodium Bismuthate solution $NaBiO_3$ (0.1M)A 7gm of solid $NaBiO_3$ was dissolved in a 0.5M HNO_3 and completed to 250ml by the same solution. Other concentrations were prepared by serial dilutions.Manganese solution Mn^{2+} 0.01M prepared from solid $Mn(NO_3)_2$. Other concentrations were prepared by serial dilutions

Apparatus

A multi-channel peristaltic pump Pharmica fine chemicals, 3-channel ,p-3 , six-way rotary injection valve, a home made flow cell,a double beam scanning spectrophotometer(Perkin-Elmer,Hitachi 200), where the source system was blocked; with a chart recorder (Perkin - Elmer recorder) were used.

General procedure

Manganese solution Mn^{2+} is injected into a stream of sodium bismuthate $NaBiO_3$ fig(1) and passed through a reaction column (100cm long), and $2ml.min^{-1}$ flow rate as an optimum condition in which some of Mn^{2+} is converted to MnO_4^- according to the reaction below:

$$2Mn^{2+} + 5NaBiO_3 + 14H^+ \rightarrow 2MnO_4^- + 5Na^+ + 5Bi^{3+} + 7H_2O$$

chemiluminescence light produced after oxidation of Luminol/KOH by MnO_4^- in the flow cell is viewed by the detector of the spectrophotometer and the peak height recorded on the chart recorder.

Results and Discussion

Effect of Bismuthate concentration

Various concentrations of bismuthate ($1*10^{-4}$ to $1*10^{-2}$)M were studied. It was found that $5*10^{-3}$ M was suitable. Fig(2) shows the chemiluminescence intensity expressed as peak height (mm) versus concentration of bismuthate.

Effect of Luminol concentration

Luminol solutions of concentrations between (10^{-4}, to$1*10^{-3}$)were tested. An$5*10^{-4}$M was selected as a suitable concentration. According to fig(3) by increasing concentration of luminol solution led to increasing light intensity and this concentration was selected as a suitable concentration.

Effect of KOH concentration

Fig(4) shows the variation of the chemiluminescence intensity expressed as peak height (mm) with the Potassium hydroxide concentration; between (0.1- 0.6)M and found that O.5M KOH was found to be suitable in which more basicity cause to quenching effect.

Effect of flow rate

The experimental parameters for maximum hemiluminescence intensity obtained above were used ،to optimize the flow rate. Flow rates of 0.5, 1, 1.5, 2 and 2.5ml min^{-1} were employed. fig(5) shows that the flow rate. 2ml. min^{-1} was found to give best sensitivity.

Effect of coil length and sample volume

Different lengths of reaction coil (50, 60 90 ،80 ،70 ،and 100)cm were tested. It was found that 100 cm was a good length to obtain high sensitivity, fig (6) explains this fact. It was observed that 60 micro liter was a good volume.

Fig (7) shows the chemiluminescence intensity as peak height(mm) were different sample volume μL.

Table (1) shows the optimum variable parameters that was observed practically

Calibration Curve

Various concentrations: (20, 30, 40, 50, 60, 70, 80 and 90) $mg.L^{-1}$ of manganese were injected at the optimum condition established above. Each measurement was repeated three times. The logarithm of the average peak height (mm) of the chemiluminescence intensity was plotted against the logarithm of the concentration of manganese ion(logarithmic graph is plotted to get more linearity as well as shortening the scale) .It was observed that the calibration curve is linear from 30 to 80 mg/L of manganese with the correlation coefficient = 0.9912 as is shown in (fig 8) was obtained.

Detection limit

Successive dilutions of 20 mgL^{-1} manganese solution were carried out for this study. It was possible to observe a clear signal for 8 mgL^{-1} of manganese (which its signal is three times the average of the blank signal).

Precision

Using optimum parameters and 50 mgL^{-1} of manganese solution, relative standard derivation founded when n=10. It was observed that RSD=1.2%.

Interferences

The optimum conditions were used. A 50mgL^{-1} of manganese solution was used and 0.1, 0.5, 1, 5, 10 and 20 mgL^{-1} of interfering ions were added for different cations and anions. It was observed that and as shown in table (1). The cations do not show intereferance effect on chemiluminescence intensity, while this phenomenon was different for anions. In which some anions like ferricyanid $[Fe(CN)_6]^{3-}$ has positive interferenace effect it means increase the chemiluminescence intensity and NO_2^- nitrite has negative interferance effect which is decrease the chemiluminescence intensity due to its reaction with

produced MnO_4^-. Table (2) and (3) show the effect of cation and anion interferences of the results that are obtained by the proposed system.

Applications

The proposed system has been successfully applied for the determination of manganese percent in steel alloys of different steel alloys that exist in Sulaimani markets.

Sampling

Different samples of steel alloys which are present in Sulaimani markets were dissolved in aqua regia solvent (1:3 HNO_3: HCl) according to the recommended procedure (5), filtrated and be ready for injection.

Determination of manganese in steel alloys

The obtained data as shown in table (4) were compared with these obtained by standard spectrophotometric method. It was found statistically that the proposed system is quite coincidence to the standard method.

The proposed flow injection with chemiluminescence detection system has been applied successfully for the determination of manganese in steels alloy. The method is reproducible, for all the measurements performed, the relative standard deviation does not exceed 0.2% ; despite of the reaction of bismuthat in acidic medium with Mn^{2+} is slow, but 90 cm coil length are quite enough to produce small amounts of MnO_4^- to oxidize luminol/KOH.

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Table(1) Optimun parameters for proposed system

Variable parameters	optimum condition
Flow rate	2 ml.min^{-}
Coil lenghth	100cm
Sample volume	60μl
KOH concentration	0.5M
Bismuthate concentration	$5*10^{-3}$ M
Luminol concentration	$5*10^{-4}$ M

Table(2): study of cations interferences on Chemiluminescence intensity

Cations	Cation concentration mgL^{-} + 50mgL^{-} Mn^{2+}					
	0.0	0.1	0.5	1	5	10
	Percent of interferences					
Fe^{2+}	0.0	0.0	0.0	+1.2	+1.28	+2.0
Fe^{3+}	0.0	0.0	0.0	0.0	+0.30	+0.37
Co^{2+}	0.0	0.0	+0.10	+0.18	+0.19	+0.20
Ag^{+}	0.0	+0.01	+0.01	+0.1	+0.12	+0.2
Cr^{3+}	0.0	0.0	0.0	0.0	0.0	0.0
Ni^{2+}	0.0	0.0	0.0	0.0	0.0	0.0
Cu^{2+}	0.0	0.0	+0.12	+0.21	+0.25	+0.31
Zn^{2+}	0.0	0.0	-0.1	-0.21	-0.25	-0.35

Table(3): Study of Anion interferences on Chemiluminescence intensity

Anions	Anions concentrations mgL^{-} + 50 mgL^{-} Mn^{2+}					
	0.0	0.1	0.5	1	5	10
	Percentage of interfernces					
NO_2^-	0.0	-0.3	-1	-2.2	-5	-15
$S_2O_3^{2-}$	0.0	0.0	0.60	0.65	0.8	0.85
$C_2O_4^{2-}$	0.0	0.0	0.0	-0.7	-0.85	-0.95
$[Fe(CN)_6]^{3-}$	0.0	0.5	1.2	+3.2	+5.2	+10
SCN^-	0.0	0.0	0.0	-0.5	-0.7	-085

Table(4): Determination of Mn% in different available steels in Sulaimani market

	Proposed system %	RSD%	Standard method %	RSD%	E%
Steel (1)	0.61	1.2	0.63	0.5	-3.7
Steel (2)	0.79	0.8	0.81	0.6	-2.4
Steel (3)	0.82	1.1	0.85	0.8	-3.5

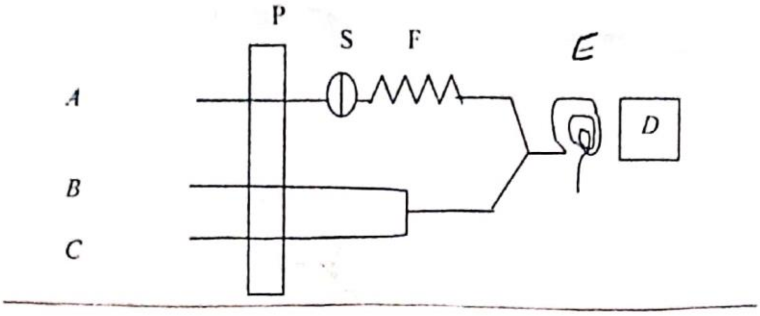
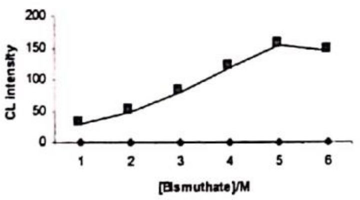
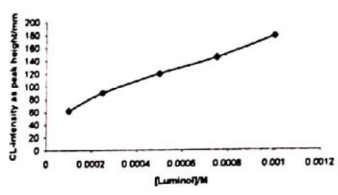


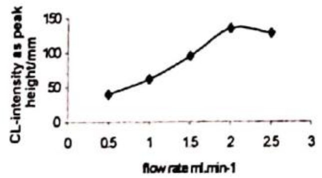
Fig (1). Schemmatic diagram of flow injection system used for the determination of Mn^{2+} ,A=$NaBiO_3$, B=luminol, C=KOH,S=sasmple solution (Mn^{2+} , F=coil length (90cm) E=flow cell, P=peristaltic pump,D=detector



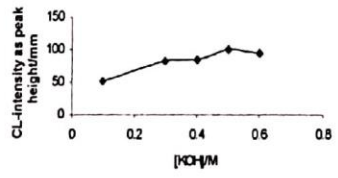
Fig(2). Effect of bismuthate on concentration on CL intensity



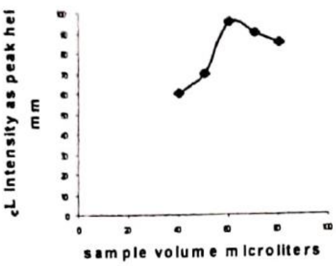
Fig(3). Effect of luminol CL intensity

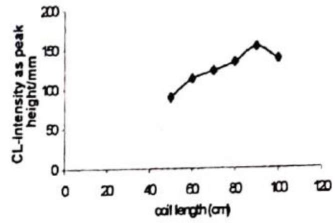


Fig(5). Effect of flow rate on CL intenstity



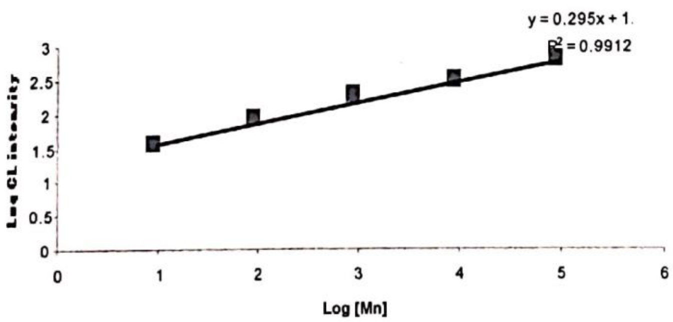
Fig(4). Effect of KOH concentration on the CL intensity





Fig(6). Effect of coil length on CL. Intensity

Fig(7).Effect of sample volume on CLintensity



Fig(8). Log-Log calibration graph for Mn^{2+}

تقدير أيون المنغنيز بطريقة الحقن الجرياني المستمر بوساطة البريق الكيميائي

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الخلاصة

لقد تم تقدير أيون المنغنيز بطريقة الحقن الجرياني المستمر و استخدم البريق الكيميائي ككاسف . حيث حقنت المحلول النموذج من أيون المنغنيز من خلال صمام الحقن الى التيار الحامل من بزموثات الصوديوم حيث يتأكسد أيون Mn^{2+} الى برمنكنات $MnO4^{-}$ والذي بدورة لة القابلية على اكسدة محلول لومينول/هايدروكسيد البوتاسيوم منتجا بريقا كيميائيا داخل الخلية . المدى الخطي كان بين 20mg/L الى 80mg/L مع اقل حد للكشف 8mg/L .الطريقة المقترحة كانت مناسبة تماما لتقدير أيون المنغنيز في الفولاذ . و بسرعة كانت ستين نموذج لكل ساعة ، مع اللانحراف القياسي 1.2% و كانت نتائج الطريقة مطابقة تماما للطرائق القياسية الشائعة.