

# Potentiometric Determination of Ascorbic acid, Malonic acid and Resorcinol Using Sulphide and Cyanide Ion-Selective Electrodes Compared with Platinum Electrode.

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## ABSTRACT

A new potentiometric method was adopted for the determination of ascorbic acid, malonic acid and resorcinol using iodine (dissolved in glacial acetic acid) as oxidant. The liberated iodide was monitored using sulphide and cyanide ion-selective electrodes compared with platinum electrode. The potential changes were sufficiently sharp (in the range of 280-300mV/0.1ml) for establishing the end points over a range of 0.001-0.100M of these reductants. The method was found accurate for determination of these reductants individually and in their mixtures.

## Introduction

Most of the reported methods for using iodine as oxidising agent are indirect, such as titrations with hypophosphite and phosphite<sup>(1)</sup>, dithionite and disulphite<sup>(2)</sup>, and metol and quinol<sup>(3)</sup>. The chemistry, metabolism and uses of ascorbic acid was reviewed<sup>(4)</sup>. Ascorbic acid can be also determined titrimetrically using two N-bromoimides<sup>(5)</sup>, chloramine T<sup>(6)</sup>, thallium (III) nitrate<sup>(7)</sup> and hexamine cobalt(III) tricarbonatocobaltate<sup>(8)</sup>. Numerous analytical techniques have been proposed for ascorbic acid determination such as spectrophotometry<sup>(9,10)</sup> fluorimetry<sup>(11)</sup>, and voltametry<sup>(12)</sup>. The reported methods for the determination of resorcinol involved oxidation with hydrogen peroxide<sup>(13)</sup>, and iodine at pH=5.7. The produced iodide was reacted with excess bromine forming  $\text{IO}_3^-$  which was determined spectrophotometrically<sup>(14)</sup> by starch-iodine procedure and titrimetrically with 0.1N  $\text{Ce}(\text{NO}_3)_4$ .

The reported methods for malonic acid determination were chromatography<sup>(16)</sup> and thallimetry<sup>(17)</sup> and the obtained  $\text{Tl(I)}$  was titrated with standard  $\text{KBrO}_3$  solution. This research aimed to find out the possibility of applying iodine (dissolved in glacial acetic acid) to the indirect potentiometric determination of : ascorbic acid, malonic acid and resorcinol. The work based on the reaction of slightly

excess of iodine with these reductants and the produced iodide was determined potentiometrically using cyanide and sulphide ion-selective electrodes compared with platinum electrode as indicator electrodes relative to  $\text{Ag/AgCl}$  double junction reference electrode.

## Experimental chemicals :

All chemicals used in this research were of highly graded (99.5% purity) imported from Fluka and BDH companies. Double distilled water was used in reagents solutions preparations. Doubled distilled water was firstly boiled, cooled and kept in tightly closed containers to minimise the traces of dissolved oxygen.

## Solutions :

0.1N of iodine : It was prepared by dissolving 3.172g of  $\text{I}_2$  in 25ml glacial acetic acid (acetic acid – iodine is preferred over ethanolic iodine due to reducing effect of ethanol). The lower concentrated solutions of iodine was prepared by successive dilutions with glacial acetic acid. These solutions were standardised against standard solutions of sodium sulphite which was prepared in boiled out double distilled water. The titration was carried out in the presence of starch (1%) end point indicator.

0.1N Ascorbic acid : A 0.0881g appropriate weight of ascorbic acid was dissolved in freshly boiled

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distilled water and standardised against excess of 0.1M thallium(III) nitrate at pH=6 followed by titration of the excess thallium(III) with 0.1M EDTA using xylenol orange as indicator(18).

**0.1N Resorcinol :** It was prepared by dissolving 0.055g in freshly boiled distilled water and standardised spectrophotometrically (15).

**0.1N Malonic acid :** It was prepared by dissolving 0.052g of solid malonic acid in freshly boiled distilled water and standardised with standard sodium hydroxide solution using phenolphthalein as indicator (18). The standardisation was confirmed thiallmetially(17).

#### **Procedure :**

A glass cell of three openings were used supplied with magnetic stirrer.

10ml of ascorbic acid ,resorcinol and malonic acid were transferred respectively to the titration cell. The solution was diluted to 40ml with distilled water (freshly boiled) and titrated with iodine solution. The potentiometric titration was followed using cyanid and sulphide selective electrodes which responded to the produced iodide ion concentrations till exceeding the equivalence points.The titration was repeated using platinum electrode v.s. saturated calomel electrode which responded to oxidation – reduction potentials. All measurements were done at room temperature (25C°).

#### **Pharmaccutical determination :**

A disk of ascorbic acid was weighed (4.5g) and dissolved in 100ml of boiled distilled water in a volumetric flask. 10ml of this solution was diluted to 40ml of distilled water and titrated with iodine solution till after end point using the same system of the former electrodes against saturated calomel electrode.

#### **Equipments:**

**pH/mV\_ meter :** Ion-analyzer type Digital from Mettler\_ TOLEDO (China) to follow potential changes through potentiometric titerations. The same instrument was used for pH measurements during titration and calibration modes.

**Electrodes :** Two ion-selective electrodes were used to monitor potential difference during titration and calibration relative to Calomel reference electrode with a precision of  $\pm 0.1$  mV as mentioned on the electrodes. These two electrodes were cyanide and

sulphide solid\_state membranes from Mettler\_ TOLEDO company. The third type is the platinum electrode in a ring shape with conductive wire to mV\_ meter from EIL company to record the oxidation – reduction potentials. Acombined glass electrode from Mettler-TOLEDO company was used to measure solutions pH through calibration and titration with a precision of  $\pm 0.01$  pH unit as clarified by the company. The Ag \ AgCl double junaction reference electrode of constant potential was from Mettler\_ TOLEDO containing 1M KNO<sub>3</sub> in its external compartment to avoid chloride ion interferences.

**Magnetic stirrer:** from minJank and kunkel company for stirring the solutions through calibration and titration processes.

**Titration cell :** It is a glass cell with cover of three openings ; two to introduce indicator and calomel reference electrodes and the third for introduction the end of the burette. The cell possesses two side openings for internal and external water from water bath for temperature adjustment with a precision of  $\pm 0.1^{\circ}\text{C}$  as written on the instrument.(Fig.1).

#### **Results and Discussion:**

Table(1) shows some physical and chemical properties of the reductants in addition to iodine used in this research. The reduction potential of iodine to iodide (0.5535 V) is higher than reduction potentials of the reductants under determination. Therefore, iodine was used as oxidising agents to determine these reductants potentiometrically by iodometric technique and the released iodide was monitored by cyanide and sulphide ion-selective electrodes in addition to platinum electrode <sup>(18)</sup> which responds to oxidation-reduction potentials. Iodine is slightly water soluble, therefore potassium iodide solution was used to increase solubility.

Because of iodide ions interference, iodine was prepared in glacial acetic acid which was proved to be suitable as oxidising agent in determination of some sulphur reducing agents <sup>(19)</sup>. Table(2) exhibits the results obtained (triplicate runs) by the adopted procedure. The data indicated reasonable precision and accuracy. In most cases, the obtained potential changes were of large order of magnitude, ranging from 200 to 300 mV\0.1 ml of titrant with s-shaped titration curves for the response of the three electrodes, thus allowing easy and accurate determination of end points . It is also found from the results that the oxidation of these reductants by iodine involved two electrons transfer

for ascorbic acid and 1electron for malonic acid and resorcinol.



The little deviations from actual values were ascribed to experimental errors. This procedure was applied to pharmaceuticals for determination of the content of ascorbic acid in a drug. The results showed successful determination with suitable accuracy (Table 3). The little difference from actual value was attributed to experimental errors.

### Conclusions:

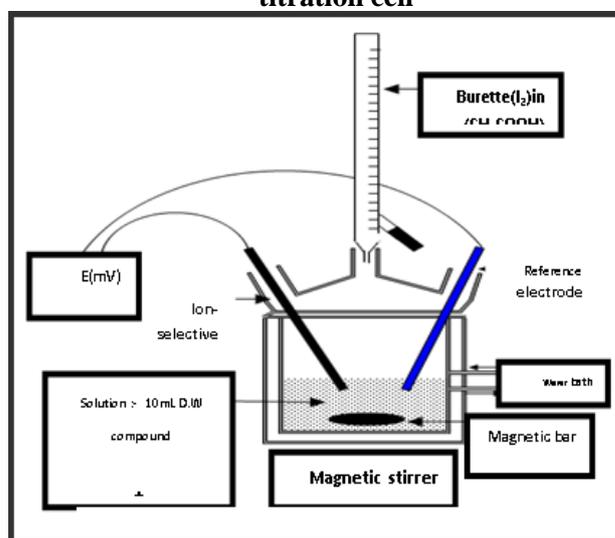
It is concluded from this research the successful use of glacial acetic acid as a solvent for iodine instead of water and ethanol. Both cyanide and sulphide ion-selective electrodes have offered an accurate results compared with pt electrode.

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**Fig.1 Schematic diagram for the potentiometric titration cell**



**Table(1) Some physical and chemical properties of ascorbic acid, resorcinol and malonic acid**

The material	Reduction potential (V)	Density (g/ml)	Purity (%)	Melting point	Solubility	Ionization constant
Ascorbic acid	0.3900	1.65	99.7	192(d)	Water Alcohol	$K_1=9.1 \times 10^{-5}$ $K_2=4.6 \times 10^{-12}$
Resorcinol	0.1500	1.272	99	110	123g/100ml water	$K=1 \times 10^{-10}$
Malonic acid	-0.4900	1.619	99.5	136	74g/100ml water	$K_1=1.4 \times 10^{-3}$ $K_2=2.0 \times 10^{-6}$

Iodine	0.5355	4.93	99.5	113.5	S=Alcohol, Benzene, Glycine, KI, MeOH, CS <sub>2</sub> , CCl <sub>4</sub>
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Table (2) : Amount of the reductants determined by potentiometric iodometric titration technique.

NO.	Reductant	Electrode	Added(mg)	Recovered(mg)	%error			
1	Ascorbic acid	Pt	88.100	86.300	-2.04			
			8.810	8.630	-2.04			
			0.881	0.863	-2.04			
			S <sup>2-</sup>	88.100	86.300	-2.04		
			8.810	8.450	-4.10			
			0.881	0.845	-4.10			
		CN <sup>-</sup>	88.100	84.5	-4.10			
			8.810	8.450	-4.10			
			0.881	0.845	-4.10			
			2	Resorcinol	Pt	55.00	52.800	-4.10
						5.500	5.280	-4.10
						0.550	0.528	-4.10
S <sup>2-</sup>	55.00	56.100				+2.00		
5.500	5.610	+2.00						
0.550	0.561	+2.00						

3	Malonic acid	Pt	52.000	49.920	-4.00	
			5.200	4.992	-4.00	
			0.520	0.4992	-4.00	
			S <sup>2-</sup>	52.000	50.960	-2.00
			5.200	5.096	-2.00	
			0.520	0.5096	-2.00	
		CN <sup>-</sup>	52.000	49.920	-4.00	
			5.200	5.096	-2.00	
			0.520	0.5096	-2.00	
			0.550	0.561	+2.00	
			5.500	5.610	+2.00	
			55.00	56.100	+2.00	

The standard deviation of the measurements were in the range of 0.602 – 1.905.

Table(3) Determination of ascorbic acid in a drug by potentiometric iodometric titration technique.

Sample No.	%Ascorbic acid	%Actual	%error
1	5.79	6.00	-3.50
2	5.80	6.00	-3.33
3	5.84	6.00	-2.67

The standard deviation of the measurements was 0.4385 and the variance = 0.1923

## التقدير الجهدي لحامض الاسكوريك وحامض المالمونيك والريسورسينول باستعمال قطبي الكبريتيد والسيانيد الانتقائيين مقارنة بقطب البلاتين.

اسماعيل خليل الهيتي و نغم خيري كريم

### الخلاصة:

طبقت طريقة جهدية جديدة لتقدير حامض الاسكوريك وحامض المالمونيك والريسورسينول باستعمال اليود (المذاب في حامض الخليك الثلجي) كعامل مؤكسد. قدر اليوديد المتحرر باستعمال قطبي الكبريتيد والسيانيد الانتقائيين مقارنة بقطب البلاتين. كان التغير في الجهد (في المدى ٢٨٠ - ٣٠٠ مللفولت/١٠,١ مللتر) حاداً بصورة كافية لمتابعة نقاط انتهاء التفاعل ( في المدى ٠,١٠٠ - ٠,٠٠١ مولاري لتراكيز هذه العوامل المختزلة. كانت الطريقة دقيقة لتقدير هذه العوامل المختزلة منفردة في محاليلها أو في مزائج محاليلها.