Determination of Chlorate by Flow Injection Analysis Via Merging zone Technique

"Study and Application"

By

Rana Saheb Khalaf

A Thesis

Submitted to the Council of College of Science

University of Babylon

In Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

September ٢٠٠٦ Sha'aban ١٤٢٧

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Supervisor

Prof. Dr. Issam Mohammad Ali Shakir Al-Hashimi

Prof. Dr. Dakhil Nasir Taha Al-Zuragani

September ٢٠٠٦ **Sha'aban ١٤٢٧**

تقدير الكلورات بتقنية الحقن الجرياني باستخدام المناطق المتداخلة دراسة وتطبيق

من قبل

رنا صاحب خلف

رسالة مقدمة إلى

مجلس كلية العلوم-جامعة بابل
وهي جزء من متطلبات نيل درجة الماجستير علوم
في علوم الكيمياء

ايلول ٢٠٠٦ **شعبان ١٤٢٧**

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باشراف

الاستاذ الدكتور	**الاستاذ الدكتور**
عصام محمد علي شاكر الهاشمي	**داخل ناصر طه الزركاني**
ايلول ٢٠٠٦	**شعبان ١٤٢٧**

الإهداء

يامن يتخفض لهما الجناح . . . . وتطمئن النفوس برهما . . . . عند الغد والرواح

شكراً أصلي لبارئ النسمات

متوسلاً حفظكما ذخراً وبركات

إليكما والدي ووالدتي

أهدي جدي . . . . وأخلاصي . . . . والوفاء

الى . . . من جفف الدموع من عيني . . . . . غارساً في نفسي الطموح

سانداً إياي بالفعل والكلمة زوجي العزيز

الى من هم سندي في شدتي . . . . وأنسي في وحدتي . . . . . . أخوتي وأخواني الى من اغرقوني بفضلهم

والد ووالدة زوجي وعائلتهما

الى النهر الذي يفيض بالعطاء . . . . . . الى من علمني سبل المعرفة والارتقاء

الى الشمعة التي تضيء من أجلهم العلم والعلماء . . . . . الى أساتذتي الافاضل

أ . د . عصام محمد علي شاكر الهاشمي

أ . د . داخل ناصر طه الزركاني

أهدي ثمرة هذا الجهد

رنا

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Praise be to Allah the Almighty for all that has been achieved.

Pray and Peace be upon the Prophet Muhammed, and his family and followers.

My cardinal and deepest thanks are due to my supervisor Dr. Issam Muhammed Ali Shakir and Dr. Dakhil Nassir Taha for their guidance and academic help.

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Finally , I heartily thank my lovely husband and all those who help me in love way or another for their continuous encouragement, support and care.

Dedication

To those who are humbly sered

And souls feel safe all the time by their respect

I pray to thank Allah

Beseeching him to keep you a treasure and blessings for you both my father and mother

I dedicate my effort ……. Sincere and gratitude

To whom who dried tears from my eye

Existing ambitions in my soul

Assisting me actively and theoretically my dear husband

To those who are my support in my difficulty

And my partner with loneliness

My brothers and sisters

To the river which is full of gift

To whom who thought me the way of knowledge and superiority

To the candle which lights for the sake of science and scientists

To my dear teachers Assist Prof. Dr. Esam Mohammad Ali Shakir Al-Hashimi

And Prof. Dr. Dakhil Nasir Taha Al-Zuragani

I present the fruit of this effort

Rana

بسم الله الرحمن الرحيم

﴿ويسألونك عن الرّوح قُل الروح من آمر ربي

وما أوتيتم من العلم الاّ قليلا﴾

صدق الله العلي العظيم

الاسراء (٨٥)

Examination Committee

We are the examining committee, certify that we have read this thesis and examined the student **Rana Saheb Khalaf** in this content, and that in our opinion it is adequate with ''Excellent'' standing as a thesis for the degree of Master in Analytical Chemistry.

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Summary

This work includes the design of a whole flow injection analysis unit. Two paths were used, first using conventional spectrophotemetric unit with home made valve and flow cell; while second unit a whole complete mini microphotometer based on radiation source, a special flow cell of ٢mm path length and a photo silicon detector. With whole complete amplification and zero set. The unit is (٣x٣x٥cm) on size.

The variable of physical and chemical of this method is based on the reaction of chlorate ion with potassium Iodide, coupling reaction in the presence of acidic medium forming I٢. Soluble has a maximum absorption at λ_{max} ٣٥٠nm.

This reaction in the first unit includes mixed hydrochloric acid (٢.٥M), potassium Iodide (٠.٥M) and flow rate (١.٩٥ ml.min$^{-١}$), for international injection unit.

Linear calibration graph for detection and measuring point with percentage linearity was in the range of (٠.٠٠٨٢٥ to ٤١٧٥ µg.ml$^{-١}$), for a sample of (١٢٧µl) volume. Detection limit of (٦.١٢x١٠$^{-٥}$µg.ml$^{-١}$) was achieved.

The relative standard deviation was ٠.٠٤١٪ at two minutes for three successive measurement of chlorate ion with its applied method.

This method was applied successful in aqueous solution, match and hypochlorite are performed.

Physical and chemical parameters for determination of chlorate ion in the second unit includes mixed sulphuric acid (١.٥M), potassium Iodide (٠.١٢M), with flow rate (٤ml.min$^{-١}$) and sample volume (٦٠μl) for four successive measurement. The linearity of calibration graph was (٥ to ٦٠٠μg.ml$^{-١}$), with detection limit about (١ μg.ml$^{-١}$) and the percentage of R.S.D = ٠.٠٩١٪.

This unit was used for determination of chlorate ion in, home made and liquid detergent.

الخلاصة

تضمنت الدراسة تصميم جهاز تحليل الحقن الجرياني والذي اشتمل جزئين: حيث تناول الجزء الاول استخدام جهاز قياس الطيف مع صمام مصنع محلياً، وخلية مصنعة محلياً (١سم)، بينما الجزء الثاني تناول وصف اجزاء منظومة مصنعة حلياً متكونة من صمام مصنع دولياً وخلية مصنعة محلياً (٢ ملم) ومضخم مصنع محلياً لتقدير ايون الكلورات. المتغيرات الفيزيائية والكيميائية لهذه الطريقة اعتمدت على تفاعل ايون الكلورات مع يوديد البوتاسيوم في الوسط الحامضي وتقدير اليود عند طول موجي (٣٥٠nm). هذا التفاعل تم تطبيقه في الوحدة الاولى تضمن مزج (٢.٥ مولاري) تركيز حامض الهيدروكلوريك و (٠.٥ مولاري) تركيز يوديد البوتاسيوم، وسرعة جريان (١.٩٥ مل.دقيقة$^{-١}$) لمنظومة الحقن مصممة دولياً.

حيث ان منحنيات المعايرة لمتابعة تغير الاستجابة مع التركيز من (٠.٠٠٨٢٥ الى ٤١٧٥ مايكروغرام.مل$^{-١}$) لأنموذج حقن بحجم (١٢٧ مايكرولتر) والحصول على حد الكشف (٦.١٢*١٠$^{-٥}$ مايكروغرام.مل$^{-١}$). الانحراف القياسي النسبي كان مساوياً الى (٠.٠٤١٪) عند زمن حقن ٢ دقيقة لثلاث قياسات متتابعة لتقدير ايون الكلورات.

هذه الطريقة طبقت بنجاح لتقدير ايون الكلورات في المحاليل المائية، الشخاط وفي محلول القاصر.

المتغيرات الفيزيائية والكيميائية لتقدير ايون الكلورات في الوحدة الثانية شمل مزج (١.٥مولاري) تركيز حامض الكبريتيك، (٠.١٢ مولاري) يوديد اتلبوتاسيوم وسرعة الجريان (٤ مل.دقيقة$^{-١}$) لحجم نموذج محقن (٦٠ مايكرولتر) لاربع قياسات متتابعة خطية منحني المعايرة كانت من (٥-٦٠٠ مايكروغرام.مل$^{-١}$) والحصول على حد الكشف (١ مايكروغرام.مل$^{-١}$)، والانحراف القياسي النسبي مساوي الى(٠.٠٩١٪). هذه الوحدة استخدمت لتقدير ايون الكلورات في محلول القاصر المستورد والمحلي.

Certification

We certify that this thesis is **(Determination of Chlorate by Flow Injection Analysis Via Merging zone Technique "Study and Application")** prepared under our supervision at the Department of Chemistry, College of Science, University of Babylon, as a partial requirement for the degree of Master of Science in Chemistry and this work never published anywhere.

Signature:

Name:Dr. Issam.M.A.Shakir

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In the view of the available recommendation , I forward this thesis for debate by the Examining Committee.

Signature:

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Address:Head of Chemistry Department , College of Science, University of Babylon.

Date: /   /٢٠٠٦

شكر وتقدير

الحمد لله الأول الذي لا أول لأوليته .. والآخر الذي لا آخر لآخرته وأحمده حمداً دائماً ما دامت السماوات والأرض وبقي الليل والنهار. وألف الصلاة والسلام على سيد المرسلين محمد (ص) الأمين وعلى خير خلقه ونجباءه أجمعين أهل بيت النبوة ومهبط الوحي وأمناءه على وحيه وخلقه أجمعين ... ومن تبعهم بإحسان ووالاهم إلى يوم الدين ... وبعد.

يسرني وأنا أضع اللمسات الأخيرة في إعداد هذه الرسالة أن أقف وقفة شكر وتقدير وامتنان إلى أستاذي الفاضلين الأستاذ الدكتور عصام محمد علي شاكر والأستاذ الدكتور داخل ناصر طه لما قدماه لي من جهد علمي رصين ومخلص وما أبداه من توجيهات سديدة من أجل إيصالي إلى هذا المستوى.. فلهما الشكر والتقدير فجزاهما الله خيراً وأدامهما ذخراً للعلم والإنسانية.

كما وأتقدم بالشكر والتقدير الى الدكتور نغم شاكر تركي العوادي/ كلية العلوم- جامعة بغداد لما قدمته لي من مساعدة في اكمال هذا البحث ولم تبخل بأي نصيحة فاسأل الله أن يمن عليها بالموفقية والنجاح في دفع عجلة العلم في بلدنا.

ويسرني أن اشكر من تحمل معي عناء الدراسة بصبره وعطائه (زوجي العزيز) وأخيراً اشكر كل من وقف معي وقفة صدق ووفاء ولم يبخل بنصيحة أو جهد .

والله ولي التوفيق

Tables of corrections

Page	line	Error	correction
Dedication		Assist Prof. Dr. Esam	Prof. Dr. Esam
Abstract		Secondly	Second
٣ Table (١.١)		Adourless	Colorless
٤		This study (uses)	It used to describe
١٣		FIA	SIA
١٥		Reaoent ١,Reaoent ٢	Reagent ١,Reagent ٢
٢٠		The second carrier can also pass through a reaction coil for furthur dispersion or the first injection for injection in the second carrier.	The carrier can also pass through a reaction coil for further dispersion or dilution for removal a silce of peack from the first injection for injection in the second carrier
٢٠		١ nal	١ ml
٢٧ table ٢.١		٨.٢١٥	٨.٢٥٩, ٢.٤٧٧
٢٧ table ٢.١		٠.٠٥	٠.٠٥ , ٠.١١٤
٢٨		volumetric flask	volumetric flask as in table (٢-٢) , (٢-٣)
٣٠ ٢.٢ apparatus	٨	Home made	Germany
٣٠ ٢.٢ apparatus	٩	Germany	Home made
٣٠ ٢.٢ apparatus	١٠	Amplifier [sketch diagram in figure (٣-١٤)]	Amplifier
٤٠	٤	Value	Valve
٤٣	٣	Potentio metric	Potentiometric
٥٠	٧ , ٨	L٢ , L١	L١, L٢
٥٥	٢	L١	L٢
٥٦	١	Table (٤-٤):The effect of reagent volume [KI] on the reaction ($ClO_{٣}^{-}$-I^{-}-$H_{٢}O^{+}$) used in determination of	Table (٤-٤):The effect of reagent volume KI on the reaction ($ClO_{٣}^{-}$-I^{-}-$H_{٢}O^{+}$) used in determination of

		chlorate ion.	chlorate ion.
٥٧	١١	Table (٤-٥): The effect of sample volume [$KClO_{٣}$] in determination of chlorate ion.	Table (٤-٥): The effect of sample volume $KClO_{٣}$ in determination of chlorate ion.
٦٣ Fig. (٤-١٠)		٦٣٧	٦٢٦.٦٦
٦٣ Fig. (٤-١٠)		Time (min)	Time (min) ٤min.
٧٠ table ٤-١١	Column ٢	Response ton=٣ $\bar{y}$ in (mV)	Response for n=٣ $\bar{y}$ in (mV)
٧٠ Table ٤-١١	Column ٤ line ٦	٢١٤.٦±٥.٧٣٦	٢١٣.٤±٥.٧٣٦
٧٠ Table ٤-١١	Column ٤ line ٧	٢١٣.٤±٥.٧٣٦	٢١٤.٦±٥.٧٣٦
٧٢ table ٤-١٢	Column ١١	Y=L.O.P	Y=L.O.D
٧٣	٣	٠.٠٥	٠.٥
٧٤	١	Figure (٤-١٤): The reproducibility of ten measurements of released iodine for (٥*١٠$^{-٢}$ml.L$^{-١}$) chlorate ion	Figure (٤-١٤): The reproducibility of ten measurements of released iodine for (٥*١٠$^{-٢}$mol.L.$^{-١}$) chlorate ion
٧٦	٧	$L_{١}$, $L_{٢}$	$L_{٢}$, $L_{١}$
٧٦	٩ , ١٠	$L_{٢}$, $L_{١}$	$L_{١}$, $L_{٢}$
٧٨ table (٤-١٦)	Column ٥	%R	%RSD
٧٩table (٤-١٧)	Column ٥	%R	%RSD
٩٢	١	Sample section volume (ml)	Sample section volume (µl)
١٠٦	٣	toward low	toward low

		concentration by amount ٦٠ ng for ٦٠µl.	concentration by amount ٦٠ ng for ٦٠µl.
١٢٦	١٠	ClO-٣-I--H٣O+	$ClO^{-}_{٣}-I^{-}-H_{٣}O^{+}$
١٢٦	١١	Khalat	Khalaf

Conclusions

and

Recommendations

Conclusions

١. FIA can be used to determine the trace concentrations of chlorate ion.

٢. The first design unit which consists of conventional spectrophotometric and homemade valve and flow cell can be used for determination of chlorate ion.

٣. The second design unit which consists of conventional valve and home made spectrophotometric and flow cell can also be used for the determination chlorate ion.

٤. The second design unit was more sensitive than the first one.

٥. Sequential injection analysis is used in the first design unit with good results.

Recommendations & further work:

١. Both design units can be used for determination of $H_٣O^+$ and iodide.

٢. The introduction of the five three-ways valve and three three-ways expand the scope of new approaches for various determinations.

٣. Sequential injection analysis can be used to determine other ions instead of chlorate ion such as $NO_٣^-$, $Fe^{+٢}$, $SO_٤^{-٢}$, ….

Conclusions

٦. FIA is used to determine the trace concentrations of ions.
٧. Using home made unit contains international valve and cell is home made (٢ mm).
٨. Comparison between international and home made unit.
٩. Sequential injection analysis is the best method in determination of chlorate ion.
١٠. The home detergent gives better results than imported one.

Recommendations:

٤. The home made unit is better than international unit to determination of low concentration ions.
٥. Using sequential injection analysis to determine another ions instead of chlorate ion.

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Chapter One

Introduction

CHAPTER ONE

١. *Introduction*

This chapter consists of two parts:

Part ((A)): This part deals with the distribution configuration, occurrence, properties, uses, generation, reactions and available methods for determination of chlorate ion.

Part ((B)) deals with the background of flow injection analysis.

Part ((A))

١A-١: Chlorate-General Introduction

The distribution configuration for chlorate ion is shown in figure (١.١).(١)

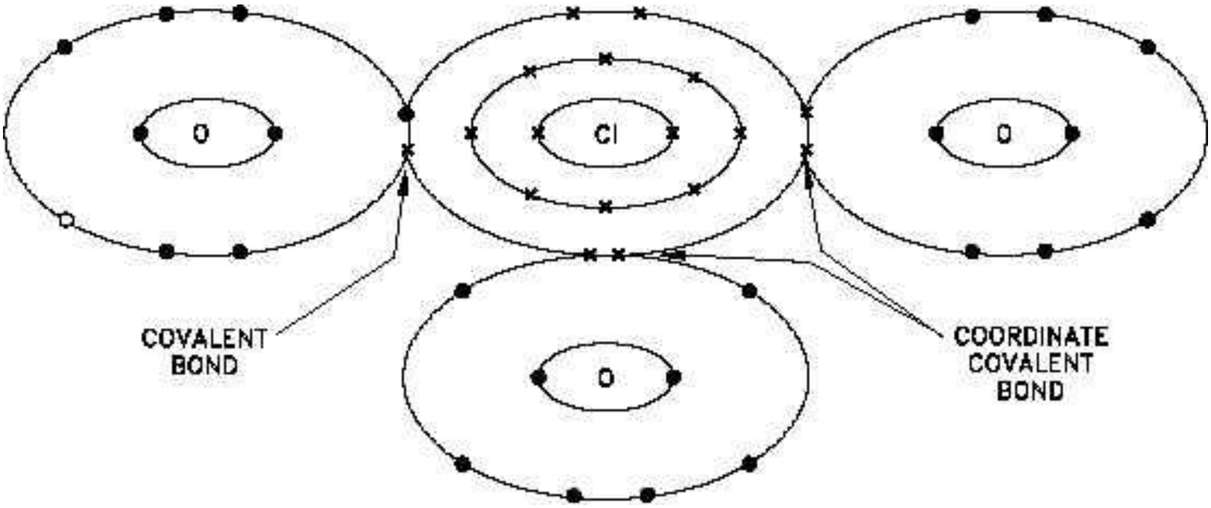


Figure (١.١) Configuration of chlorate ion.

The chlorates have been used historically as a herbicides to kill all terrestrial plants(٢), they also have a damaging effect when discharged to the recipient(٣) and the chlorates are oxidizing agents and all of their compounds are water soluble(٤).

١A-٢: Occurrence

The fate of chlorates and their toxicity is linked closely to nitrate levels in the water(٥) and the critical nitrate levels appear to range from ٥ µg.L$^{-١}$

where chlorate transport is rapid, to ٨٠ µg.L$^{-١}$, which almost completely inhibits nitrate transport(٦,٧).

Recent monitoring data indicate that typical surface water concentrations of chlorates are about ٠.٠٤ mg.L$^{-١}$ and about ٠.٠٢ mg.L$^{-١}$ for the Rehine and Ijssel rivers in the Netherlands(٨,٩,١٠).

١A-٣: Properties

Chlorates are a colorless, cubic or trigonal crystals or a white powder. The crystals are also reported to be pale-yellow or white which may be attributed to an impurities(١١). Table (١.١) shows the properties of chlorate compound.

Table (١.١) Properties of chlorate compound(١٢-١٥).

Colour	Boiling point b.p.°C	Melting point M.P. °C	Molecular weight M.wt g/mol	Density g/ml
a colorless	١٢٢ °C	٢٤٨ °C	١٠٦.٤٤ g/mol	٢.٤٩٠ g/ml

Chlorate is highly soluble in water; it is not toxic to bacterial suspension at a concentrations below ٧٠٠ mg.L$^{-١}$(١٦) and the chlorate anion is unstable in water and decomposes to form oxy chloride ion and oxygen(١٧).

١A-٤: Uses

Chlorate is used extensively for a variety of purposes; it used as a herbicide or defoliant, released when chlorine dioxide ($ClO_{٢}$) is used as a bleaching agent in paper and pulp industry(١٨). Also it is used as the terminal electron acceptor(١٩,٢٠).

It used in the manufacture of matches, explosive, dyeing, printing of fabrics, tanning and finishing of leather(٢١, ٢٢, ٢٣).

١A-٥: Formation of chlorate

Chlorine dioxide oxidizes the organic material forming chlorite, which can then be oxidized to chlorate by ozone(٢٤) or by hypochlorite(٢٥). When the combination of chlorine dioxide and these disnifectant were used, chlorate is formed as a by product of chlorine dioxide generation(٢٦). It can be present in a commercial hypochlorite solutions(٢٧, ٢٨), ozonation of water with a chlorine residual(٢٩), and chlorine dioxide residual(٣٠), also results in the formation of chlorate.

It can be formed by decomposes of sodium hypochlorite by effect of temperature (٣١) .

$$3\,OCl^- \rightarrow ClO_3{}^- + 2\,Cl^-$$

And when excess of chlorine is present, the intermediate will form chlorate according to reactions below(٣٢-٣٥).

$$Cl_2O_2 + H_2O \rightarrow ClO_3{}^- + Cl^- + 2H^+$$

$$Cl_2O_2 + HOCl \rightarrow ClO_3^- + Cl_2 + H^+$$

chlorate ion can also be formed by reaction between chlorine dioxide and chlorine; therefore, that reaction may account for a fraction of the $ClO_٣^-$ in $ClO_٢$ treated samples(٣٦-٣٨).

١A-٦: Reactions of chlorate ion at different chemical media(٣٩, ٤٠, ٤١). This reactions can be indicated table (١.٢).

Table (١.٢) Reactions of chlorate ion.

Reaction media or reagent used	Main reaction equation	Reaction product	Remarks
١.$H_٢SO_٤$ (concentrated)	$٢KClO_٣+٢H_٢SO_٤ \rightarrow ClO_٢+$ $HClO_٤+٢KHSO_٤+H^+$	Greenish-yellow gas	Evolved gas form orange-yellow solution with $H_٢SO_٤$
٢. HCl (concentrated)	$٢KClO_٣+٦HCl \rightarrow ٣Cl_٢+٣H_٢O+KCl$		Give a yellow colour due to the liberated $Cl_٢$ gas acid
٣. $NaNO_٢$ (solution)	$KClO_٣+٣NaNO_٢ \rightarrow KCl+٣NaNO_٣$	Chlorate reduction to chloride	
٤.$AgNO_٣$ mixture $HNO_٣+NaNO_٢$ (solution)	$KClO_٣+AgNO_٣+HNO_٣+NaNO_٢ \rightarrow$ $AgCl\downarrow+KNO_٣+HNO_٢+NaNO_٣+O_٣$	White precipitate of silver chloride	Reduction of chlorate to chloride
٥. Potassium Iodide (solution)	$ClO_٣^-+٦I^-+٦H^+ \rightarrow Cl^-+٣I_٢+٣H_٢O$	Pale yellow colour	Iodine libration
٦. Ferrous sulphate (solution)	$KClO_٣+٦FeSO_٤+٣H_٢SO_٤ \rightarrow KCl+$ $٣Fe_٢(SO_٤)_٣+٣H_٢O$	Formation of chloride	Reduction of chlorate to chloride
٧. Indigo test	$KClO_٣+H_٢SO_٤ \rightarrow Cl_٢$ or $HClO_٣$	A pale-blue colour is form	The chlorate is reduced by the sulphuric acid to chlorine or to hydrochloride and the later bleaches the indigo
٨. Aniline sulphate test		A deep-blue colour	
٩. Manganous-sulphate-phosphoric acid test	$٦Mn^{٢+}+١٢PO_٤^{٣-}+٦H^++ClO_٣^- \rightarrow Cl^-$ $+٣H_٢O+٦[Mn(PO_٤)_٢]^{٣-}$	Violet-colour	To form mangani-phosphate ion and reductionof chlorate to chloride

١٠. Action of heat (٤٢,٤٣, ٤٤)	$٢KClO_٣ \rightarrow ٢KCl+٣O_٢$ $٢KClO_٣ \rightarrow KClO_٤+KCl+O_٢$	White product	Form chloride and oxygen Form perchlorate

١A-٧: Determination of chlorates

Different classical methods were used for the determination of chlorate ion. Table (١.٣) tabulates some of the available methods.

Table (١.٣) Determination of chlorate ion.

Base of the method	Main reaction scheme	Determination of product	References No.
١.Volumetric method	$ClO^{-}_{٣}+٦I^{-}+٦H^{+}\rightarrow Cl^{-}+٣I_{٢}+٣H_{٢}O$ $ClO^{-}_{٣}+٦Fe^{٢+}+٦H^{+}\rightarrow Cl^{-}+٦Fe^{٣+}+٣H_{٢}O$	- Determination of released iodine by titration with standard sodium thiosulphate solution -The excess ($Fe^{٢+}$) ion is determined by titration with standard dichromate solution	٤٥ ٤٦
٢. Gravimetric method	$ClO^{-}_{٣}+ ٦Fe^{٢+}+ AgNO_{٣}+٣H^{+}\rightarrow AgCl +٣OH^{-}+Fe(NO_{٣})_{٢}$	- By precipitation as silver chloride (AgCl).	٤٧
٣.Ion chromatography with post column reaction	$٦I^{-}+ClO^{-}_{٣}+ ٦H^{+} \rightarrow ٣I_{٢}+Cl^{-}+٣H_{٢}O$ $I_{٢}+I^{-}\rightarrow I_{٣}^{-}$	-Chlorate is analyzed by ion chromatography followed by an osmate catalyzed post column reaction of chlorate with iodide.	٤٨
٤.Biological reduction method	$٣ClO^{-}_{٣}+ ٣H_{٢}\rightarrow ٣H_{٢}O+Cl_{٢}+O_{٢}$	-Determination of high conc. Of chlorate ion in waste water by using micro. Organisms chlorate as an electron acceptor and hydrogen gas as a reducing agent.	٤٩
٥.Flow injection analysis		-Determination of chlorate by iodometry method in FIA	٥٠, ٥١

Part ((B))

١B-١: Flow Injection Analysis

FIA (Flow Injection Analysis) is a widely used technique for the determination tracing elements and the designation of FIA was proposed in ١٩٧٥ by Ruzicka and Hansen(٥٢,٥٣,٥٤), and defined it "information gathering from a concentration gradient formed from an injected, well defined zone of a fluid, dispersed into a continuous unsegmented stream of a carrier(٥٥)".

The simplest flow analyzer consists of a pump, which is used to propel the carrier stream through a narrow tube, an injection valve, a micro reactor in which the sample, zone disperses and reacts with the components of the carrier stream, forming species that are sensed by a flow through a detector. The obtained signal is recorded on any read out system(٥٦, ٥٧) . Basic flow injection system is shown in figure (١.٢).

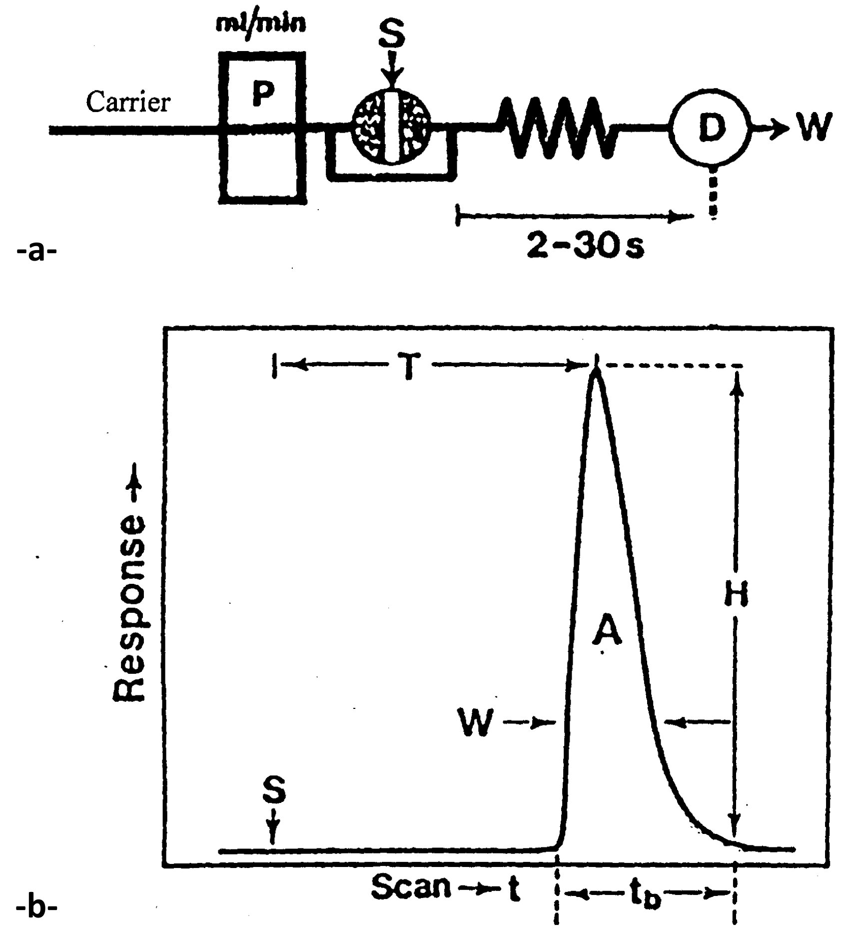


Figure (١-٢): A schematic diagram of the basic flow injection system

a: The simplest single flow injection analysis manifold utilizing a carrier stream of reagent.

b- The analog output has the form of a peak

Figure (١.٣) shows the main stages that could be used in flow injection analysis(٥٨, ٥٩).

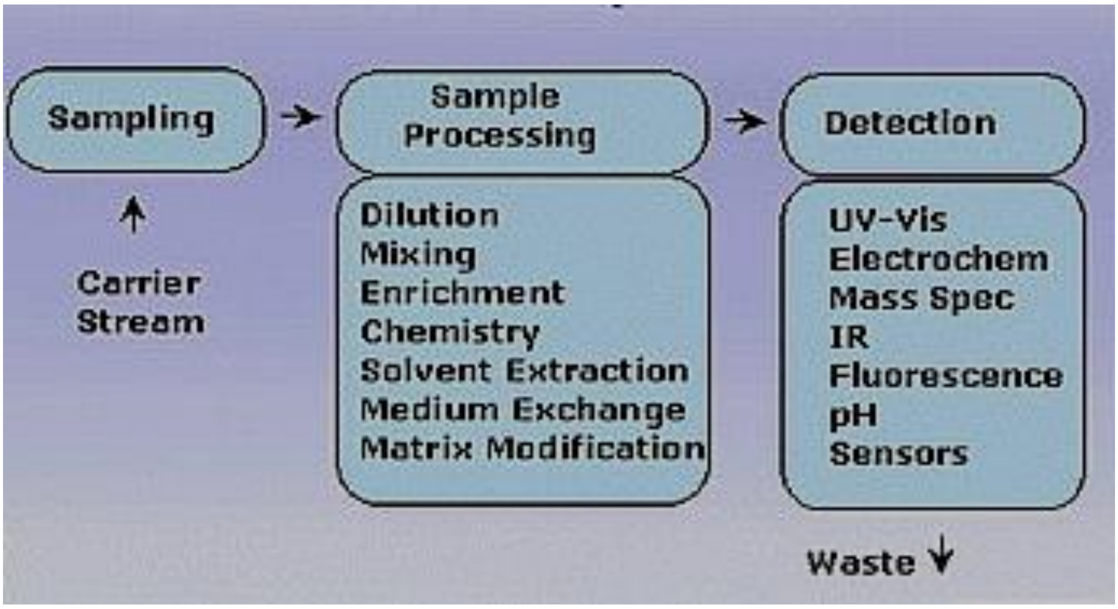


Figure (١-٣): Main steps in flow injection analysis

There are two types of continuous-flow methods, segmented and un segmented.

The segmented flow method commercialized by technicon in the "Auto analyzer" system, which corresponds to the classical version, was first described by Skegg's in ١٩٥٧(٦٠), the samples were propelled sequentially and air bubbles separate (segment) the flow(٦١). A wash cycle between samples was also included. The air bubbles were usually removed before they reach the detector cell(٦٢), as in figure (١.٤).

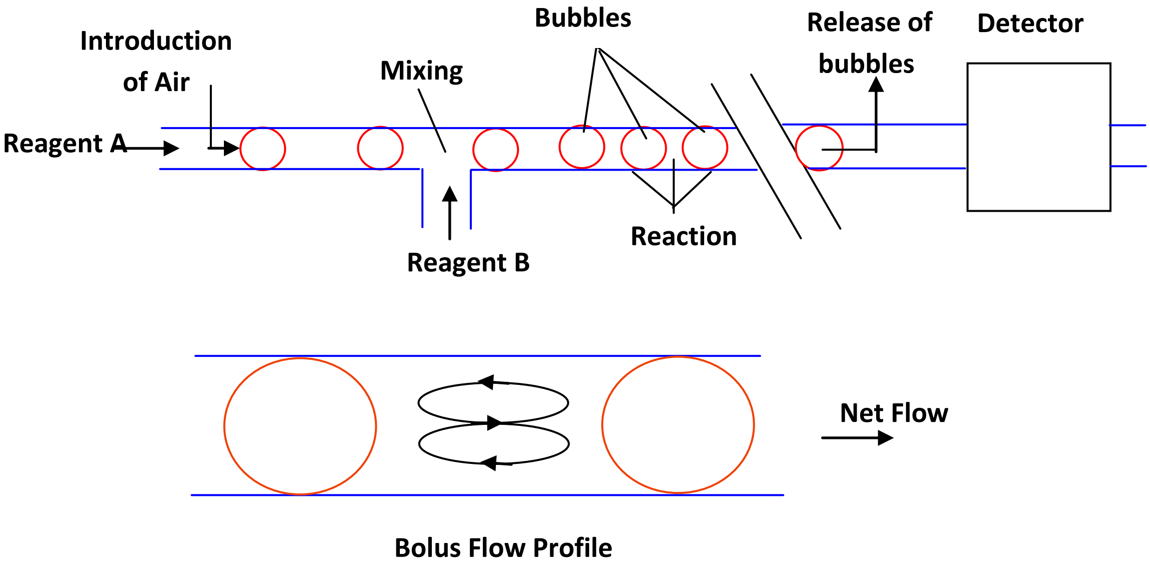


Figure (١-٤): Air-segmented continuous flow analysis

While un segmented-flow methods, described for the first time in ١٩٧٤, are narrow and referred to as flow injection analysis methods and differ from segmented flow method.

The flow is not segmented by air bubbles, the sample is injected instead of propelled and neither physical (flow homogenization) nor chemical equilibrium has been attained by the time and the signal is recorded(٦٣, ٦٤, ٦٥). Figure (١.٥) shows the laminar flow for un segmented flow analysis.

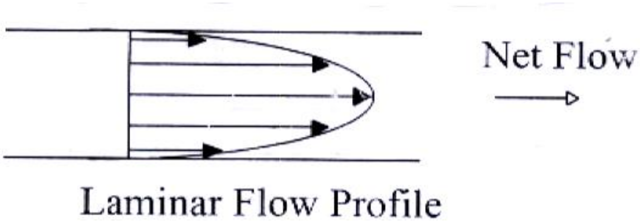


Figure (١-٥): Laminar flow profile for un segmented flow analysis

١B-٢: Comparison between two chief continuous analyses segmented (sequential) (SFA) and un-segmented (FIA):

Figure (١.٦) can be used to describe the basic components and principles of (FIA).

It's a simple and versatile analytical technology for automating wet chemical analysis, based on the physical and chemical manipulation of a dispersed sample zone formed from the injection of the sample a flowing carrier stream detection down stream(٦٦, ٦٧).

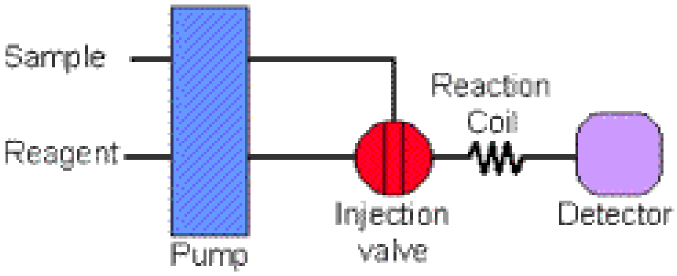


Figure (١-٦): Simple flow injection analysis (un-segmented).

Sequential Injection Analysis (Segmented) is a new generation of FIA; this approach is to automate the sample manipulation which arose from a need to simplify manifolds(٦٨, ٦٩). Figure (١.٧) shows the main explantary idea of the technique.

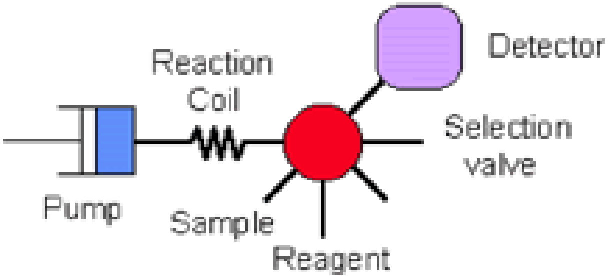


Figure (١-٧): Simple Sequential Injection Analysis.

It should be stressed that (FIA) offers higher sample through put, uses smaller amounts of reagent, provides a layer number analytical data and opens new possibilities.

A detailed summary is presented in table (١.٤).

Table (١.٤) Comparison between (SFA) and (FIA).

Parameter	SFA	FIA	Ref.
Sample introduction	Aspiration	Injection	٧٠
Sample volume	٠.٢-٢.٠ ml	١٠-١٠٠ ml	٧١
Response time	٢.٠-٣٠٠ min.	٣-٦٠ sec.	٧٢
Bore tubling	٢.٠ mm	٠.٥-٠.٧ mm	٧٣
Detection	At equilibrium (homogeneity)	With controlled (dispersion)	٧٤
Sample through put	≤٨٠ sampler/hr	≤٣٠٠ sampler/hr	٧٥
Precision	١-٢٪	١-٢ %	٧٦
Reagent consumption	High	Low	٧٧
Wash-out cycle	Essential	Not required	٧٨
Continuous kinetic analysis	Not feasible	Stopped flow	٧٩
Titrations	Not possible	Possible	٨٠
Data produced	Peak height	Peak height Peak area-peak with peak to peak distance.	٨٠

The comparison between (FIA) and (SIA) can be noticed in the dispersion of the sample zone that is attained in both. It is worth noting that at the moment of injection in an (FIA) experiment, an un dispersed plug of sample is introduced into the carrier stream, while in (SIA) already during aspiration of the sample into the holding coil dispersion begins to take place and the flow reversal that happens when the sample is sent off, plays a dramatic role in mixing the sample with the carrier(٨١,٨٢).

١B-٣: Development stages for FIA and Injection zone

١B-٣-١: Flow Injection Analysis (FIA)

The first generation of FIA techniques is also probably the most widely utilized(٨٣). In it's simplest form, the sample zone is injected into a flowing carrier stream of reagent. As the injected zone moves down stream, the sample solution disperses into the reagent, causing the product to be formed. The modern flow injection analysis system usually consists of a high quality multichannel peristaltic pump, an injection valve, a coild reactor, a detector such as a photometric cell and an auto sampler, additional components may include a flow through heater to increase the speed of chemical reactions, columns for sample reduction, de bubblers and filters for particulate removal(٨٤).

Figure (١.٨) Shows this generation and the emerging zone for it is shown in figure (١.٩).

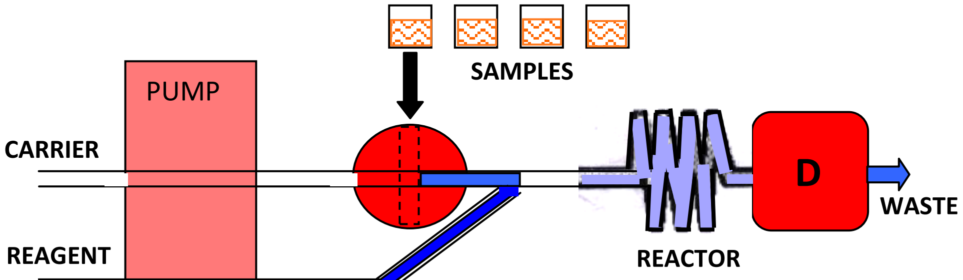


Figure (١-٨): Flow Injection Analysis system.

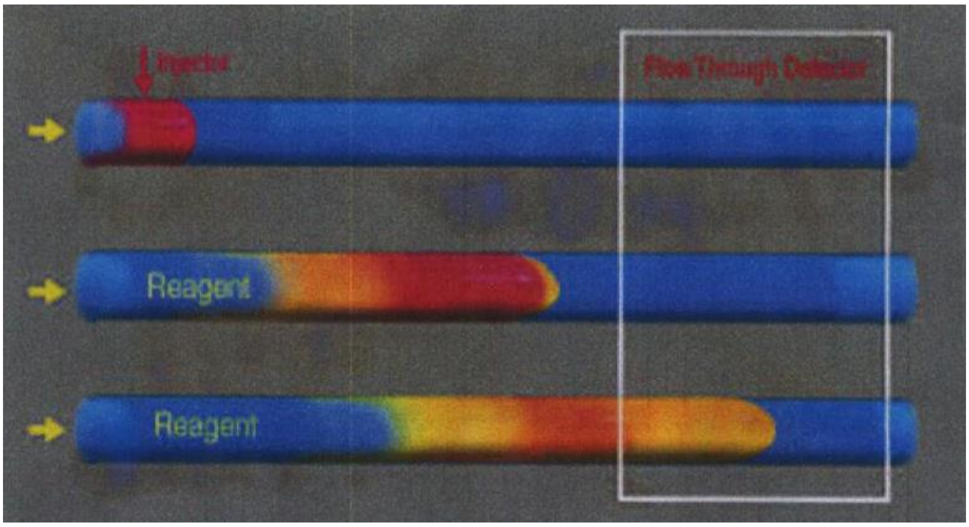


Figure (١-٩): Emerging zone in flow injection analysis.

١B-٣-٢: Sequential Injection Analysis (SIA)

SIA is the second generation approach to flow injection analysis compatible assays. It usually consists of a single-channel high precision, bidirectional pump, a holding coil, a multiposition valve represented in (#١, #٢, #٥) and a flow through detector(٨٥).

This generation is indicated in figure (١.١٠).

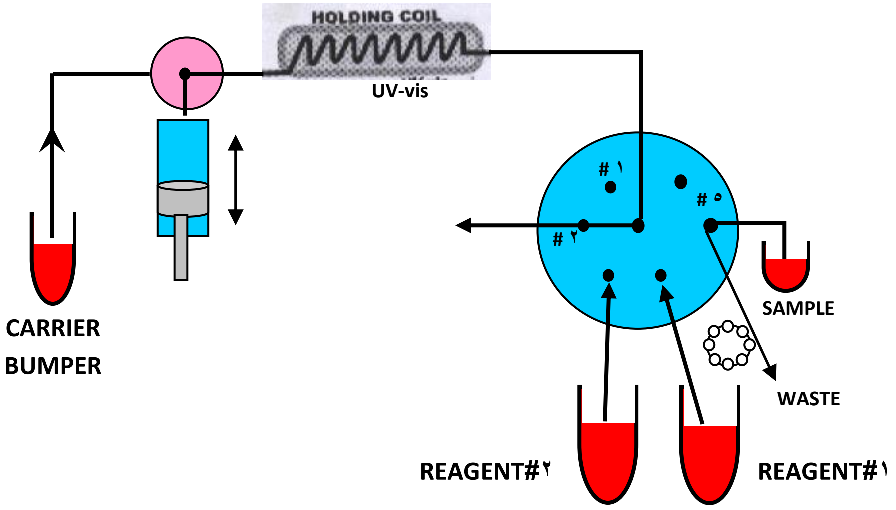


Figure (١-١٠): Sequential Injection Analysis system.

The system is initially filled with a carrier stream into which zone of sample and a zone of reagents (S), as in figure (١.١١-A) , are sequentially aspirated into a holding coil, forming a linear stack, these zones become overlapped due to the parabolic profile induced by differences between flow velocities of adjacent stream lines such as in figure (١.١١-B,C).

Flow reversals and flow accerleration furthur promote mixing. The multiposition valve is then switched to the detector position and the flow direction is reversed, propelling the sample/reagent zones through the flow cell which is indicated in figure (١.١١-D, E).

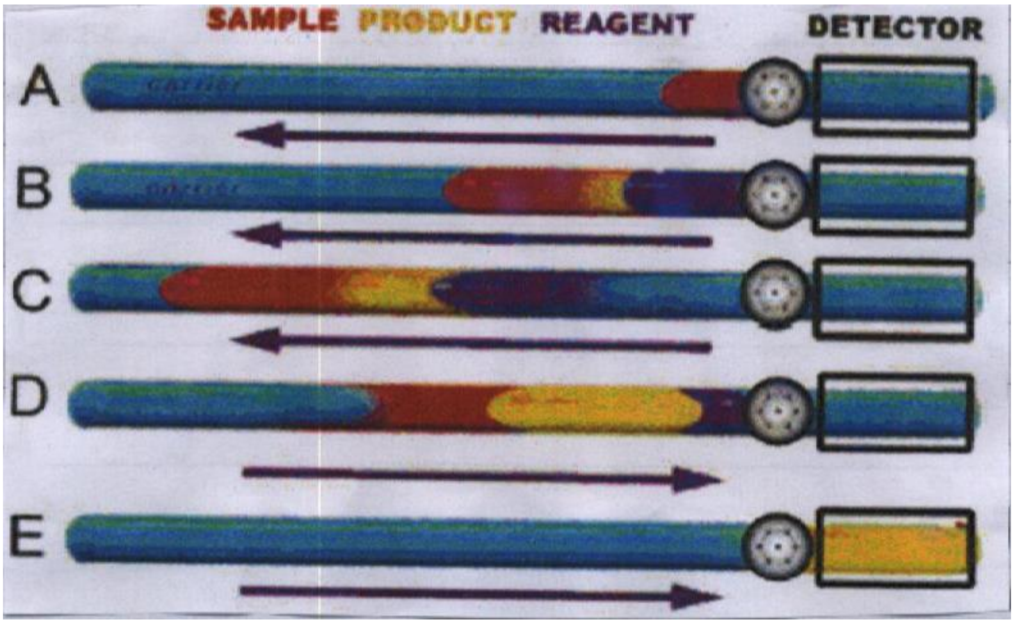


Figure (١-١١): Sequential Injection Programmed.

١B-٣-٣: Bead Injection Analysis (BIA)

BIA is the third generation and it is based on monitoring of (UV-Vis-IR) spectra of micro beads as they selectively capture a biomolecule of choice(٨٧).

To perform this assays, beads with a suitable interactant immobilized on their surface are trapped with in a micro flow cell, where a solution containing bio molecule of choice is passed over bead surfaces by a precisely controlled flow, where reaction proceeds on surface of bead giving rise to reactant product(٨٨,٨٩). Figure (١.١٢) shows third generation of bead injection analysis.

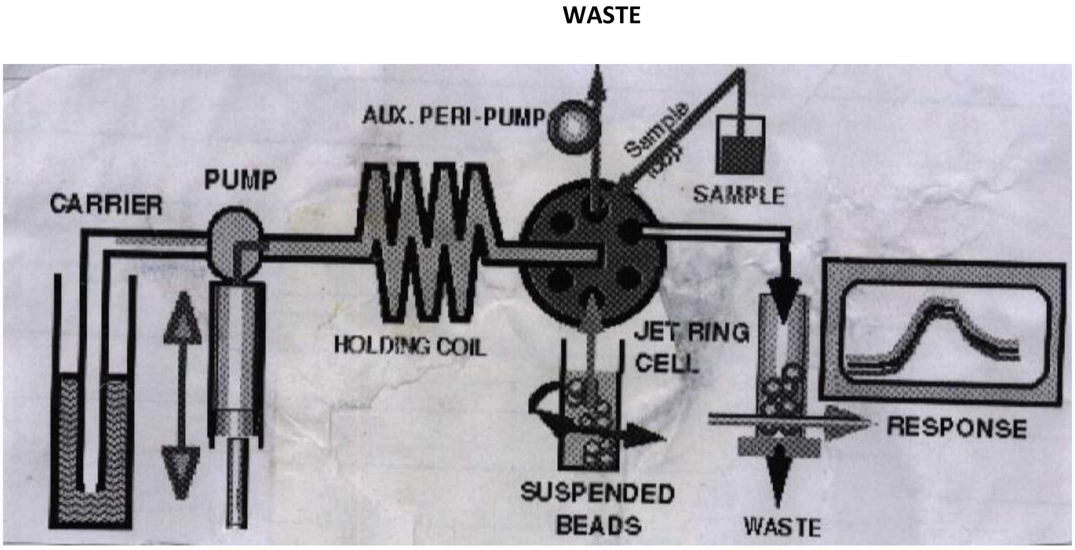


Figure (١-١٢):Bead injection analysis.

١B-٣-٤: Laboratory- On a valve

It is the fourth generation and it has been designed to miniaturized flow injection, sequential injection and bead injection, all with in a single monolithic mezzo fabricated component(٩٠).

The precisely fabricated instrument integrates a flow through injection port, working channels and flow through cell in a strategically designed structure, that allows sample dilution, reagent addition, mixing, incubation and reaction rate measurements to be carried out under computer control in the forward, reversed flow/stopped flow regime(٩١, ٩٢, ٩٣).

Figure (١-١٣): Laturature fourth generation.

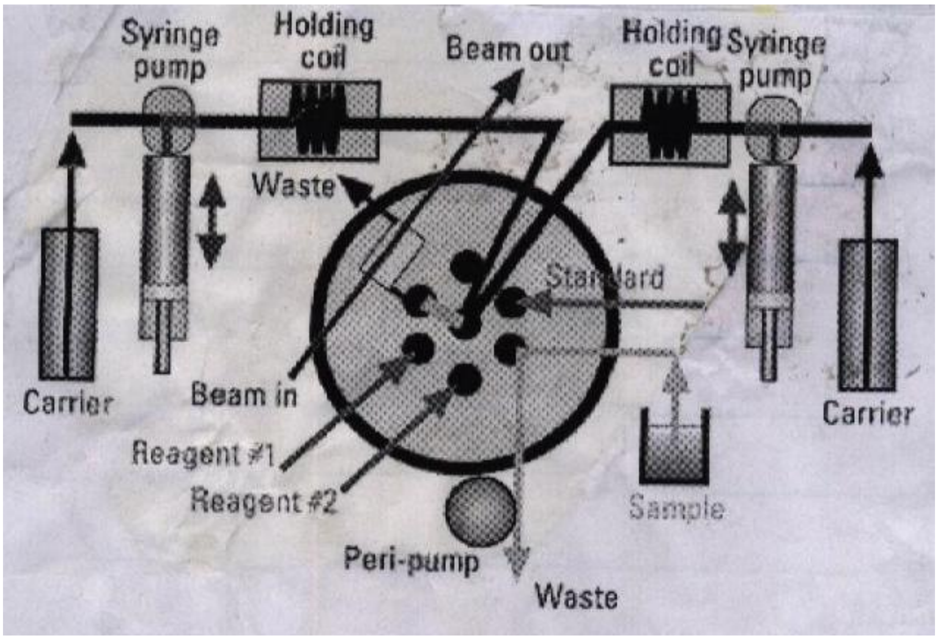


Figure (١-١٣): Laboratory-on a valve.

The sampling zone in flow injection analysis is a relatively simple and powerful technique for dilution. It is similar to the (heart-cut) technique used in chromatography.

It requires two sample injection valves set up(٩٤-٩٨), as depicted in to the following figure (١.١٤).

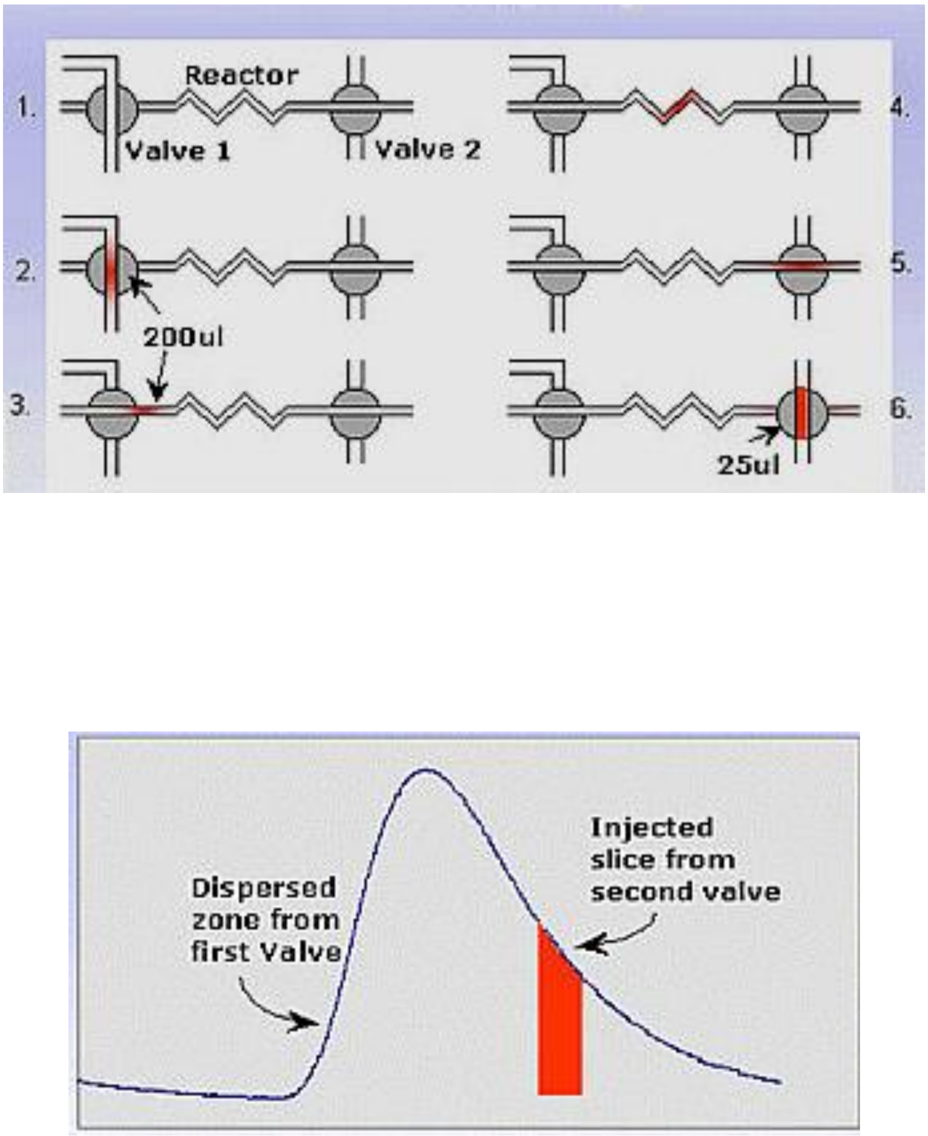


Figure (١-١٤): Zone sampling

In this first valve, a relatively large sample is injected, which then flow down dispersed by the reaction coil. As the dispersed sample zone fills the smaller sample loop of the second valve, an " a liquot" of the zone is injected into a second carrier stream (٩٩).

The second carrier can also pass through a reaction coil for furthur dispersion or the first injection for injection in the second carrier.

Dilutions by a factor of several hundred can be achieved. Precise timing of the two valves is important, requiring soft ware or an electronic time for optimum precision(١٠٠, ١٠١).

A gradient chamber is a simple device for dilution in FIA and SIA, as depicted in figure (١-١٥).

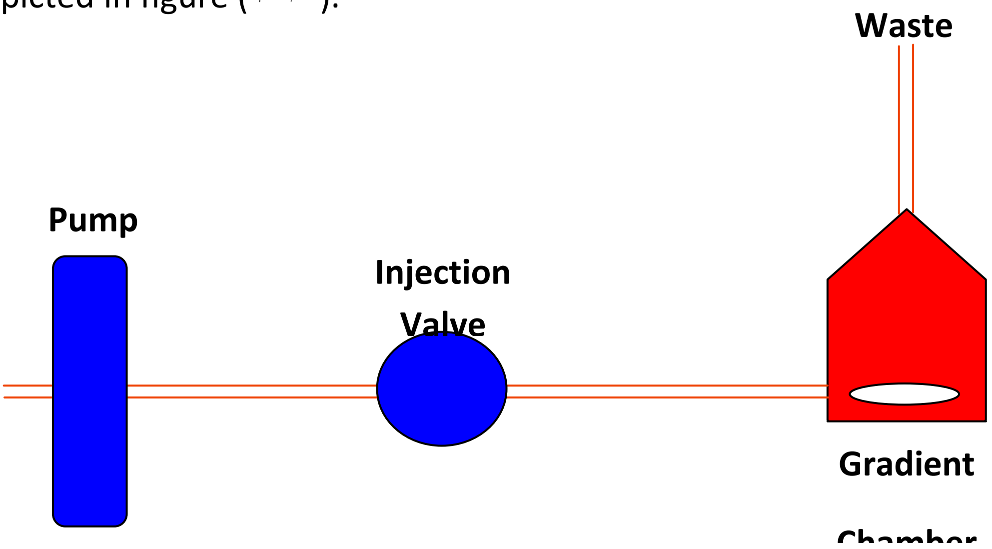


Figure (١-١٥): Gradient Chamber

The gradient chamber is small mixing vessel, generally with a stirring bar, an inlet and outlet for the carrier stream. The volume of the chamber is generally ١ml or less. Sample is injected into the carrier and undergoes a large dispersion as it mixes with the much greater volume of the gradient chamber.

Dilutions by a factor of several hundred can be achieved with good precision(١٠٢).

١B-٤: Dispersion in flow injection analysis

The term dispersion coefficient (D) is defined as " the ratio of the concentration of the constituent of interest in a fluid element of the injected zone before and after dispersion(١٠٣)". Expression of it is by equation (١.١):

$$D=C_o/C\text{…………(١.١)}$$

Where (C_o) is the original concentration of the constituent in the solution before dispersion, and (C) is the concentration of that fluid element of the dispersed fluid zone from which analytical read out is extracted. When the fluid element with the highest concentration is used for reading out, equation (١.٢) is expressed as:

$$D=C_o/C_{max}\text{…………(١.٢)}$$

Where (C_{max}) is the concentration of the constituent at peak maximum(١٠٤).

There are two processes that contribute to dispersion:

First: pressure-driven (Laminar) flow in an open tube causes a parabolic flow profile, where solvent near the walls is stationary and solvent in the center moves with twice the average velocity.

The longer a solute passes through a tube, the more spread out it becomes. In the absence of diffusion, sample would be found along the entire length of the tube.

Second: The other source of dispersion is diffusion, which acts in two ways:

١. Diffusion along the length of the tube acts to dilute and spread the sample.
٢. Diffusion in the radial direction acts to relax the parabolic profile.

The dispersion process typical of flow injection analysis system is shown in figure (١.١٦).

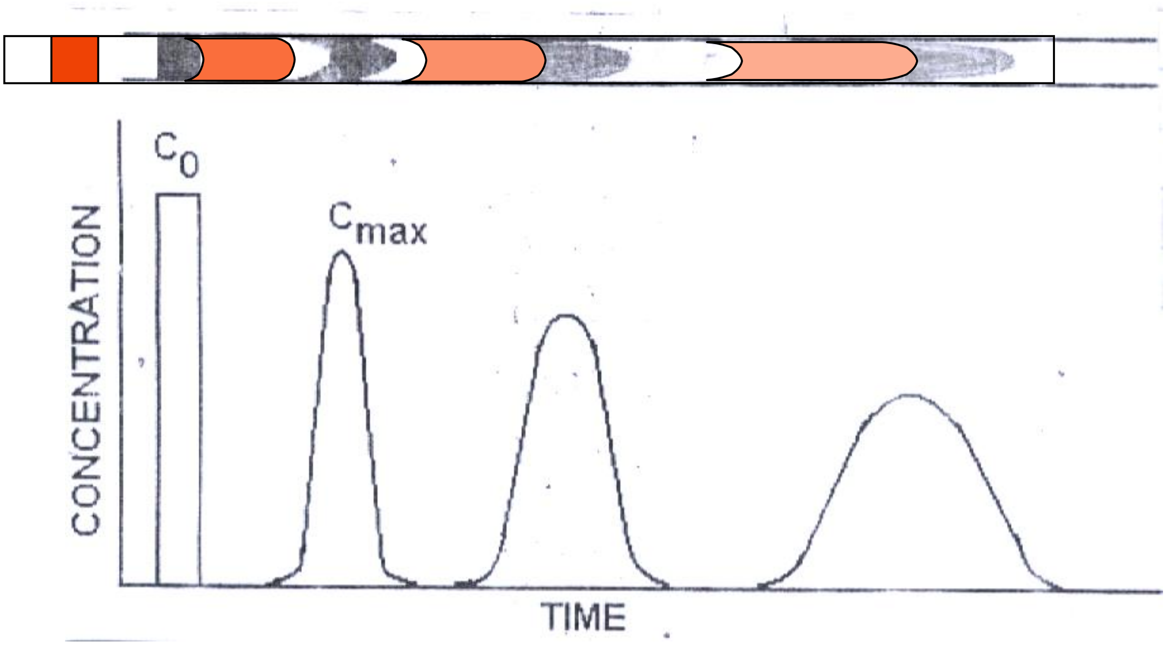


Figure (١-١٦): The typical dispersion process of (FIA) system

The sample is injected in a plug with concentration (C_o). The portion of the sample in the center of the tube moves down stream most quickly, while the sample at the tube wall is stationary(١٠٥).

Diffusion acts to relax the concentration profile in to a gaussion-shaped function.

The peak area is constant. Dispersion causes an increase in peak width and decrease in peak height.

There are three types of dispersion:

١. Limited dispersion

In this case, the system is designed to keep D<٣; it has several advantages over direct infusion of the sample.

- The signal becomes modulated, which helps to reduce the effects of drift in the instrument and figure (١.١٧) showed that.
- Sample and standard can be sequentially analyzed.
- An auto sampler can be used to automate sample injection.

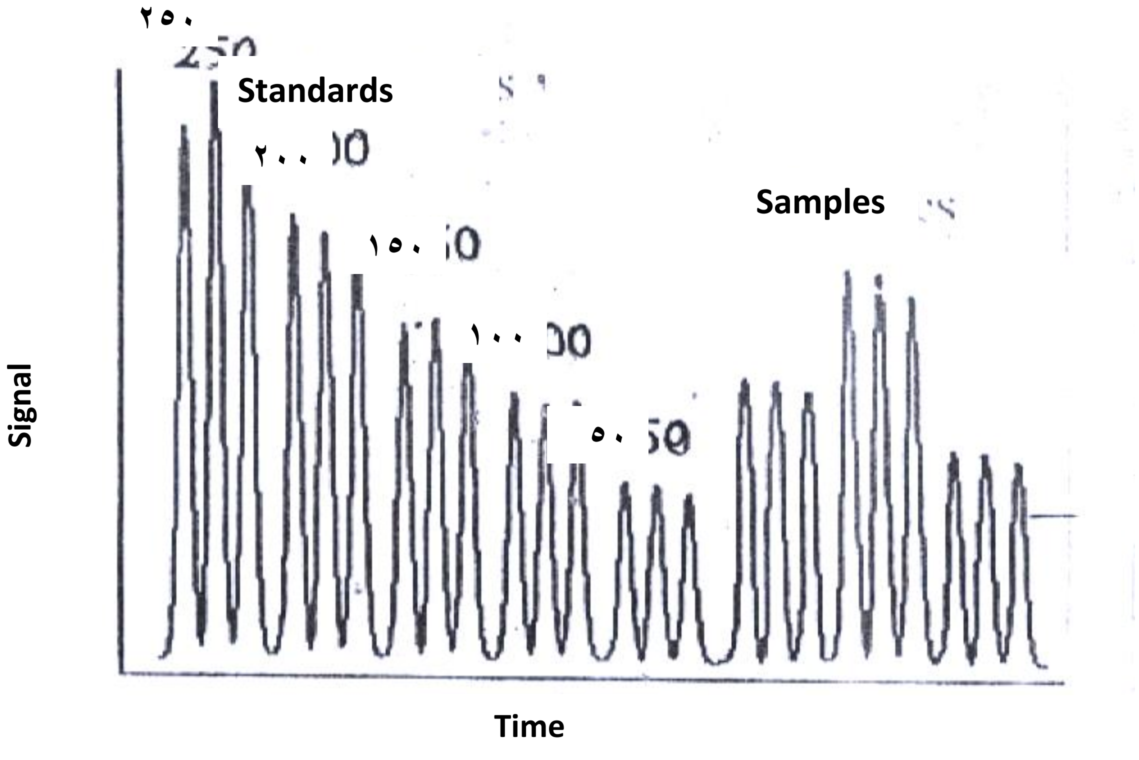


Figure (١-١٧): Signal modulated that appeared in limited dispersion

٢. Medium dispersion: D=(٣-١٠) is used when reactions are performed in the system.

In one stream flow injection analysis, the sample is injected directly into the reagent stream and mixing occurs by dispersion as in the figure (١.١٨).

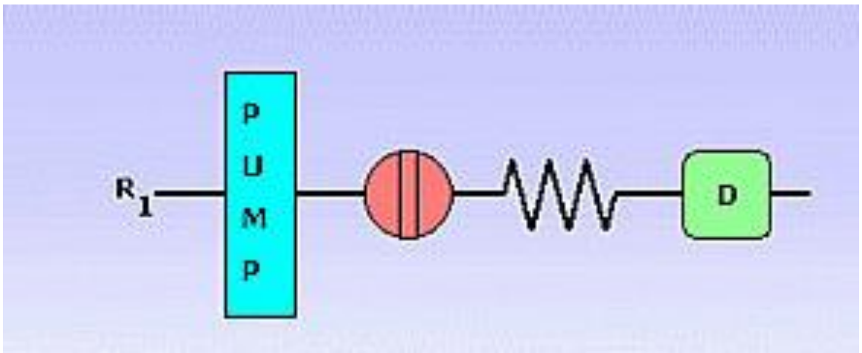


Figure (١-١٨): Single stream FIA

(R١: Reagent ١, V: Valve, R.C .: Reaction Coil, D: Detector)

In two stream FIA, the sample is injected into buffer, while reagent is introduced in a separate stream; mixing is more efficient in this system(١٠٦), as in the figure (١.١٩).

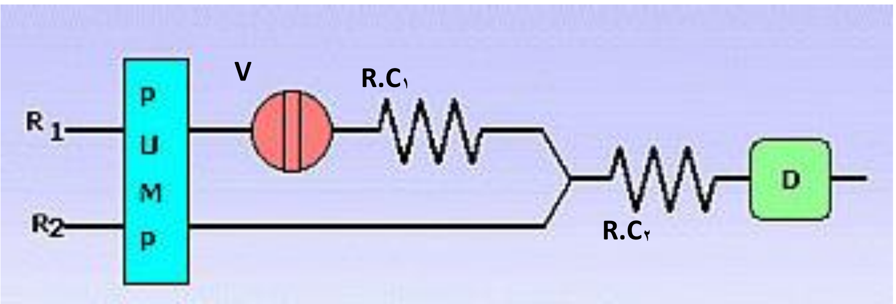


Figure (١-١٩): Two stream FIA

(R١: Reagent ١, R٢: Reagent ٢, V: Valve, R.C .: Reaction Coil,

D: Detector)

٣. Large dispersion: (D=>١٠) FIA

Best for reactions needing time to equilibrate:

-Long reactors.

- Low-flow rates-(slow).

- Small sample volumes but high dispersion-(not used much)(١٠٧).

١B-٥: Advantages of automation

١. Low cost and simple in instrumentation.(١٠٨)

٢. Low scheduled maintenance requirement.

٣. Accurate and precise sample manipulation.(١٠٩)

٤. Quality control measures can be included to assure the integrity of the analytical results.

٥. Applicable to abroad range of compounds by using a variety of reactions and simple photometric and electrochemical detectors(١١٠).

٦. Constant flushing of the manifold lines minimizes the risk of fouling(١١١).

٧. A wide range of useful manifold components allows complex operations such as dilution, trace enrichment, gas permeation, dialysis and several others to be incorporated into the analyzer manifold(١١١).

٢- Aim of research

This study aimed to:

١. Build up flow injection unit based on five-three ways valve which all together forms the home made injection valve. Also reaction cells were home made by using two loops.

٢. Design of flow injection unit based on cell and spectrophotometer.

٣. Style of flow injection unit depend on three-ways valve injection using one loop.

٤. Home made design of sequential injection unit depend on three-ways valve and cells using one loop.

٥. Determination of chlorate ion in an aqueous solutions, in safety matches and in hypochlorite solution locally manufactured (from Babylon company and Al-Fourat company) and an imported hypochlorite solution.

Chapter Two

Chemicals and Apparatus

٢.١: Chemicals

All the chemicals used were analytical reagent grade and distilled water was used throughout the study.

٢.١.١ Potassium Iodide

Potassium Iodide (٠.٥M) and (٠.١٥M) were prepared by dissolving (٨.٢٥٩g, ٢.٤٧٧g) in distilled water and completed to (١٠٠ml) in volumetric flask.

٢.١.٢ Potassium chlorate

Potassium chlorate (٠.٠٥M) and (٠.١١M) were prepared by dissolving (٠.٣٠g, ٠.٣٥g) in distilled water and completed it to (٥٠ml) in volumetric flask.

٢.١.٣ Hydrochloric acid

(٢.٥M) was dilute (٥٥.٢ml) of (٣٥٪) HCl (sp.gr ١.١٨) with distilled water in a (٢٥٠ml) volumetric flask.

٢.١.٣ Sulphric acid

(١.٥M) was dilute (٢٠.٥٤ml) of (٣٥٪) $H_{٢}SO_{٤}$ (sp.gr ١.٨٢٥) with distilled water in a (٢٥٠ml) volumetric flask.

-Interfering ions solutions

All the solutions were prepared at the concentration of ١٠٠ ppm by dissolving an appropriate amount of each substance in distilled water and completed to ١٠٠ ml volumetric flask as in table (٢-١) , (٢-٢).

Table (٢-١) Anion interfering solutions

Substances	Chemical formula	Interfering ion	Molecular weight	Weight (g)	Purity %	Company
Potassium permenganate	$KMnO_٤$	$MnO_٤^-$	١٥٨.٠٣	٠.٠١٣٢	٩٩٪	BDH
Potassium chromate	$K_٢CrO_٤$	$CrO_٤^{--}$	١٩٤.١٩	٠.٠١٦٧	٩٩.٥٪	BDH
Potassium sulphate	$K_٢SO_٤$	$SO_٤^{--}$	١٧٤.٢٧	٠.٠١٨١	١٠٠٪	Fluka
Potassium iodate	$KIO_٣$	$IO_٣^-$	٢١٤.٠٠	٠.٠١٢٢	٩٩.٥٪	Riedal-DeHAEN
Potassium nitrate	$KNO_٣$	$NO_٣^-$	١٠١.١٠	٠.٠١٦٣	١٠٠٪	Riedal-DeHAEN
Potassium chloride	KCl	Cl^-	٧٤.٥٩	٠.٠٢٠٩	٩٩.٥٪	Riedal-DeHAEN
Potassium bromide	KBr	Br^-	١١٥.٤٠	٠.٠١٤٨	٩٩.٥٪	BAKER Analyzed

Table (٢-٢) Cation interfering solutions.

Substances	Chemical formula	Interfering ion	Molecular weight	Weight (g)	Purity %	Company
-Cadmium nitrate	$Cd(NO_٣)_٢.٤H_٢O$	$Cd^{+٢}$	٣٠٨.٤٧	٠.٠٢٧٤	٩٩٪	MERCK
-Copper nitrate	$Cu(NO_٣)_٢$	$Cu^{+٢}$	١٨٧.٥٠	٠.٠٢٩٥	٩٥٪	MERCK
-Cobalt nitrate	$Co(NO_٣)_٢.٦H_٢O$	$Co^{+٢}$	٢٩١.٠٤	٠.٠٤٩٣	٩٨٪	MERCK
-Ferric nitrate	$Fe\ (NO_٣)_٣$	$Fe^{+٣}$	٢٤٥.٠٠	٠.٠٤١٥	٩٨٪	MERCK
-Ammonium nitrate	$NH_٤NO_٣$	$NH_٤^{+}$	٨٠.٠٠	٠.٠٤٤٤	٩٩٪	FLUKA
-Sodium nitrate	$NaNO_٣$	Na^{+}	٨٥.٠٠	٠.٠٣٦٩	٩٩٪	RIEDAL-DEHAEN
-Lead nitrate	$Pb(NO_٣)_٢$	$Pb^{+٢}$	٣٣١.٠٠	٠.٠١٥٩	٩٩٪	BDH
-Silver nitrate	$AgNO_٣$	Ag^{+}	١٦٩.٨٠	٠.٠١٥٧	٩٩.٨٪	PANREAC
-Potassium nitrate	$KNO_٣$	K^{+}	١٠١.١٠	٠.٠٢٥٨	١٠٠٪	RIEDAL-DEHAEN
-Tin chloride	$SnCl_٢$	$Sn^{+٢}$	١٨٩.٦٩	٠.٠١٥٩	٩٨٪	FLUKA
-Manganese chloride	$MnCl_٢$	$Mn^{+٢}$	١٢٦.٠٠	٠.٠٢٢٩	٩٨٪	FLUKA
-Zinc sulphate	$ZnSO_٤$	$Zn^{+٢}$	١٦١.٣٠	٠.٠٢٤٧	٩٩.٥	MERCK

٢.٢: Apparatus

No.	Instrument or Equipment	Company
١.	Tubing pump model (Ismatic)	Germany
٢.	Spectronic ٢١ (UV-Vis)	Milton Roy U.S.A
٣.	X-T Flat bed recorder No. (١٠٣٢ Siemens)	Germany
٤.	٥-ways injection valve (Merging zone version)	Home made
٥.	٣-ways injection valve (Merging zone version)	Home made
٦.	Reaction coil made from glass, I.D=١.٥ mm, O.D=٦ mm, Length= ١٠٠ cm	Home made
٧.	Flow injection cells: a- ١ cm path length b-٢ mm path length	Home made
٨.	Balance, Sartorius, BL ٢١٠٥	Germany
٩.	Tubes: A-sample loop made from teflon (١ mm I.D) :B: Glasses (٢ mm I.D) :C- Nipples	Home made
١٠.	Amplifier	Home made

Chapter Three

Unit design

CHAPTER THREE

This chapter includes components of unit used in flow injection analysis and falls in two parts:

Part A:

It deals with the first unit which consists of pump, valves (home made), cell (١ cm) (home made), international spectronic, and recorder.

Part B:

It deals with the second unit which is composed of pump, international valve, cell (٢ mm) (home made), spectronic (home made), recorder.

Part ((A))

٣A- The components of the first unit:

This unit is composed of few channels perstaltic pump used to pump the carrier stream (acid solution) through the valve, variable flow rates can be obtained and this pump is shown in figure (٣.١).

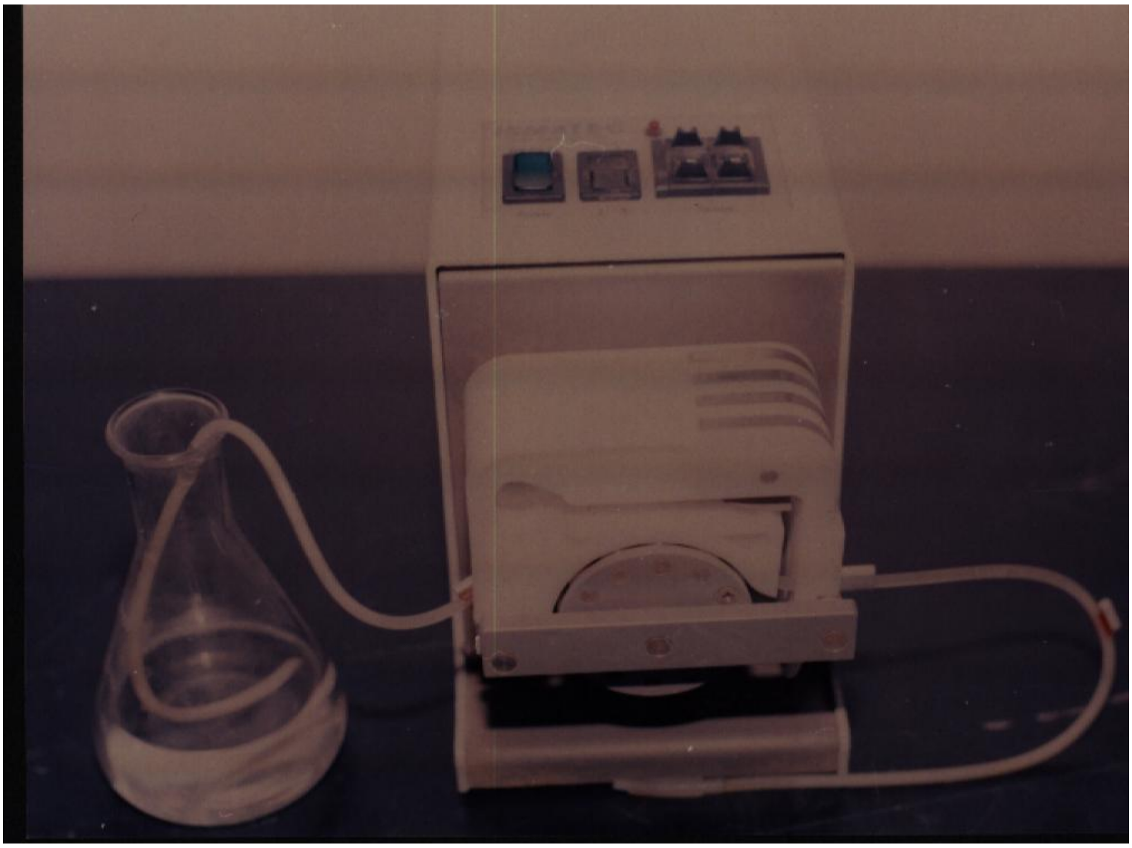
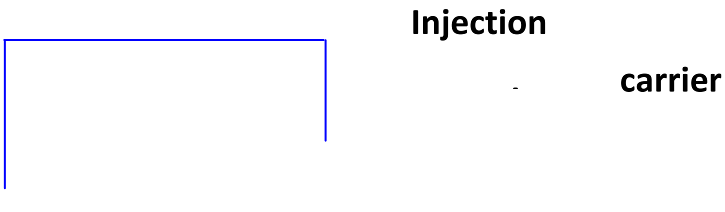


Figure (٣-١) Pump of flow injection analysis

The other part of this unit is five three- ways valve which is composed of five valve and two loops ($L_{١}$) and ($L_{٢}$). ($L_{١}$) represents the interior loop that passes through it sample solution (Chlorate ion ($ClO_{٣}^{-}$)) (١٢٧ μl) and ($L_{٢}$) represents exterior loop that passes through it reagent solution (potassium iodide (KI)) (٣١.٤ μl) and using valve (٢) to inject the sample ($ClO_{٣}^{-}$) as in figure (٣-٢) and reagent show in figure (٣-٣) by valve (٣) and valve (٤) after moving it by angle (٩٠º) to the left of the valve, valve (٥) is used to remove any quantity remained after filling ($L_{١}$) and ($L_{٢}$).



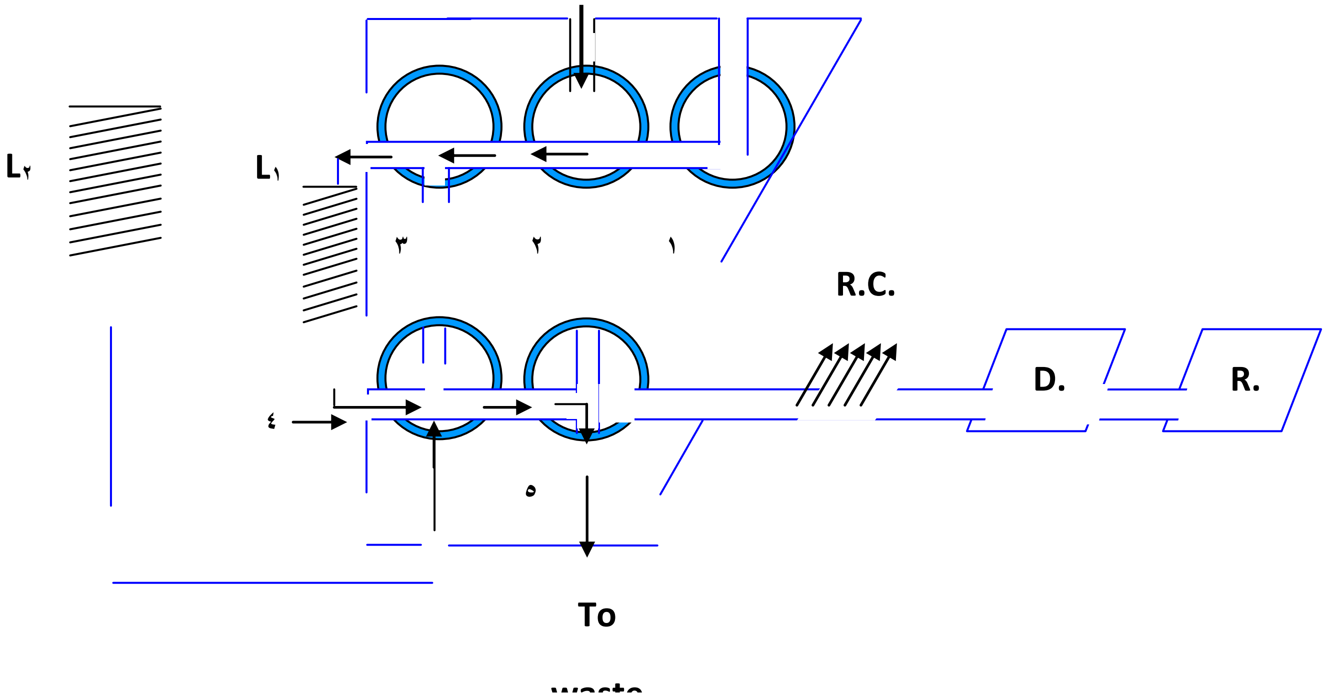


Figure (٣-٢): Injection the sample in loop (١)

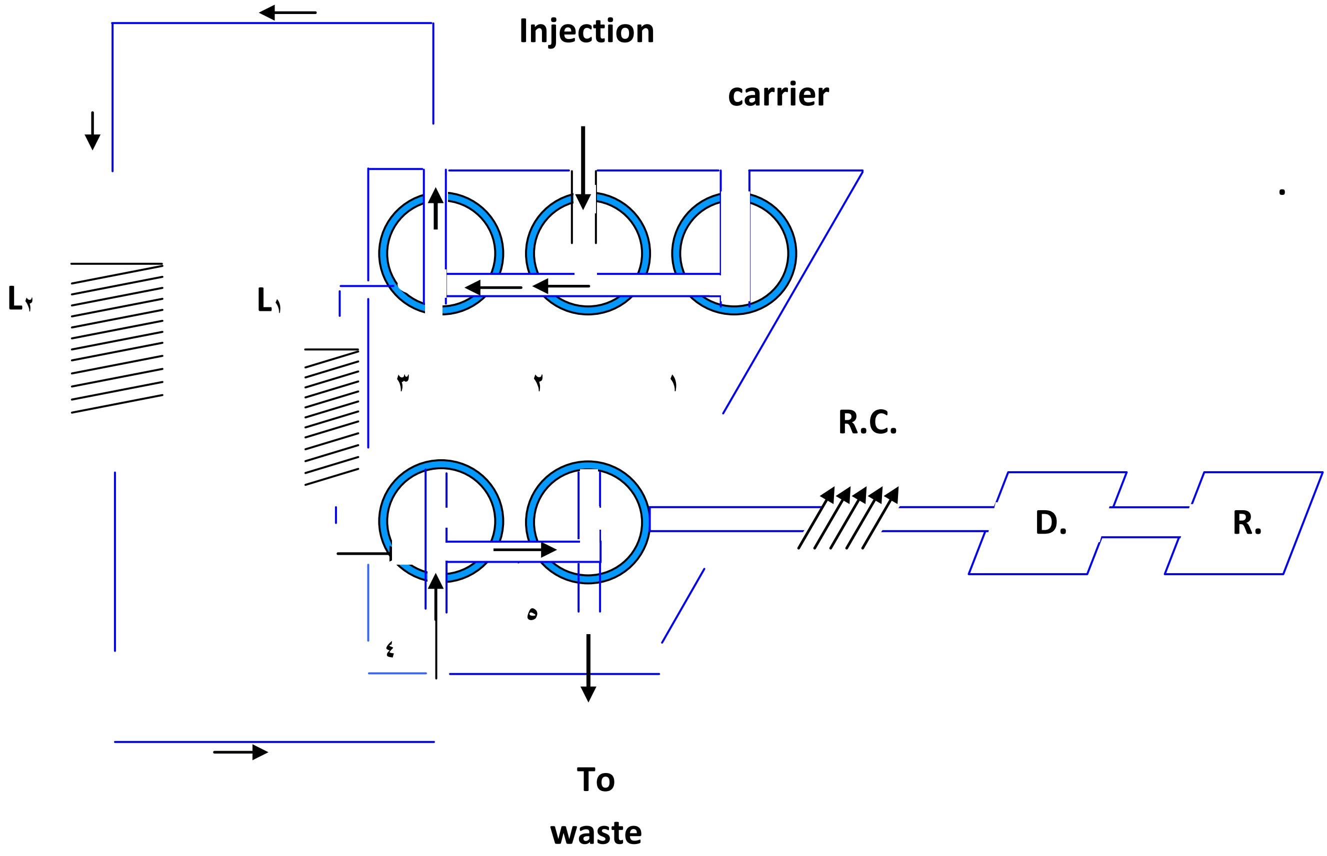


Figure (٣-٣): Injection the reagent in loop (٢)

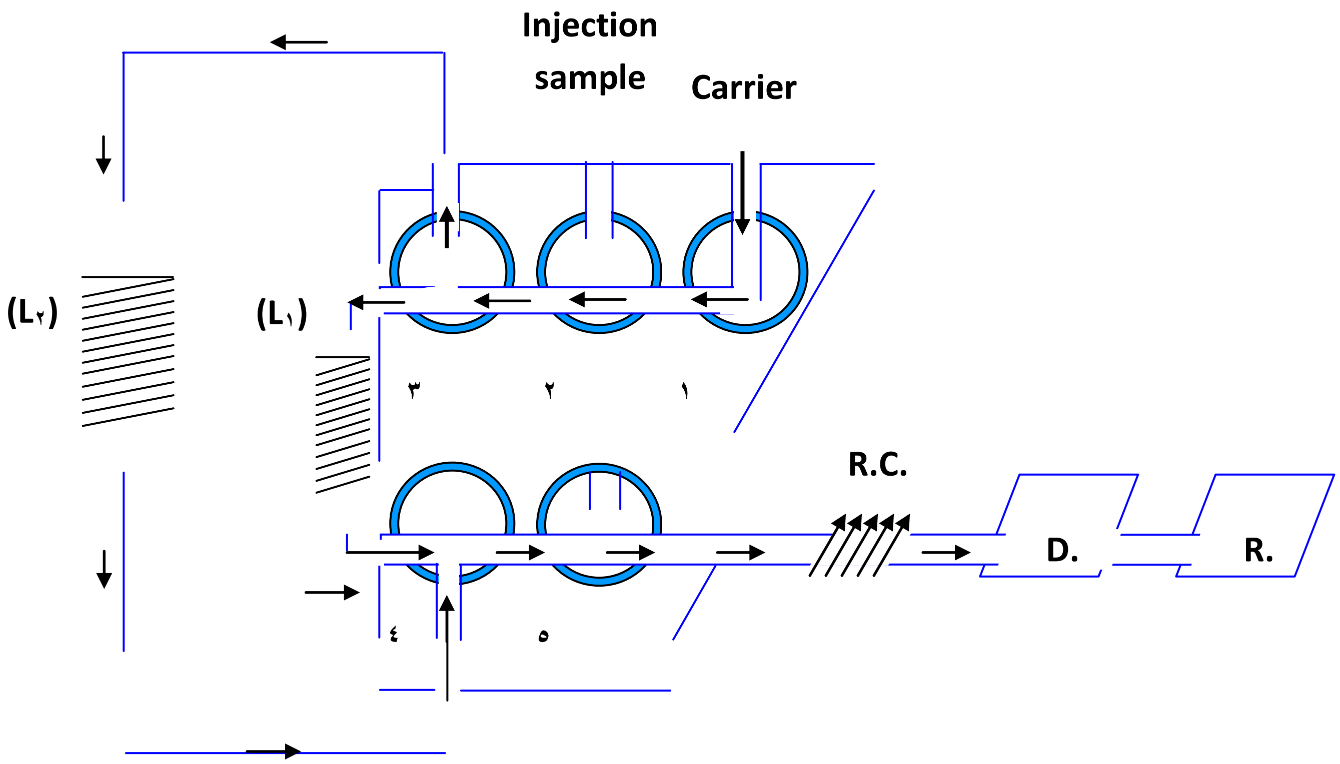


Figure (٣-٤): Shows the introduction of sample into the reaction manifold

Valve (١) is used to pass the carrier solution (Hydrochloric acid ٢.٥ M) through it to both loops and from it to manifold unit as shown in figure (٣-٤).

This valve which proves quite an alternative cheap, simple replaceable and easy to handle.

Three-Three ways valve has been used in this project; it is composed of one loop and three valves.

Valve (٢) is used for injecting the sample volume and the carrier solution (composed of acid solution and the reagent), the sample volume (١٢٧µl) was injected in the loop and valve (٣) is used to remove any volume of sample remains after injection the loop as shown in figure (٣-٥).

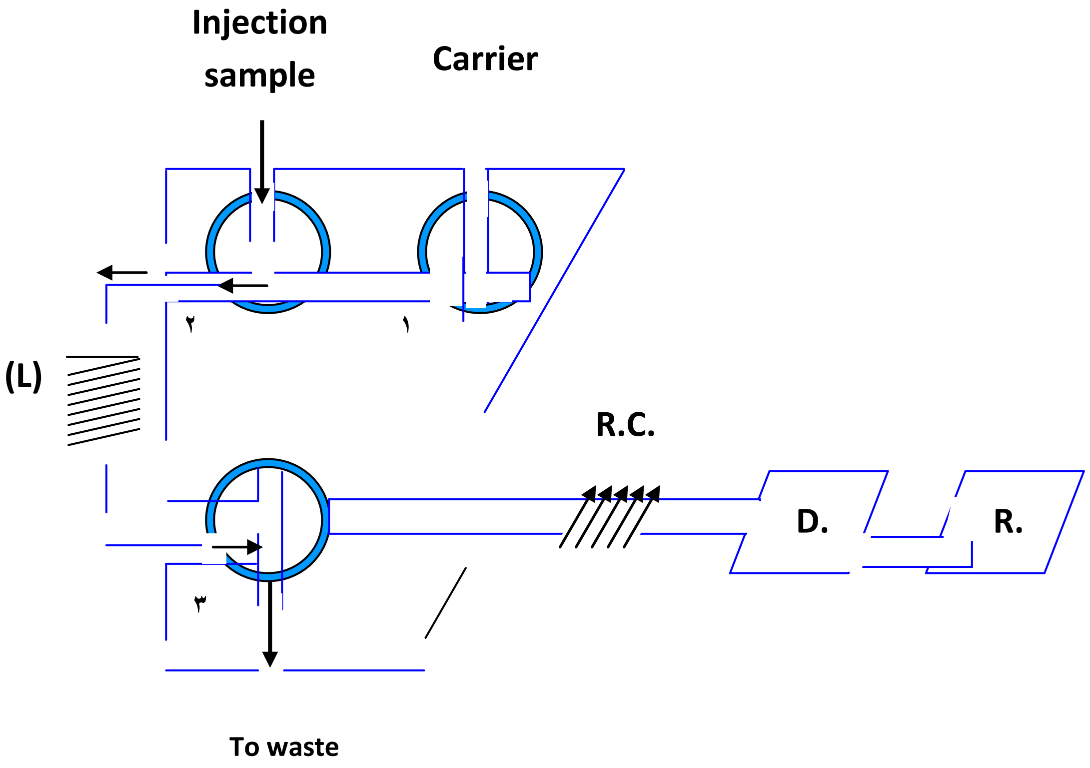


Figure (٣-٥): Injection of sample in the loop using three Three-ways valve.

Valve (١) passes the carrier solution from it to sample solution and through valve (٣) then to the manifold unit and measures the absorbance at ٣٥٠ nm as in figure (٣-٦).

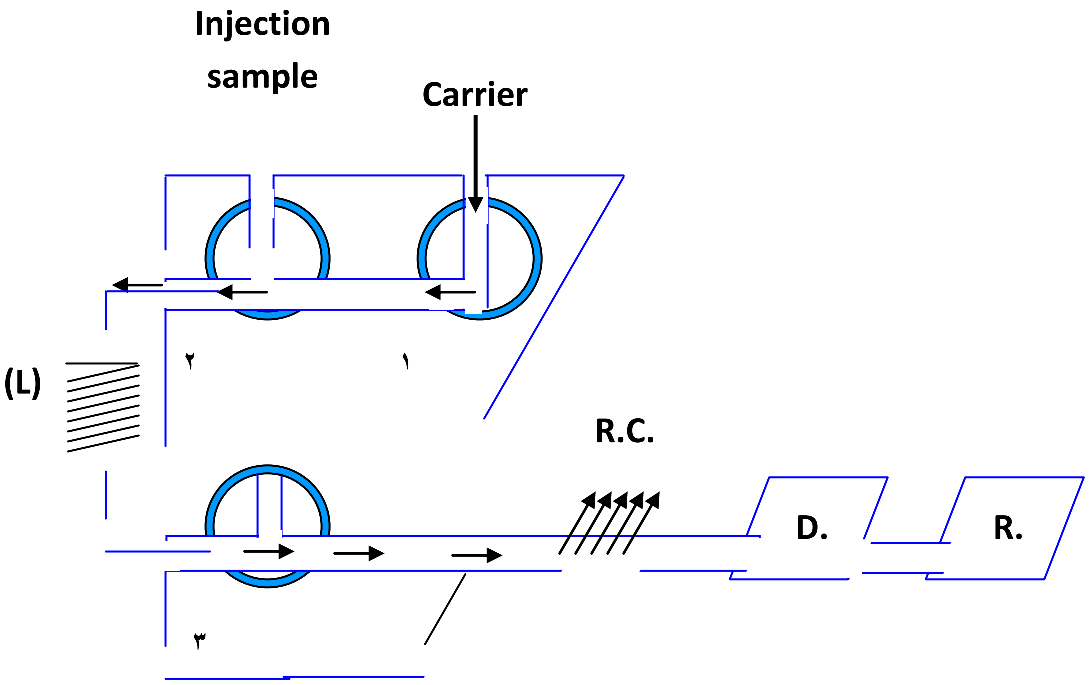


Figure (٣-٦): Introduction of sample in to reaction manifold

From five three- ways valve to reaction coil (RC: ١٠٠ cm in length with ٢ mm I.D) where the main reaction is conducted as shown in figure (٣-٧).

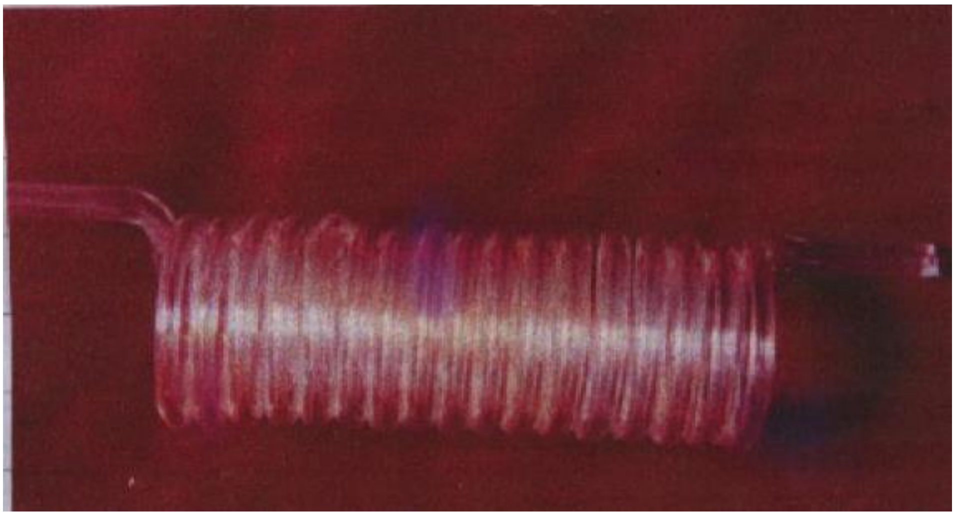


Figure (٣-٧): Reaction coil.

The next part flow-through cell that consists of two ends. The lower end represents the entry for the liquid and the upper end represents the going out of the liquid. The contact with the area of the passing light is made of quartize.

This cell gave acceptable repeatability through the work conducted in this project as shown in figure (٣-٨).

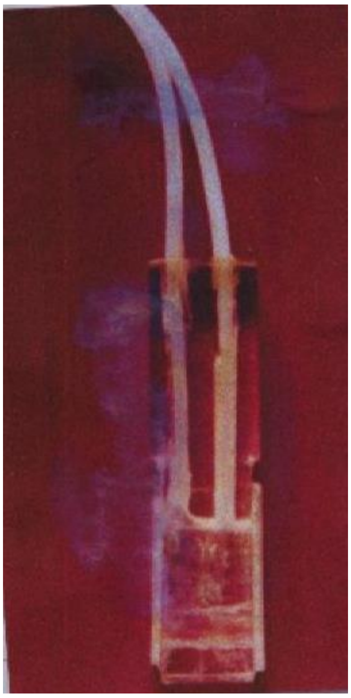


Figure (٣-٨): Absorption cell.

The absorbance that is obtained from spectrophotometer can be measured the signal by recorder. The whole components forming the unit are shown in the figure (٣-٩).

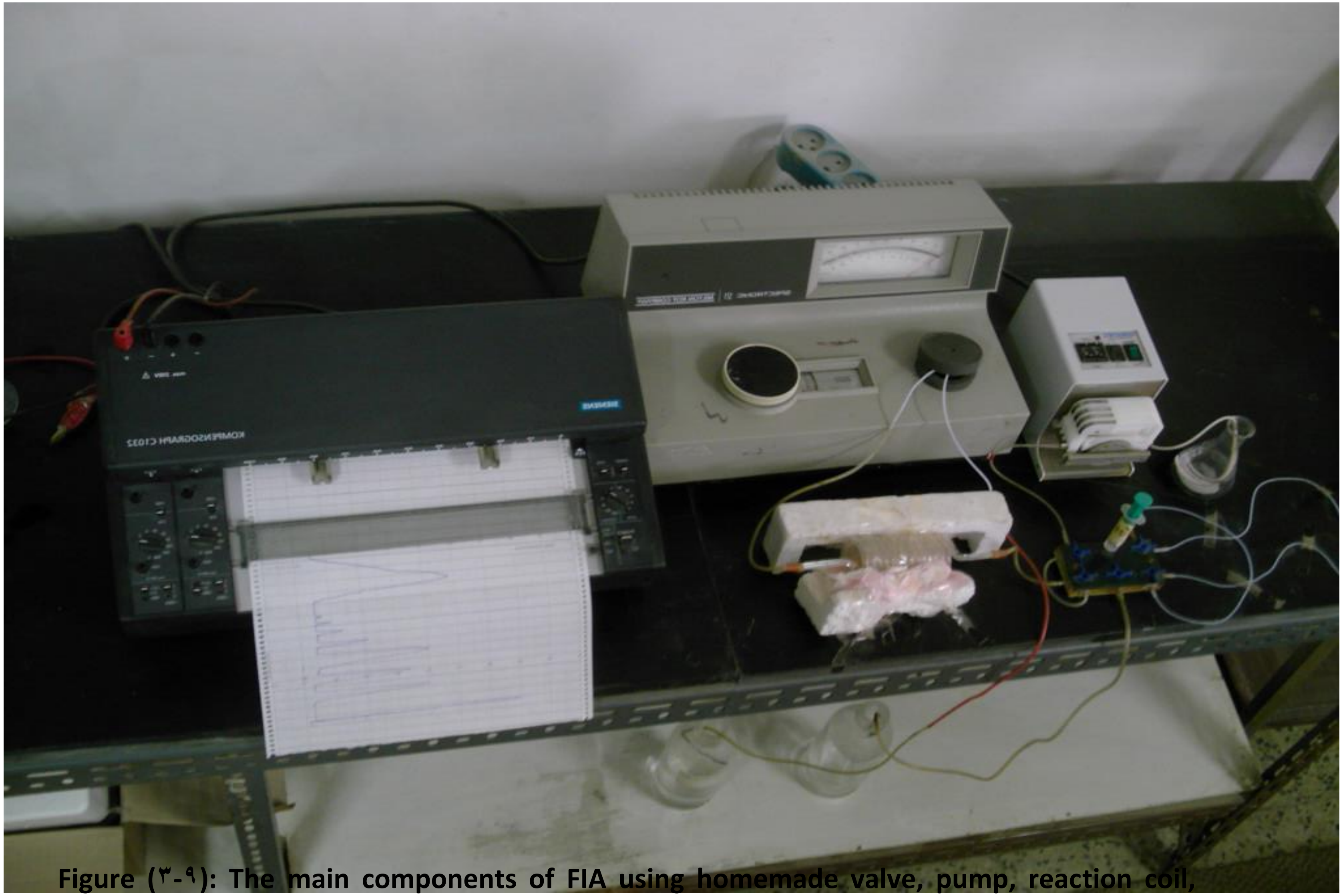


Figure (٣-٩): The main components of FIA using homemade valve, pump, reaction coil, homemade cell (١ cm), detector & recorder.

Eventually, the unit show in figure (٣.٩) was used to determine the chlorate ion and knowledge the degree of dispersion and detection limit of this method.

Fast and slow chart speed was used in order to notice any hidden shoulder in the profile (i.e pure release for one product or multi release or multi reaction product) as in figure (٣-١٠).

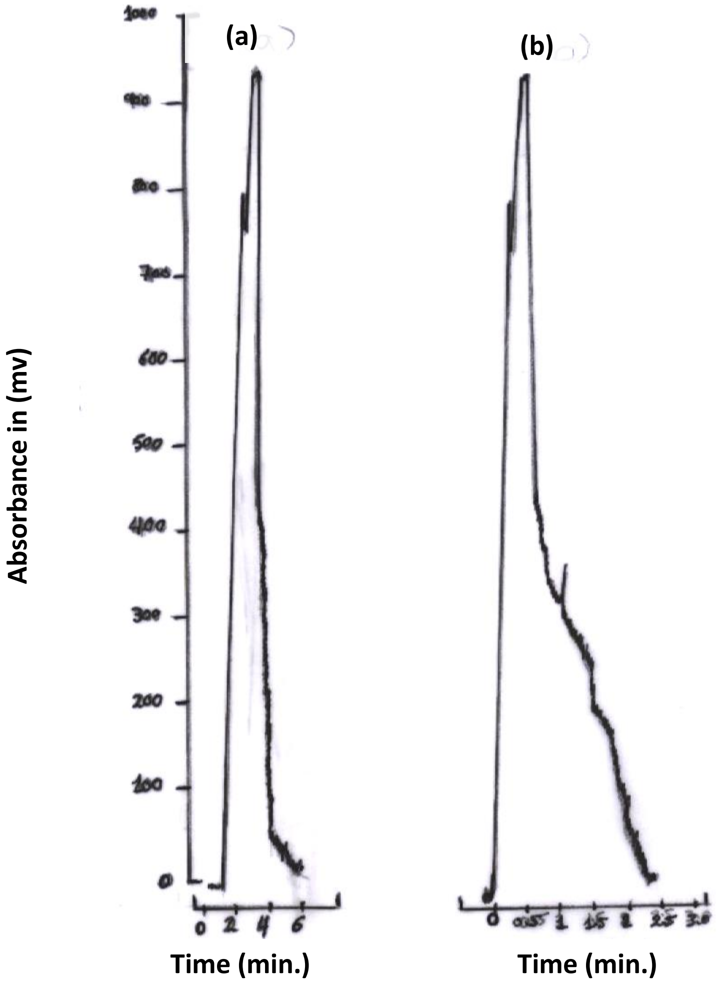


Figure (٣-١٠): Absorbance time profile of the released I٢ using FIA

a: Fast chart speed (٦min.)

b- Slow chart speed (٣min.)

Part ((B))

٣B - The components of the second unit:

This unit that is home made consists of three ways, the first way represents passing of sulphuric acid solution, while the second way passes reagent solution (potassium iodide) and the third way acts as transfer current for injected sample through an injection valve that has international design as shown in figure (٣-١١).

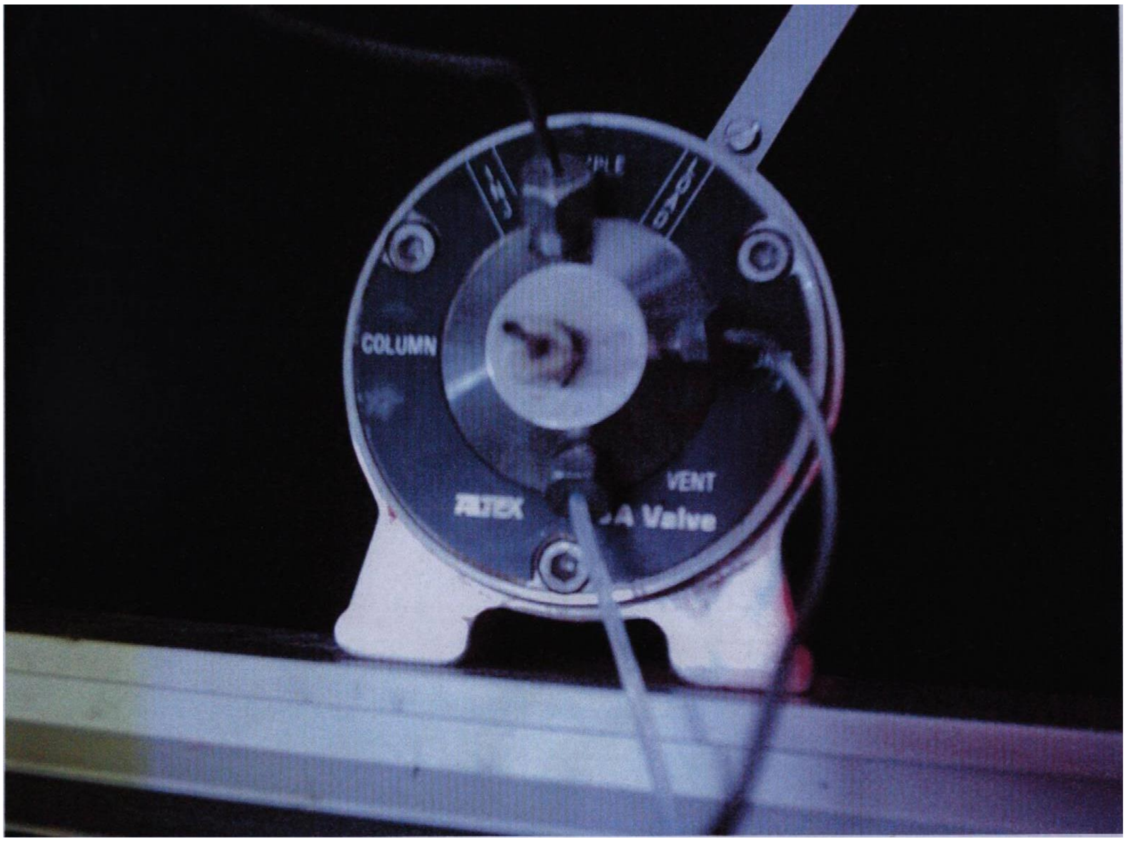


Figure (٣-١١): An injection valve

After passing acid and reagent solution through pump, figure (٣-١), which is composed of many rates and from it we can choose the optimum rate for reaction ($\mathrm{ClO}^{-}_{٣}$-I^{-}-$\mathrm{H}_{٣}\mathrm{O}^{+}$).

Then acid and reagent solutions move toward primary mixing coil after merging out from primary mixing coil will meet transfer current of sample section that represents the third way of design unit. Now these components form the reaction and it mixes in secondary mixing coil and then to completion reaction coil that is made of Teflon whose length is (١.٢ mm). Figure (٣-١٢) indicates injection point.

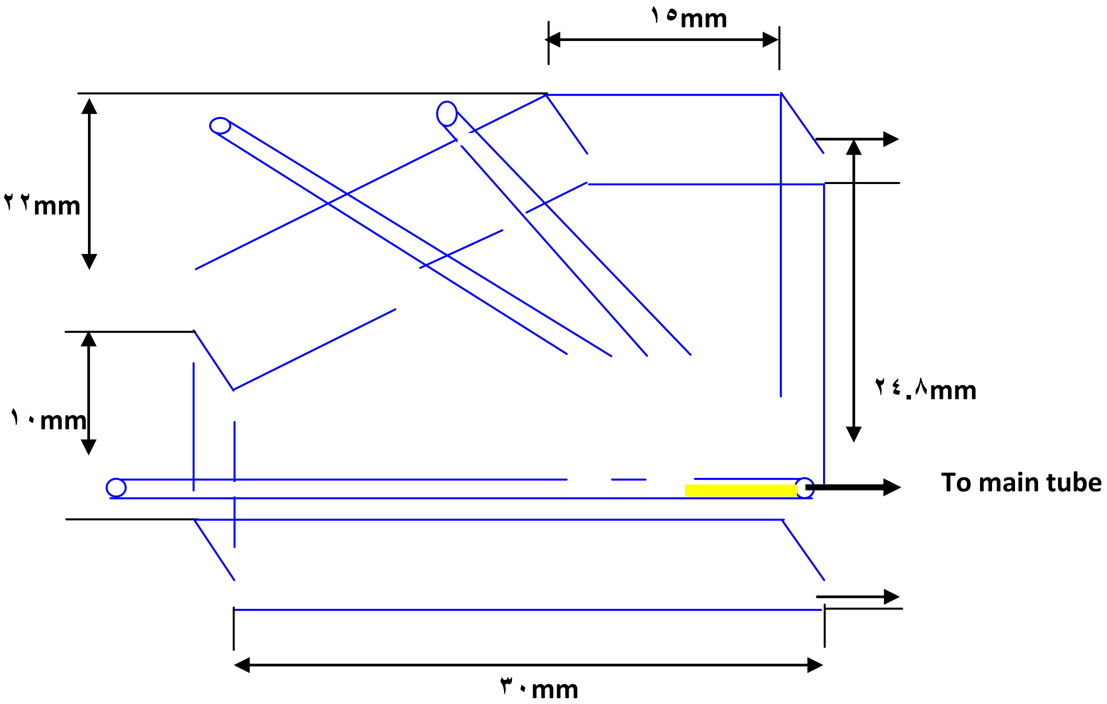


Figure (٣-١٢): Schematic sketch indicating the dimension of the injection point

A homemade flow through cell made of quartiz was used. Attached to one face a source (LED) blue, while the opposite side a photo silicone detector. Figure (٣-١٣) shows a schematic represents this cell.

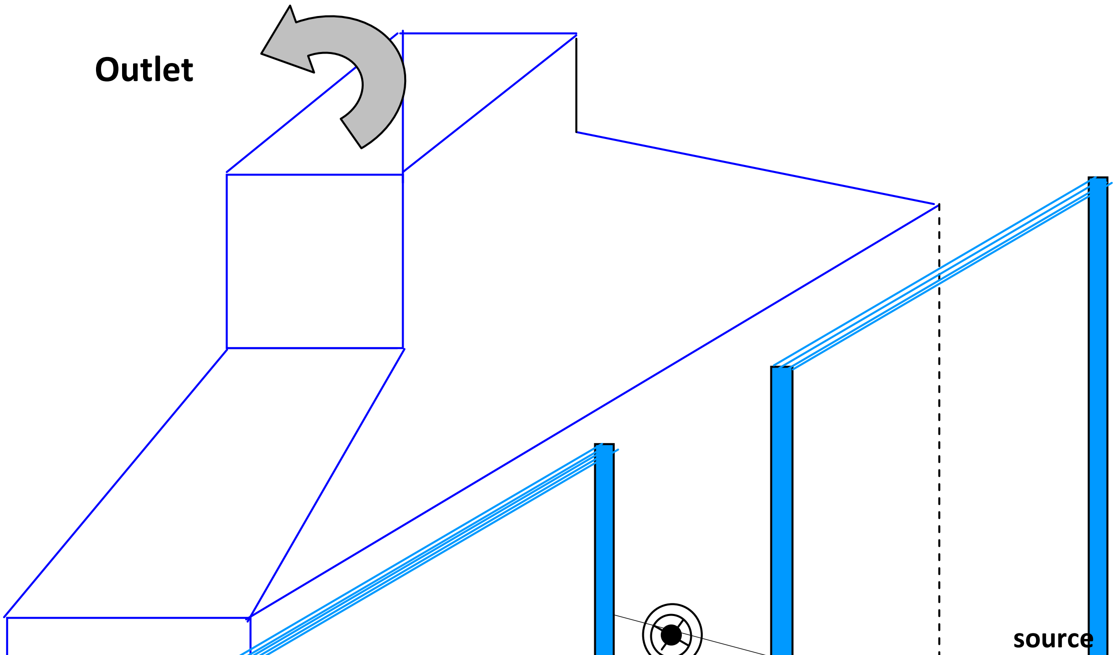


Figure (٣-١٣): Reaction cell is larger than real cell by ٢٥ time (path length ٢mm)

The output signal from photo silicone detector (Psd) passes to an amplifier followed by a read out device in our case X-T-potentiometric recorder was used.

The following figures (٣-١٤) and (٣-١٥) show the schematic diagram and shape of style unit.

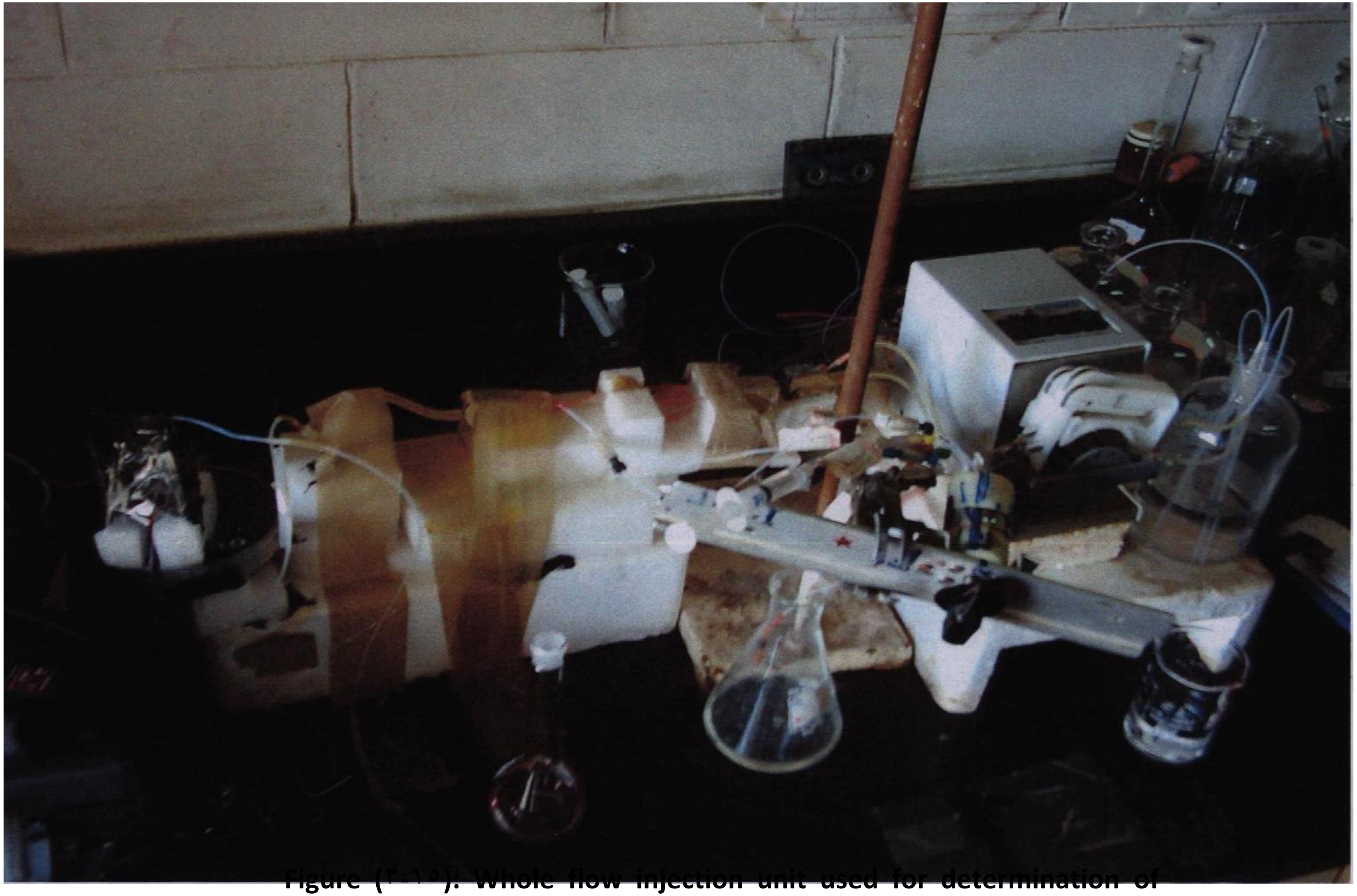


Figure (٣-١٥): Whole flow injection unit used for determination of chlorate ion.

Figure (٣-١٤) shows a complete flow injection unit for the determination of released iodine for the chlorate ion determination. Electronic unit in determination, is also shown in figure (٣-١٤).

Fast and slow chart speed was used in order to notice any hidden shoulder in the profile (i.e pure release for one product or multi release or multi reaction product as shown in figure (٣-١٦).

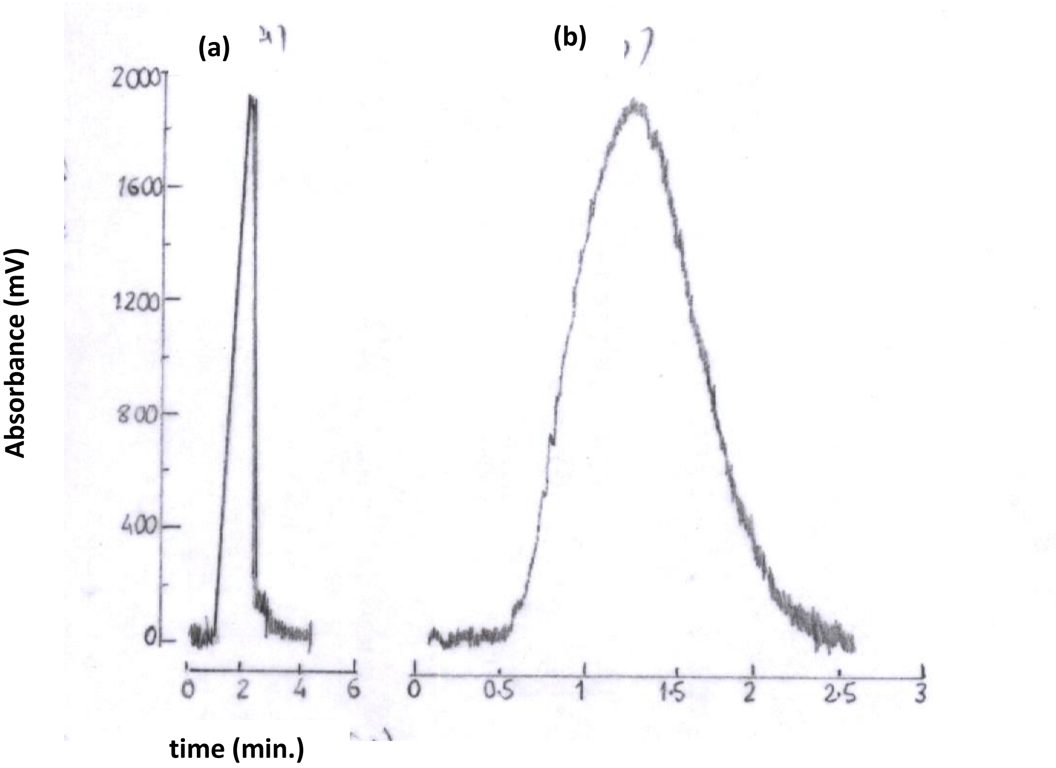


Figure (٣-١٦) Absorbance time profile of signal obtained for the released iodine from chlorate determination.

a. Fast chart speed (٤min.)

b. Slow chart speed (٢.٥min.)

Chapter Four

Results and Discussion

CHAPTER FOUR

This chapter is divided into two parts:

Part ((A)):

This part treats results, discussion and applications for unit used in part ((A)) of chapter three.

Part ((B)):

Part B deals with results, discussion and applications for the unit used in part ((B)) of chapter three.

Part ((A))

٤A-١: The study of the dispersion phenomenon in sample zone and comparison between FIA and SIA:

To measure the dispersion value in different sample zones of (٤١٧٥, ٤١٧.٥, ٤١.٧٥ µg.ml$^{-١}$) chlorate ion, two experiments were carried out by using unit in figure (٣-٩).

In the first experiment after mixing of reactants ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) and form iodine that passes through manifold unit giving continuous response of constant concentration for chlorate ion; this indicates non-existence of dispersion effect by convection or diffusion. This measurement represents (C_o). While the second experiment includes injecting different concentration of

(٤١٧٥, ٤١٧.٥, ٤١.٧٥ $\mu g.ml^{-١}$) chlorate ion in the interior loop ($L_١$) and ٣١.٤ μl of (٠.٥ $mol.L^{-١}$) potassium iodide (KI) in the exterior loop ($L_٢$), by using of (٢.٥ $mol.L^{-١}$) hydrochloric acid (HCl) as a carrier stream. The obtained value from this experiment represents intensity response for sample injected (C_{max}) as shown in figure (٤-١).

The equation used to calculate dispersion (D) is:

$$D = \frac{C_o}{C_{max}}$$

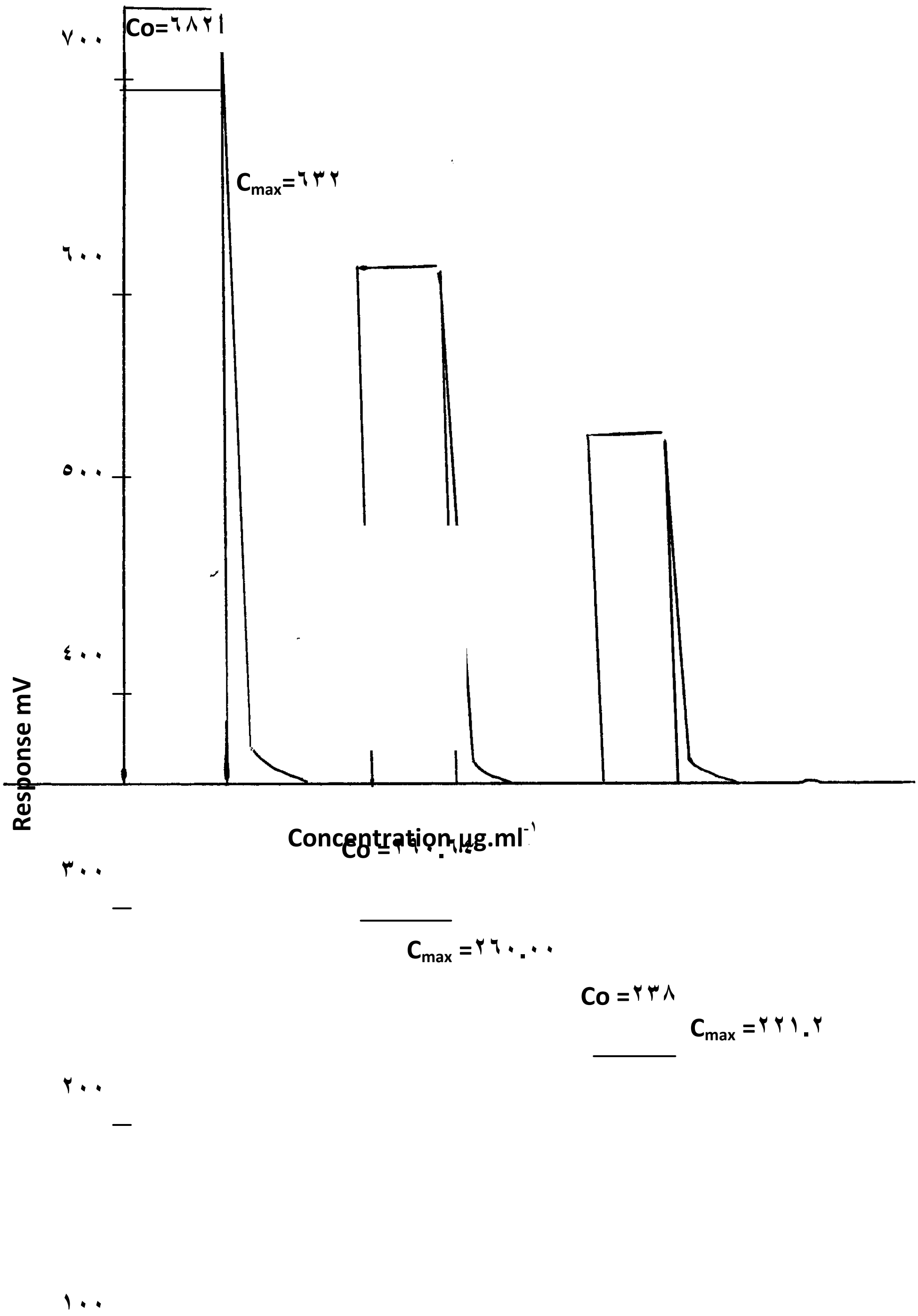
As in table (٤-١), these values fall in limit state of dispersion.

Table (٤-١): The dispersion of (٤١٧٥, ٤١٧.٥, ٤١.٧٥ $\mu g.ml^{-١}$) chlorate ion for system ($ClO_٣^- - I^- - H_٣O^+$).

Chlorate ion concentration ($\mu g.ml^{-١}$)	Response in (mV)		Dispersion (D) $D = \frac{C_o}{C_{max}}$
	C_o (mV)	C_{max} (mV)	
٤١٧٥	٦٨٢	٦٣٢	١.٠٧٩١

٤١٧.٥	٢٩٠.٦٤	٢٦٠	١.١١٧٨
٤١.٧٥	٢٣٨	٢٢١.٢	١.٠٧٥٩

The optimum value obtained from dispersion of (٤١.٧٥ μg.ml⁻¹) chlorate ion.

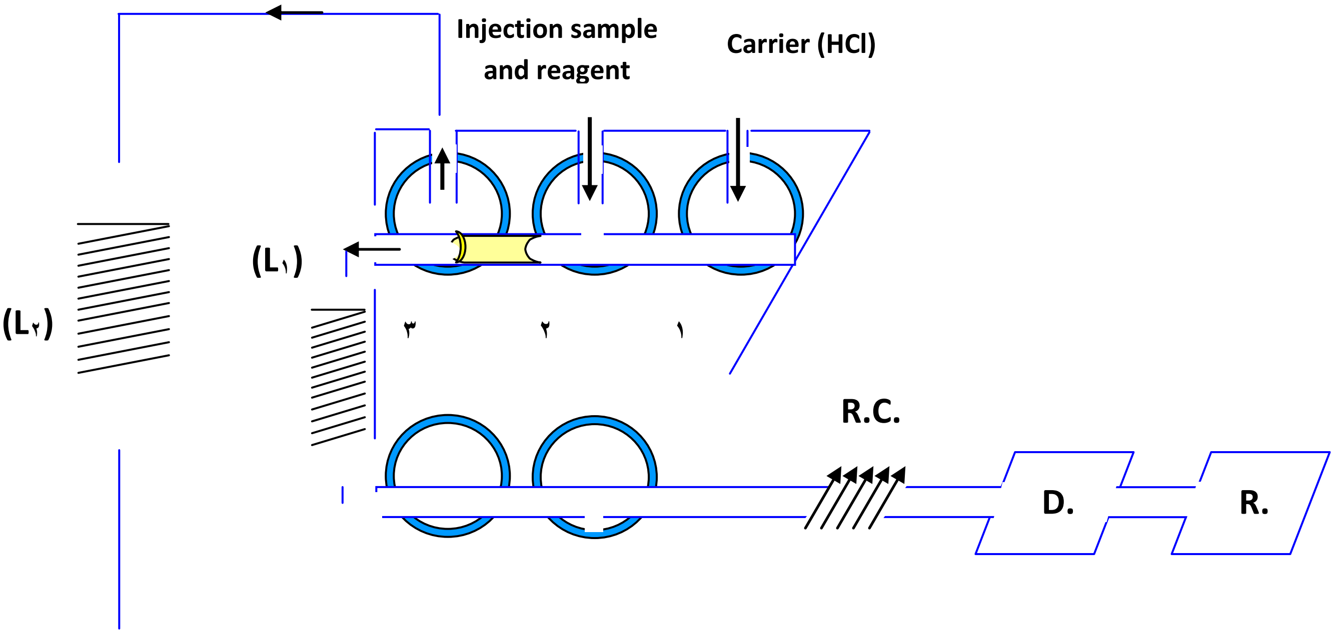


٤١٧٥ ٤١٧.٥ ٤١.٧٥

Figure (٤-١) The dispersion of chlorate Ion using (٤١٧٥, ٤١٧.٥, ٤١.٧٥ µg.ml$^{-١}$) in the system of ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$).

And the comparison between flow injection analysis and sequential injection analysis that can be noticed in the dispersion of the sample zone that is attained is shown in figures (٤-٢) and (٤-٣).

Figure (٤-٢ a, b, c) indicating new valve (Five three- ways valve) is homemade and injected (٤١٧٥, ٤١٧.٥, ٤١.٧٥ µg.ml$^{-١}$) of chlorate ion and (٠.٥ M) of potassium iodide using (٢.٥ M) of hydrochloric acid as a carrier stream In figure (٤-٢ a,b) injected chlorate ion in ($L_{١}$) and potassium iodide in ($L_{٢}$) and toward the arrow, while figure (٤-٢ c) shows pushing process the carrier (HCl) to sample and reagent and shape sample section.



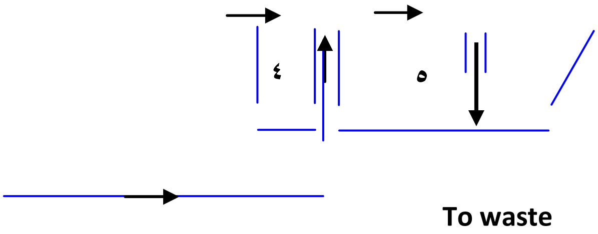
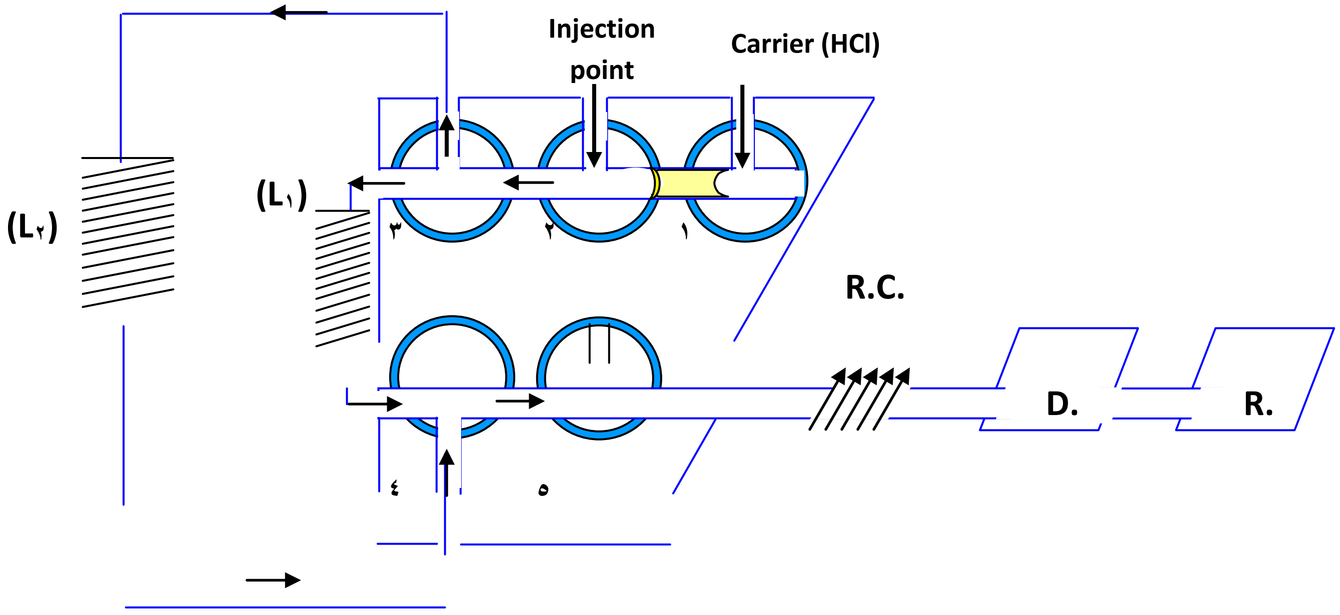
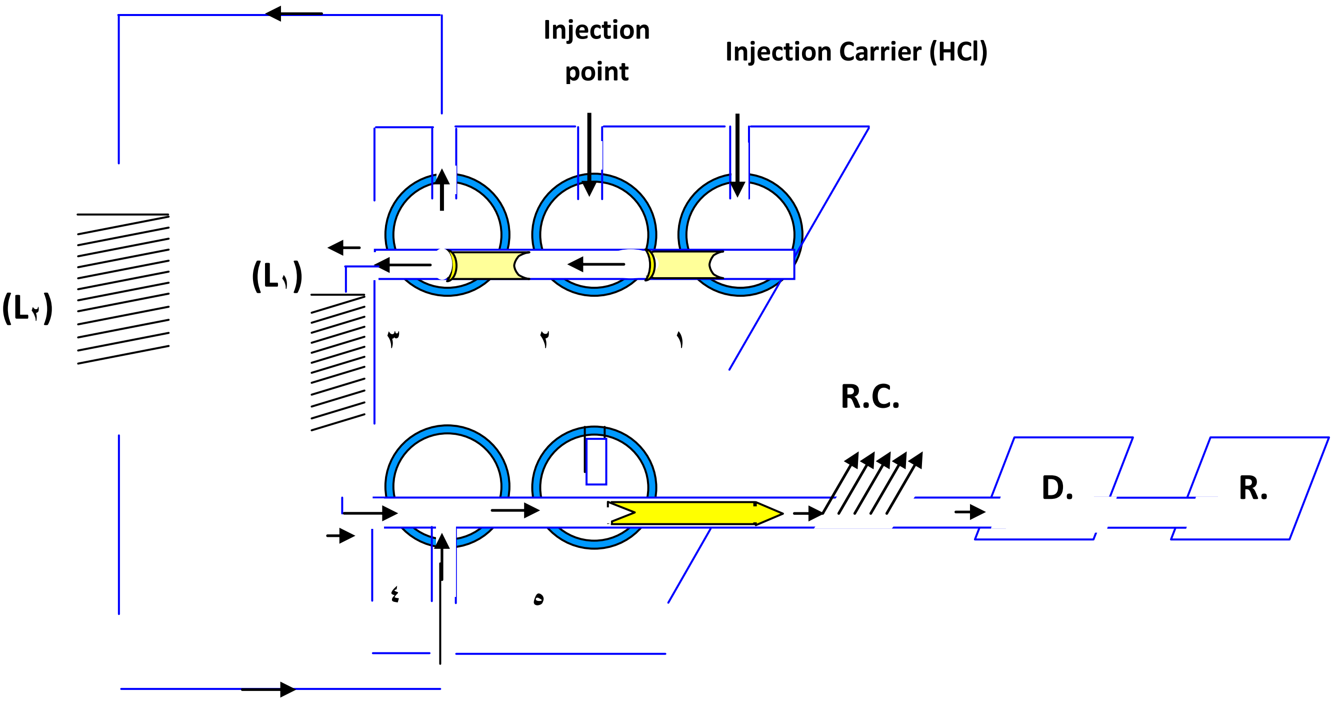


Figure (٤-٢) (a): Injection samples and reagent



(٤-٢) (b)



(٤-٢) (c)

Figure (٤-٢ a,b,c): The dispersion of sample zone in FIA critically

where: a: Injection sample and reagent.

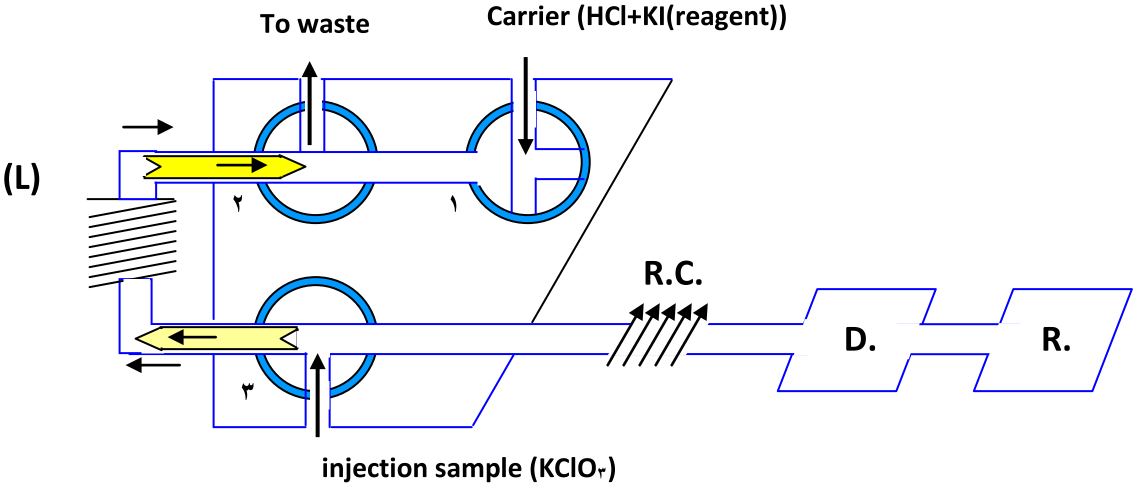
b- Injection carrier solution .

c- Dispersion of sample zone that attained in FIA.

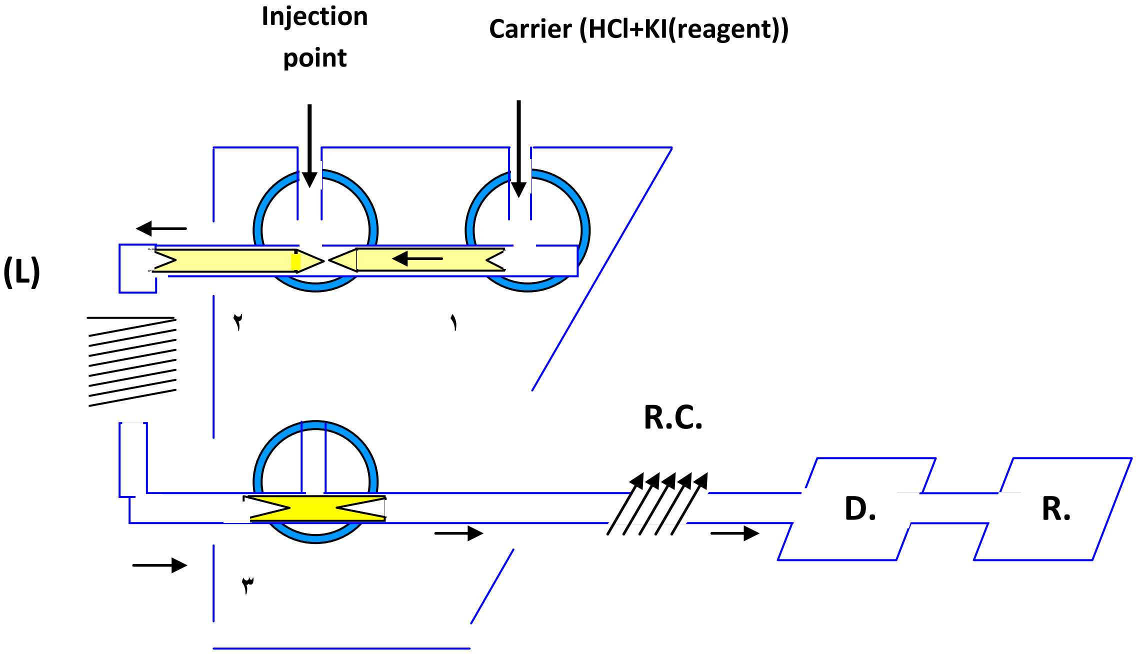
While figure (٤-٣ a, b) is three three-ways valve (homemade) injection (٤١٧٥, ٤١٧.٥, ٤١.٧٥ µg.ml$^{-١}$) of sample and (٠.٥ M) of potassium iodide (reagent) in opposite direction as in figure (٤-٣ a).

Whereas figure (٤-٣ b) indicates injection carrier to push the sample and reagent for other parts of unit and by this process noticed the shape of sample section that indicating the decreasing in dispersion.

Through these experiments in figures (٤-٢ a, b, c) and (٤-٣ a, b) we noticed the value of absorbance for released iodine to system ($ClO_٣^{-}$-I^{-}-$H_٣O^{+}$) at ٣٥٠ nm, as in table (٤-٢).



(٤-٣) (a)



(٤-٣) (b)

Figure (٤-٣ a,b): dispersion of sample zone in SIA practically

where: a: Injection sample.

b- Injection carrier solution in SIA

Figure (٤-٤), shows the comparison between FIA and SIA in dispersion of sample zone theoretically.(١١٢)

And table (٤-١) shows the difference between FIA and SIA practically.

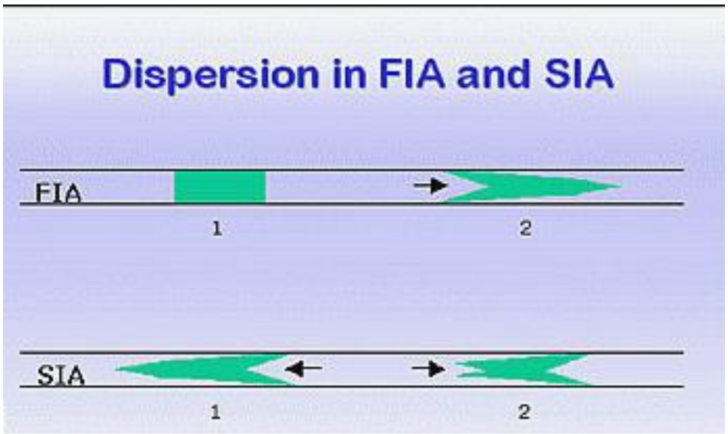


Figure (٤-٤): Comparison between FIA and SIA theoretically.

Table (٤-٢): The difference in absorbance of iodine between FIA and SIA practically using (٢.٥ M) of HCl and (٠.٥ M) of KI at ٣٥٠ nm.

Conc. Of $ClO_{٣}^{-}$ μg.ml$^{-١}$	Absorbance (FIA)	Absorbance (SIA)

	mV	mV
٤١٧.٥	٢٦٠, ٢٦٠, ٢٦٠	٧٠٠, ٧٠٠, ٧٠٠
٤١٧٥	٦٣٢, ٦٣٢, ٦٣٢	٨٨٠, ٨٨٠, ٨٨٠

٤A-٢: Physical parameters:

٤A-٢-١: Effect of flow-rate:

Flow-rate is studied by using different flow rates extends from (١.٣-٥.٥ ml.min$^{-١}$) using (١٢٧ µl) of (٠.٠٥ M) of chlorate ion and (٣١.٤ µl) of (٠.٥ M) of potassium iodide and (٢.٠M) of hydrochloric acid.

Table (٤-٣) and figure (٤-٥) show that ١.٩٥ ml.min$^{-١}$ is the optimum flow-rate to obtain the best absorbance.

Table (٤-٣): Variation of absorbance of released iodine expressed as average peak height (mV) versus flow rate at constant concentration of potassium iodide (٠.٥ M), concentration of acid (٢.٠ M) and chlorate ion (٠.٠٥M).

Flow-rate ml.min$^{-١}$	Absorbance (mV)			$\overline{Y}$	SD	%RSD	$\bar{y} \pm t \frac{\sigma_{n-1}}{\sqrt{n}}$
١.٣٠	٥٢٤	٥٢٤	٥٢٤	٥٢٤	٠	٠	٥٢٤

١.٩٥	٥٦٨	٥٦٨	٥٦٨	٥٦٨	٠	٠	٥٦٨
٢.٥٠	٥٠٨	٥٠٨	٥٠٨	٥٠٨	٠	٠	٥٠٨
٣.٠٠	٤٤٨	٤٤٨	٤٤٨	٤٤٨	٠	٠	٤٤٨
٣.٣٥	٤٢٤	٤٢٤	٤٢٤	٤٢٤	٠	٠	٤٢٤
٣.٩٥	٣٦٠	٣٦٠	٣٦٠	٣٦٠	٠	٠	٣٦٠
٤.٦٥	٣٠٤	٣٠٤	٣٠٤	٣٠٤	٠	٠	٣٠٤
٥.٥٠	٢٨٨	٢٨٨	٢٨٨	٢٨٨	٠	٠	٢٨٨

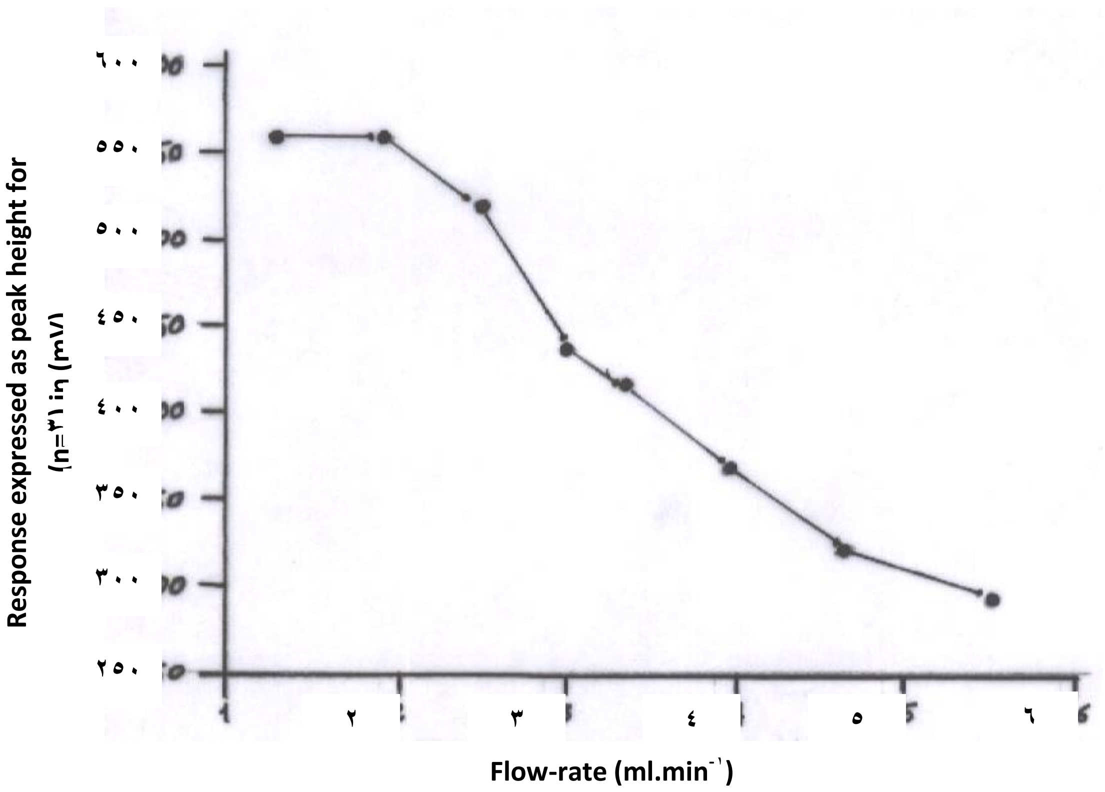


Figure (٤-٥): The effect of flow rate

٤A-٢-٢: The effect of reagent volume (KI):

A set of injected volumes of potassium iodide ranging from (١٥.٧١-٥٥.٠٠µl) by changing the length of iodide loop ($L_١$) were evaluated using (١٢٧ µl) of (٠.٠٥ M) of chlorate ion, (٢.٥ M) of hydrochloric acid as a main carrier stream and flow-rate (١.٩٥ $ml.min^{-١}$). Figure (٤-٦) and table (٤-٤) show the variation of absorbance of released iodine expressed as peak height in (mV) (average of three measurements) versus the reagent volume. A reagent volume of (٣١.٤ µl) is chosen as the optimum value.

Table (٤-٤):The effect of reagent volume KI on the reaction ($ClO_٣^- - I^- - H_٢O^+$) used in determination of chlorate ion.

Volume of reagent (µl)	Absorbance ($I_٢$) (mV)			$\overline{Y}$	SD	%RSD	$\bar{y} \pm t \frac{\sigma_{n-1}}{\sqrt{n}}$
١٥.٧١	٦١٨.٠	٦١٨.٠	٦١٨.٠	٦١٨.٠	٠	٠	٦١٨.٠
٢٣.٥٦	٦١٦.٠	٦١٤.٠	٦٠٠.٠	٦١٠.٠	٨.٧١٧	١.٤٢٩	٦١٠±٢١.٦٥٦
٣١.٤٠	٦٢٢.٤	٦٢٤.٠	٦٢٤.٠	٦٢٣.٤	٠.٩٢٣	٠.١٤٨	٦٢٣.٤±٢.٢٩٣
٣٩.٢٠	٥٤٢.٠	٥٤٠.٠	٥٤٠.٠	٥٤٠.٦	١.١٥٤	٠.٢١٣	٥٤٠.٦±٢.٨٦٧
٥٥.٠٠	٥٧٢.٠	٥٧٢.٠	٥٧٢.٨	٥٧٢.٢	٠.٤٦١	٠.٠٨٠	٥٧٢.٢±١.١٤٥

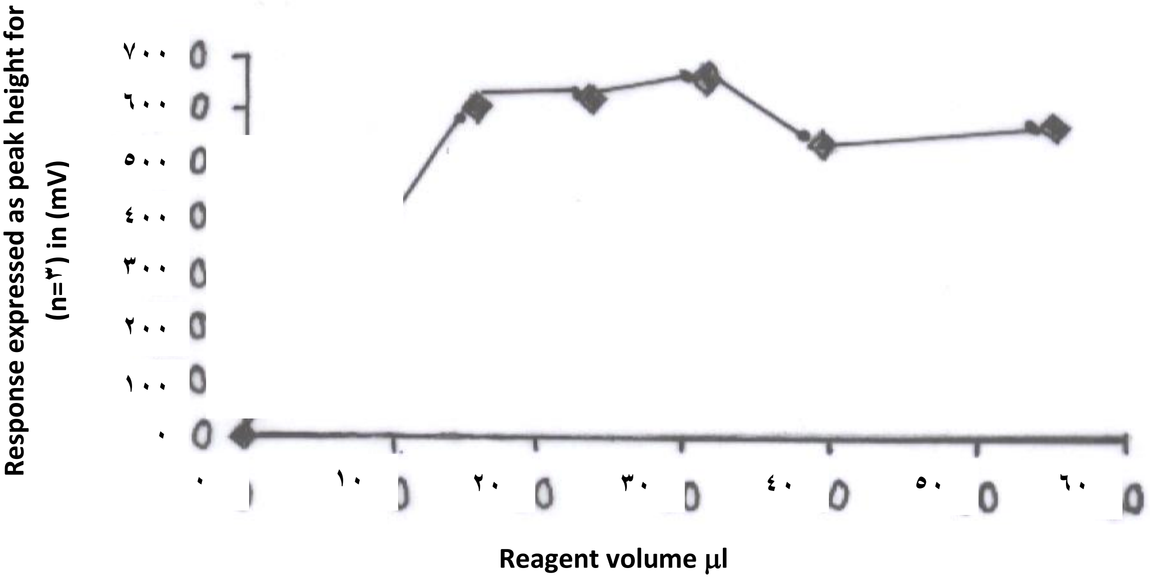


Figure (٤-٦): Effect of reagent volume (KI)

٤A-٢-٣ Effect of sample volume:

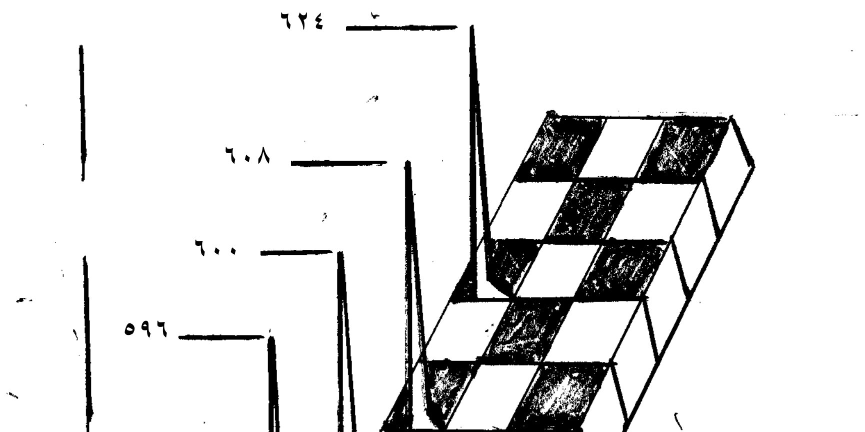
The effect of sample volume is examined in the range from (٣٦.٤-١٢٧.٠ µl) by changing the lengths of sample loop (١) using (٠.٠٥M) of chlorate ion, (٣١.٤ µl) of (٠.٥ M) of potassium iodide, (٢.٥ M) of hydrochloric acid as a carrier stream and flow-rate (١.٩٥ ml.min$^{-١}$).

Table (٤-٥) and figure (٤-٧) show the variation of absorbance of released iodine expressed as peak height in (mV) (n=٣) versus the sample volume.

(١٢٧ µl) of chlorate ion is chosen as an optimum volume, while at increasing the volume larger than (١٢٧µl) will decrease in intensity of response.

Table (٤-٥): The effect of sample volume $KClO_{٣}$ in determination of chlorate ion.

Volume of sample (µl)	Absorbance ($I_{٢}$) (mV)			$\overline{Y}$	SD	%RSD	$\bar{y} \pm t \frac{\sigma_{n-1}}{\sqrt{n}}$
٣٦.٤	٥٩٢	٥٩٢	٥٩١.٢	٥٩١.٧	٠.٥١٩	٠.٠٨٧	٥٩١.٧±١.٢٨٩
٥٤.٦	٥٩٦	٥٩٥.٦	٥٩٨	٥٩٦.٥	١.٢٨٥	٠.٢١٥	٥٩٦.٥±٣.١٩٢
٧٢.٨	٦٠٠	٦٠٠	٦٠٠	٦٠٠.٠	٠.٠٠٠	٠.٠٠٠	٦٠٠
٩١.٠	٦٠٨	٦٠٨	٦٠٨	٦٠٨.٠	٠.٠٠٠	٠.٠٠٠	٦٠٨
١٢٧.٠	٦٢٤	٦٢٣.٢	٦٢٤	٦٢٣.٧	٠.٤٦١	٠.٠٧٤	٦٢٣.٧±١.١٤٥



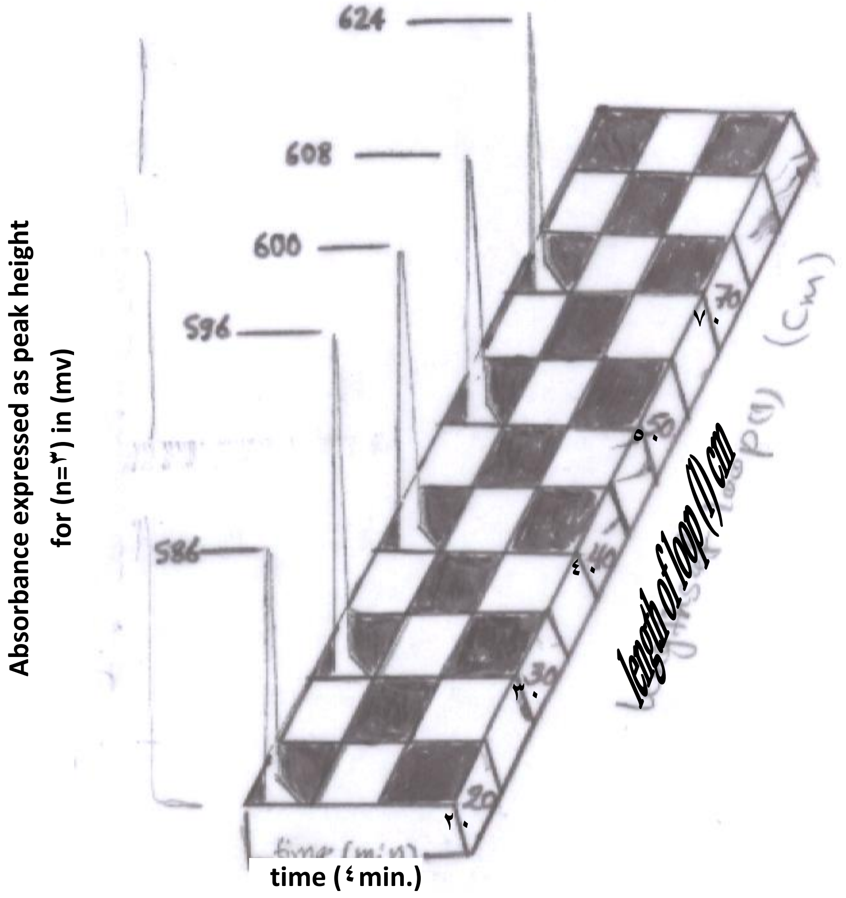


Figure (٤-٧): The effect of $ClO_{٣}^{-}$ volume concentration

٤A-٢-٤: Effect of interior loop shape:

Interior loop represents loop (١) for chlorate ion ($ClO_{٣}^{-}$); in this experiment loop (١) is used as a helix shape and other time is linear shape, and shows the difference between the two peaks that were obtained in both cases.

Table (٤-٦) and figures (٤-٨) and (٤-٩) show the difference in the absorbance by using the different shape.

From this experiment, linear loop (١) is more important than helix loop (١), because the linear shape gives a nice narrow peak with higher response and without shoulder, figure (٤-٩) shows the shape of the loop.

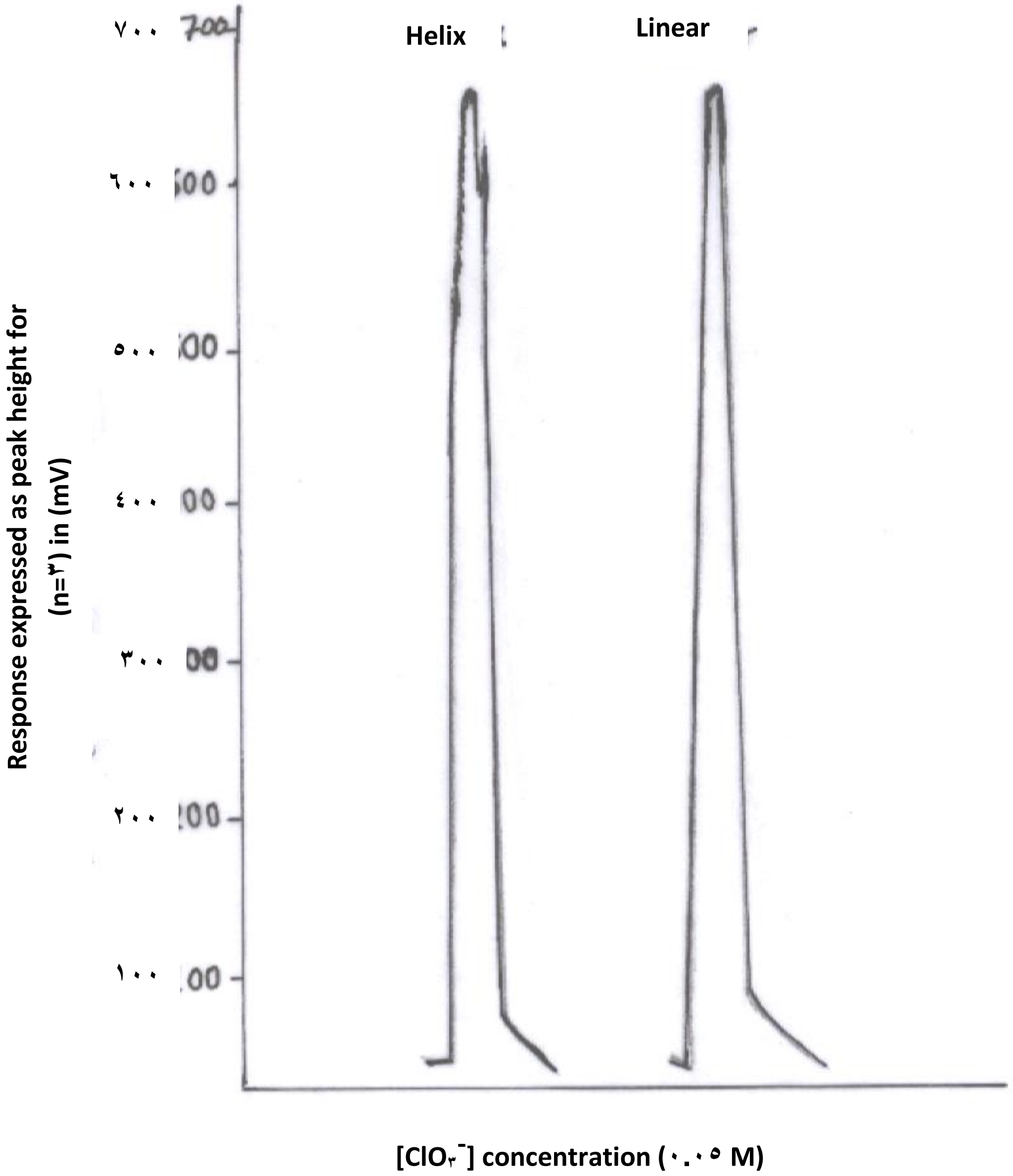
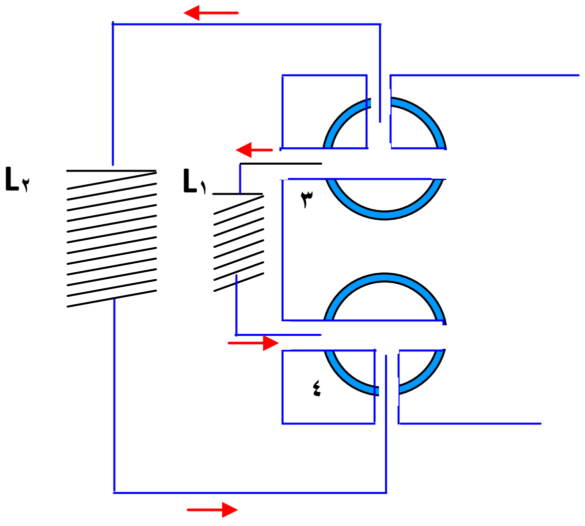


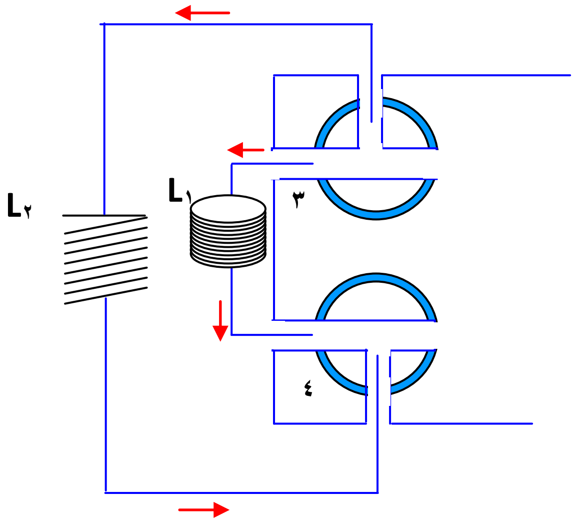
Figure (٤-٨): The difference in response between linear and helix loop(١)

Table (٤-٦): Variation of absorbance of released iodine at (λ=٣٥٠ nm) expressed as average peak height (mV) versus the shape of loop (١) at concentration of sample (٠.٠٥M), carrier [HCl] (٢.٥ M) and reagent KI (٠.٥ M) and flow rate (١.٩٥ ml.min$^{-١}$).

Shape of loop (١)	Absorbance ($I_٢$) in (mV)			$\overline{Y}$	SD	%RSD	$\bar{y} \pm t\frac{\sigma_{n-1}}{\sqrt{n}}$
Helix	٦٠٠	٦٠٨.٠	٦٠٦.٠	٦٠٤.٦	٤.١٦٣	٠.٦٨٨	٦٠٤.٦±١٠.٣٤٢
Linear	٦٢٠	٦١٩.٦	٦٢٠.٠	٦١٩.٨	٠.٢٣٠	٠.٠٣٧	٦١٩.٨±٠.٥٧١



(a) Linear of loop (١)



(b) Helix of loop (١)

Figure (٤-٩): The difference in shape of loop (١)

a- Linear shape

b- Helix shape

٤A-٢-٥: Effect of reaction coil length

By changing the reaction coil length from (٥٠-٢٠٠ cm), it has been showen that the sensitivity of the method for the determination chlorate ion increases with the increase of length of the reaction coil by using (٠.٠٥M) of chlorate ion, (٠.٥ M) of potassium iodide, (٢.٥ M) of hydrochloric acid and flow rate (١.٩٥ $ml.min^{-١}$); this was due to the long residence time resulting from the increase in the reaction yield that was up to (١٠٠ cm), increase and base width of response will increase too due to the dispersion from the results.

Table (٤-٧) and figure (٤-١٠) show the absorbance in (mV) versus reaction coil length (cm).

(١٠٠ cm) length is selected for reaction coil as an optimum length.

Table (٤-٧): The effect of reaction coil length on the released iodine in the determination of chlorate ion

Length of coil (cm)	Absorbance ($I_{٢}$) (mV)	$\overline{Y}$	SD	%RSD	$\bar{y} \pm t\frac{\sigma_{n-1}}{\sqrt{n}}$

٥٠	٦٢٢	٦٣٦	٥٩٦	٦١٨.٠٠	٢٠.٢٩٧	٣.٢٨٤	٦١٨±٥٠.٤٢٦
١٠٠	٦٢٦	٦٢٨	٦٢٦	٦٢٦.٦٦	١.١٥٤	٠.١٨٤	٦٢٦.٦٦±٢.٨٦٨
١٥٠	٦٣٦	٦٣٢	٦٤٠	٦٣٦.٠٠	٤.٠٠٠	٠.٦٢٨	٦٣٦±٩.٩٣٧
٢٠٠	٦٤٠	٦٣٦	٦٣٢	٦٣٦.٠٠	٤.٠٠٠	٠.٦٢٨	٦٣٦±٩.٩٣٧

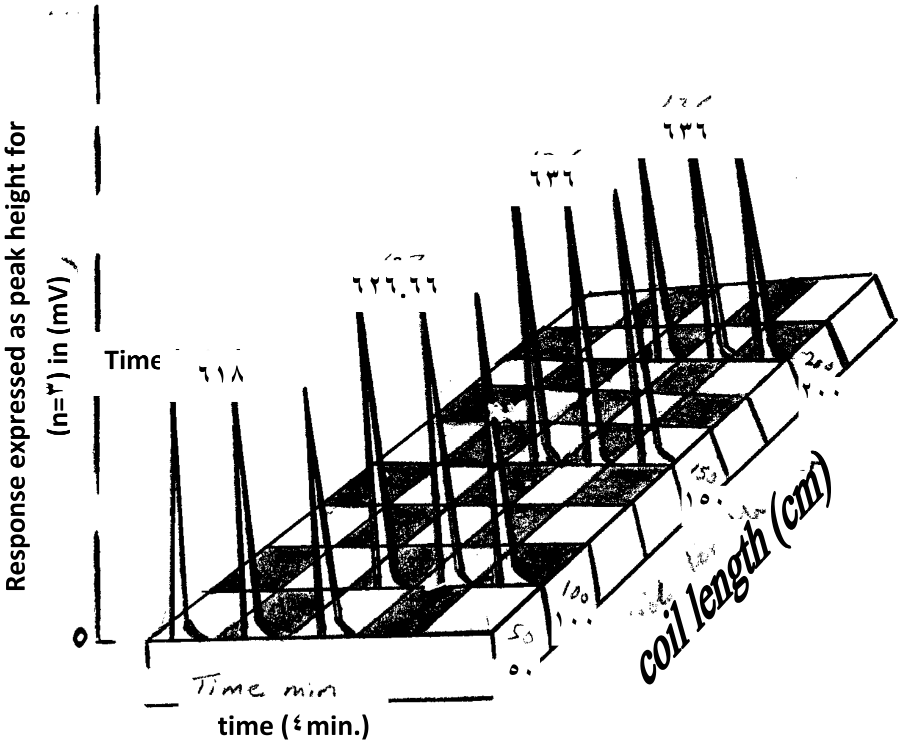


Figure (٤-١٠): The effect of the reaction coil length

٤A-٢-٦: Effect of temperature

The reaction of (٠.٥ M) potassium iodide and (٢.٥ M) of hydrochloric acid as a carrier stream with (١٢٧ µl) of (٠.٠٥M) chlorate ion is done in different temperature by use optimum condition obtained previously former. It was found that there was no effect of temperature between (٢٠-٥٠ ºC) on the reaction, as shown in table (٤-٨).

Table (٤-٨): The effect of temperature on the absorbance of iodine released in the reaction system ($ClO_{٣}^{-}-I^{-}-H_{٣}O^{+}$).

Temperature °C	Absorbance ($I_{٢}$) (mV)			$\bar{Y}$	SD	%RSD	$\bar{y} \pm t \frac{\sigma_{n-1}}{\sqrt{n}}$
٢٠	٣٢٨.٠	٣٢٨.٠	٣٢٧.٦	٣٢٧.٨٦	٠.٢٣٠	٠.٠٧٠	٣٢٧.٨٦±٠.٠٥٧١
٣٠	٣٢٧.٦	٣٢٧.٦	٣٢٨.٠	٣٢٧.٧٣	٠.٢٣٠	٠.٠٧٠	٣٢٧.٧٣±٠.٠٥٧١
٤٠	٣٢٨.٤	٣٢٨.٠	٣٢٨.٠	٣٢٨.١٣	٠.٢٣٠	٠.٠٧٠	٣٢٨.١٣±٠.٠٥٧٣
٥٠	٣٢٨.٠	٣٢٧.٦	٣٢٨.٠	٣٢٧.٨٦	٠.٢٣٠	٠.٠٧٠	٣٢٧.٨٦±٠.٠٥٧٣

٤A-٣: Chemical parameters:

٤A-٣-١: Influence of acid concentration

Variable acid concentrations (١.٠-٢.٥ M) are used in the reaction of (٠.٠٥M) chlorate ion with (٠.٥ M) of potassium iodide and flow rate (١.٩٥ ml.min$^{-١}$) to release the iodine which is measured at ٣٥٠ nm.

The results showed that the concentration of iodine generated increase swiftly with acid concentration up to (٢.٢٥ M) and the absorbance will be constant when the concentration is larger than (٢.٥ M).

(٢.٥ M) of acid is selected for this study. Table (٤-٩) and figure (٤-١١) show the variation of absorbance of released iodine expressed as average peak height in (mV) versus the concentration of (HCl).

Table (٤-٩): The effect of hydrochloric acid concentration on the peak height in the reaction of $(ClO_{٣}^{-}-I^{-}-H_{٣}O^{+})$.

Conc. of HCl (mol.$L^{-١}$)	Absorbance $I_{٢}$ (mV)			$\overline{Y}$	SD	%RSD	$\bar{y} \pm t \frac{\sigma_{n-1}}{\sqrt{n}}$
١.٠٠	٢٢٠	٢٢٨	٢٢٦	٢٢٤.٦٦	٤.١٦٣	١.٥٨٣	٢٢٤.٦٦±١٠.٣٤٣
١.٥٠	٣١٢	٣١٠	٣١٤	٣١٢.٠٠	٢.٠٠٠	٠.٦٤١	٣١٢.٠٠±٤.٩٦٨
٢.٠٠	٤٨٠	٤٨٦	٤٨٤	٤٨٣.٣٣	٣.٠٥٥	٠.٦٣٢	٤٨٣.٣٣±٧.٥٨٩
٢.٢٥	٥٩٨	٥٩٨	٥٩٨	٥٩٨.٠٠	٠.٠٠٠	٠.٠٠٠	٥٩٨
٢.٥٠	٦٠٤	٦٠٦	٦٠٤	٦٠٤.٦٦	١.١٥٤	٠.١٩٠	٦٠٤.٦٦±٢.٨٦٨

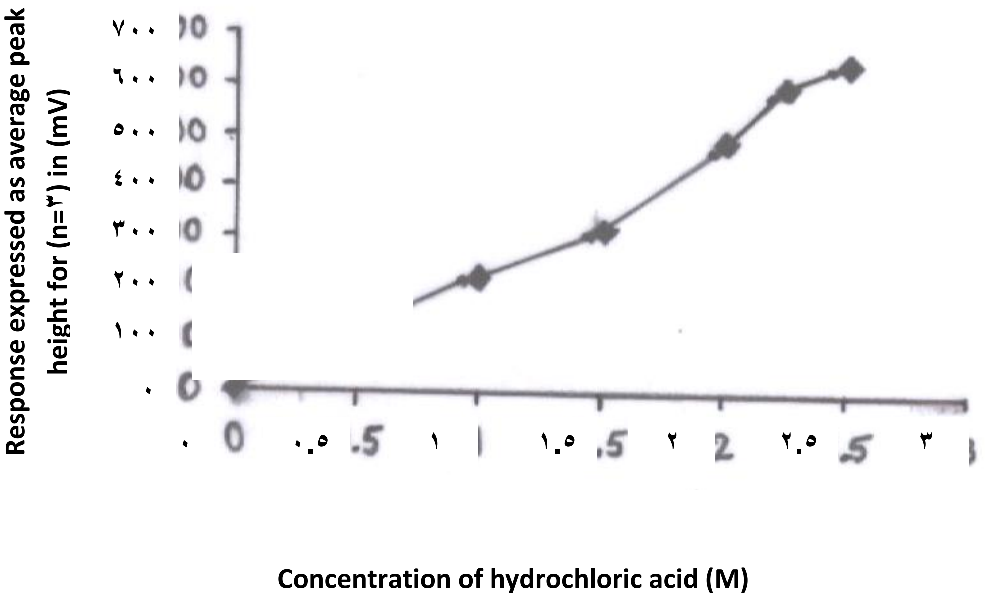


Figure (٤-١١) Effect of hydrochloric acid concentration

٤A-٣-٢: The effect of potassium iodide concentration

The effect of potassium iodide concentration for absorption measurements is studied in the range of (٠.٠٢٥-٠.٦٢٥ M) that can be used in the second loop (٣١.٤ µl).

By using (١٢٧ µl) of (٠.٠٥M) chlorate ion, (٢.٥ M) of hydrochloric acid is used as a carrier stream and flow-rate(١.٩٥ ml.min$^{-١}$).

Figure (٤-١٢) shows the variation of absorbance expressed as average peak height (n=٣) in mV versus the molar concentration of potassium iodide solution.

The results showed that by increasing potassium iodide concentration up to (٠.٥ M) the absorbance of the released iodine increased, and at higher than the value is decreased.

(٠.٥ M) of potassium iodide concentration is selected for the further study and the results are shown in the table (٤-١٠).

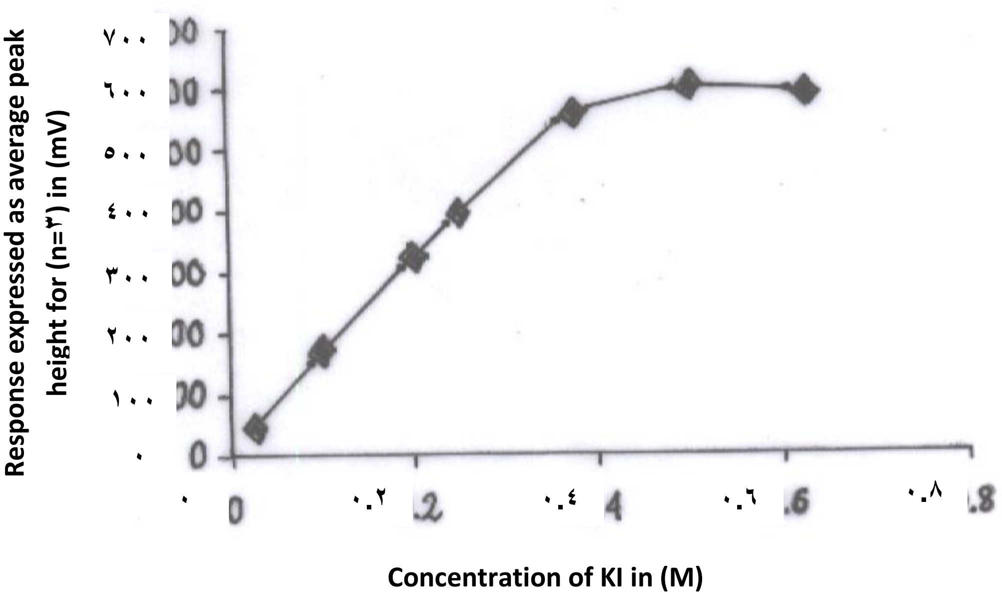


Figure (٤-١٢) Effect of potassium iodide concentration

Table (٤-١٠): The effect of potassium iodide concentration on the system (ClO$_٣^-$-I$^-$-H$_٣$O$^+$) used in determination of chlorate ion.

Conc. of KI (mol.L$^{-١}$)	Absorbance (mV)			$\overline{Y}$	SD	%RSD	$\bar{y} \pm t\frac{\sigma_{n-1}}{\sqrt{n}}$
٠.٠٢٥	٤٤.٤	٤٤.٠	٤٤.٠	٤٤.١٣	٠.٢٣٠	٠.٥٢٣	٤٤.١٣±٠.٥٧١

٠.١٠٠	١٦٨.٠	١٦٨.٠	١٦٤.٠	١٦٦.٦٦	٠.٣٠٩	١.٣٨٥	١٦٦.٦٦±٠.٧٦٧
٠.٢٠٠	٣٢٤.٠	٣٢٦.٠	٣٢٢.٠	٣٢٤.٠٠	٢.٠٠٠	٠.٦١٧	٣٢٤±٤.٩٦٨
٠.٢٥٠	٣٩٢.٠	٤٠٠.٠	٣٩٤.٠	٣٩٥.٣٣	٤.١٦٣	١.٠٥٣	٣٩٥.٣٣±١٠.٣٤٣
٠.٣٧٥	٥٥٦.٠	٥٥٨.٠	٥٥٦.٠	٥٥٦.٦٦	١.١٥٤	٠.٢٠٧	٥٥٦.٦٦±٢.٨٦٨
٠.٥٠٠	٦٠٠.٠	٦٠٠.٠	٦٠٠.٠	٦٠٠.٠٠	٠.٠٠٠	٠.٠٠٠	٦٠٠
٠.٦٢٥	٥٨٥.٦	٥٨٥.٠	٥٨٥.٠	٥٨٥.٨٠	٠.٢٣٠	٠.٠٣٩	٥٨٥.٨±٠.٥٧١

٤A-٤ : Calibration graph:

A series of potassium chlorate solutions of the range (٠.٠٠٨٣٥-٤١٧٥μg.$ml^{-١}$) were prepared from stock solutions under the optimum conditions of reagent and manifold variables, by repeating the measurement of each concentration three times as indicated in table (٤-١١).

The typical detector response for iodine is shown in figure (٤-١٣). The treatment of the results in linear regression terms is shown in table (٤-١٢).

Table (٤-١١): Results of Changing the response with concentration

[ClO$_{٣}^{-}$] ppm	Response for n=٣ $\bar{y}$ in (mV)	$\sigma_{n-١}$ / %RSD	$\bar{y} \pm t_{0.05} \frac{\sigma_{n-1}}{\sqrt{n}}$	$\hat{y}$ predicted in (mV)
٠	٠	٠	٠	٥٥.٥٨
٠.٠٠٨٣٥	٢٠٨	٠	٢٠٨	٢١٣.٨١
٠.٠٤	٢٠٩.٣	٢.٣٠٩ ١.١٠٣	٢٠٩.٣±٥.٧٣٦	٢١٣.٨٢
٠.٠٨	٢١٢	٠	٢١٢	٢١٣.٨٣
٠.٤٢	٢١٣.٤	٢.٣٠٩ ١.٠٨٢	٢١٣.٤±٥.٧٣٦	٢١٣.٨٧
٠.٨٤	٢١٤.٦	٢.٣٠٩ ١.٠٧٥	٢١٤.٦±٥.٧٣٦	٢١٣.٩١
٤.١٨	٢١٥.٣	١.١٥٤ ٠.٥٣٦	٢١٥.٣±٢.٨٦٧	٢١٤.٢٤
٨.٣٥	٢١٦	٠	٢١٦	٢١٤.٦٦
١٦.٧	٢١٧.٣	٢.٣٠٩ ١.٠٦٢	٢١٧.٣±٥.٧٣٦	٢١٥.٥
٤١.٧٥	٢٢٠	٠	٢٢٠	٢١٨.٠١
٦٦.٨	٢٢١.٣	٢.٣٠٩ ١.٠٤٣	٢٢١.٣±٥.٧٣٦	٢٢٠.٥
٨٣.٥	٢٢٢.٦	٢.٣٠٩ ١.٠٣٧	٢٢٢.٦±٥.٧٣٦	٢٢٢.١٩
١٦٧	٢٣٢	٠	٢٣٢	٢٣٠.٥
٤١٧.٥	٢٦٠	٠	٢٦٠	٢٥٥.٦٥
٦٦٨	٢٨١.٣	٢.٣٠٩ ٠.٨٢٠	٢٨١.٣±٥.٧٣٦	٢٨٠.٧٥

٢٩٧.٤٨	٢٩٧.٣±٥.٧٣٦	٢.٣٠٩ ٠.٧٧٦	٢٩٧.٣	٨٣٥
٣٨١.١٣	٣٨٠	٠	٣٨٠	١٦٧٠
٦٣٢.٠٩	٦٣٢	٠	٦٣٢	٤١٧٥

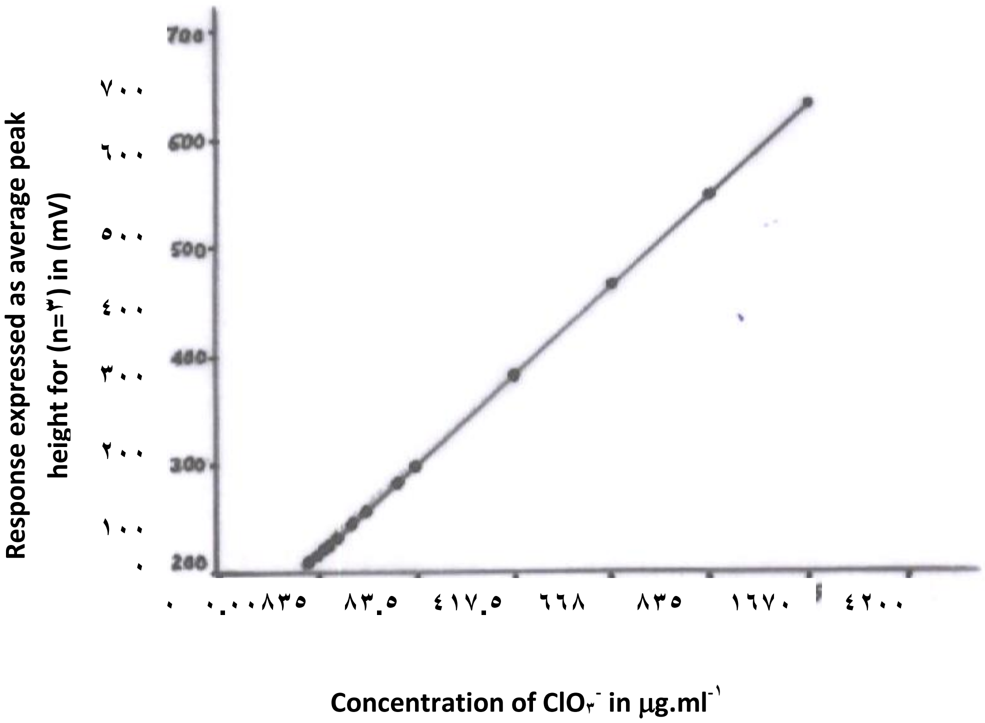


Figure (٤-١٣) Determination of chlorate ion by changing the response with concentration for system ($ClO_{٣}^{-}$- I^{-}-$H_{٣}O^{+}$)

Table (٤-١٢) Changing the response with concentration for obtaining on the calibration curve

<table>
<tr><td colspan="2">Lowest value theoretically can begin it calibration curve x=٥DL µg.ml$^{-١}$</td><td>٢٥*١٠$^{-١٠}$ mol.L$^{-١}$</td></tr>
<tr><td rowspan="3">Detection limit each ١٥µL</td><td>Theoretically from linear equation y=L.O.D.=$Y_B + ٣S_B$ at confidence limit ٩٥٪</td><td>٢٢١.٠ mol.L$^{-١}$</td></tr>
<tr><td>Theoretically from equation D.L= $\frac{3S_D}{slope}$</td><td>١.٠٧*١٠$^{-٦}$ mol.L$^{-١}$</td></tr>
<tr><td>Theoretically from dilution to low conc. In calibration curve</td><td>٦.١٢*١٠$^{-٥}$ µg.ml$^{-١}$</td></tr>
<tr><td colspan="2">Conc. Allowed to reach it calibration curve (١٠٪r→r)</td><td>٠.٩٩٩٧→٠.٨٩٩٧٣</td></tr>
<tr><td colspan="2">T calculate from $t = \frac{|t|\sqrt{n-2}}{\sqrt{1-r^2}}$</td><td>٧٠٥.٤</td></tr>
<tr><td colspan="2">T from table at confidence limit ٩٥٪ for (n-٢)</td><td>٤.٣٠٣</td></tr>
<tr><td colspan="2">Correlation coefficient and percentage of linearity %r^{٢}</td><td>٠.٩٩٩٧
٪٩٩.٩٤</td></tr>
<tr><td colspan="2">No. of $[ClO_{٢}^{-}]$ measured</td><td>٢٥</td></tr>
<tr><td colspan="2">Linear equation at confidence limit ٩٥٪ Abs.I. (mV)=(a±Sat)+(b±Sbt) $[ClO_{٢}^{-}]$ µg.ml$^{-١}$</td><td>٢١٣.٨٢٨٨٩±١.٥٨٢*٤.٣٠٣+٨٣٦٥.٢٨±٠.٣٨١*٤.٣٠٣</td></tr>
</table>

Range of [$ClO_٣^-$] in μg.ml$^{-١}$ in calibration curve (range)	٠.٠٠٠٨٣٥→٤١٧٥
[$ClO_٣^-$] in μg.ml$^{-١}$ measured	٤.١٥*١٠$^{-٥}$→٤١٧٥

٤A-٥: Reproducibility

Reproducibility is studied in determination of chlorate ion via measurement of released iodine from system ($ClO_٣^-$-I^--$H_٣O^+$) by using (٠.٠٥M) of chlorate ion, (٠.٥M) of potassium iodide, (٢.٥ M) of hydrochloric acid with flow-rate of ١.٩٥ ml.min$^{-١}$.

The relative standard deviation (R.S.D.) for replicate injections (n=١٠) is found to be ٠.٠٤٣٢ as in table (٤-١٣).

Table (٤-١٣): The reproducibility for this method using in determination of chlorate ion by system ($ClO_٣^-$-I^--$H_٣O^+$).

Conc. of $ClO_٣^-$ in (μg.ml$^{-١}$)	Peak height (cm) for n=١٠	Peak height (mV) for n=١٠	$\overline{Y}$ (mV)	$\sigma_{n-١}$	%RSD	$\bar{y} \pm t\frac{\sigma_{n-1}}{\sqrt{n}}$
٤١٧٥	١٥.٦	٦٢٤	٦٢٤	٠.٢٦٩٩	٠.٠٤٣٢	٦٢٤±٠.١٩٢٩

The mean percentage recovery of chlorate ion concentration of ٩٩.٩٦ % is obtained as shown in figure (٤-١٤).

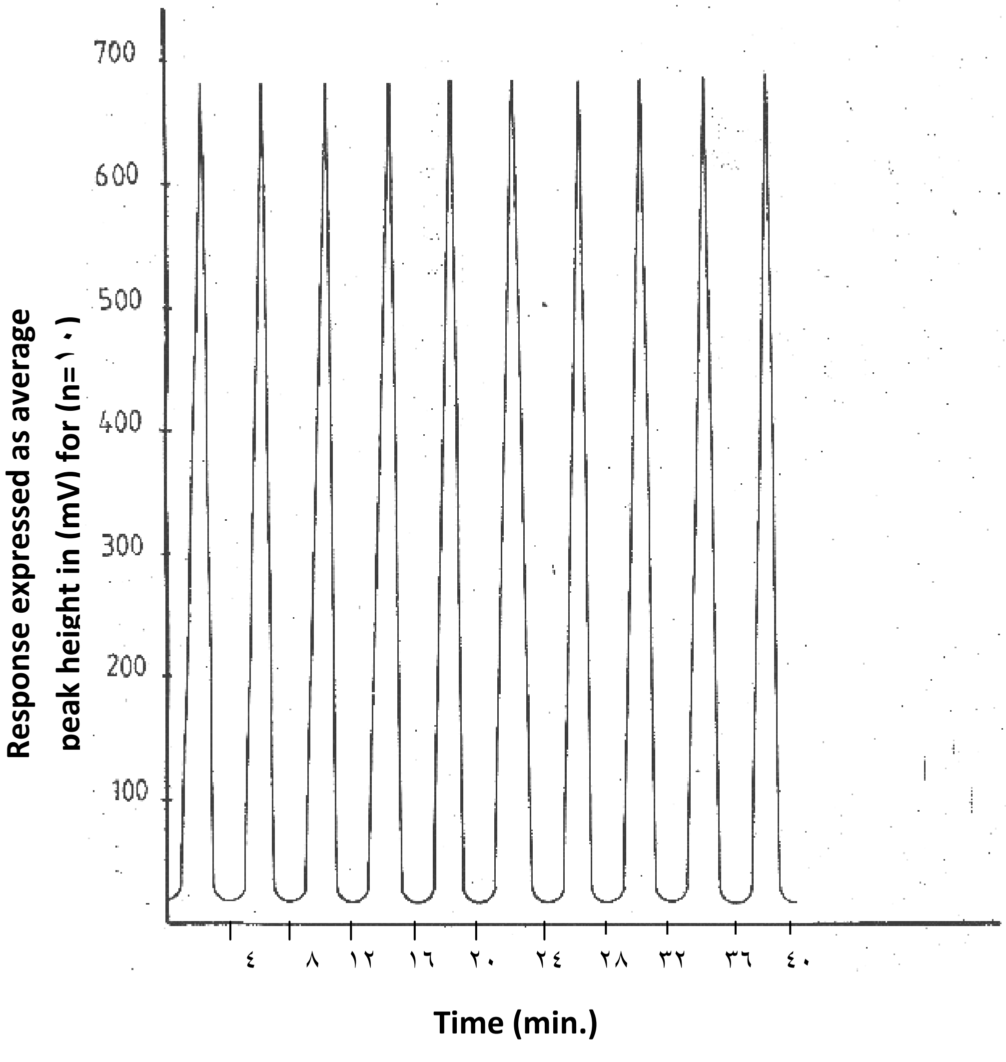

Response expressed as average peak height in (mV) for (n=١٠)
700
600
500
400
300
200
100
٤
٨
١٢
١٦
٢٠
٢٤
٢٨
٣٢
٣٦
٤٠
Time (min.)

Figure (٤-١٤): The reproducibility of ten measurements of released iodine for ($٥*١٠^{-٢}$ M) chlorate ion

٤A-٦: Detection limit(١١٤)

detection limit (DL) is defined as the concentration corresponding to a signal three times the noise level of the background, in fact, it is the point at which we can make a decision on whether the element or the compound is present or not. Three times the detection limit is often called the limit of determination (LOD). In the determination of chlorate ion, the LOD found is $٥×١٠^{-١٠}$ mol.$L^{-١}$ and its mean is ($٦.١٢×١٠^{-٥}$ ppm in µg.$ml^{-١}$).

٤A-٧: Study of the interference

Many of foreign ions are studied in this method to ensure the validity of the proposed method for the determination of chlorate ion. The effect of various foreign ions on the determination of (٤١٧٥ µg.$ml^{-١}$) of chlorate ion is studied and table (٤-١٤) shows the results of this study by using many cations and anions. It can be seen that there is no serious interference at the studied level.

Table (٤-١٤): Effect of interfering ions

Interference Effect %												**Conc. of cation fold**
$CO^{+٢}$	$Cd^{+٢}$	$Cu^{+٢}$	$Mn^{+٢}$	$Sn^{+٢}$	$Pb^{+٢}$	$Zn^{+٢}$	$Fe^{+٣}$	$NH_{٤}^{+}$	K^{+}	Na^{+}	Ag^{+}	
٠	٠	-١.٣	-٠.٨	-١.٥	-١.٥	٠	+٠.٧	+٠.٢	-٠.٤	+٣.٥	٠	١
-٠.٤	+٠.٢	-١.٢	-١.٠	-٢.٥	-١.٠	٠	+٠.٨	+٢.٤٢	-٠.٤	+١.٧٥	٠	٢
+٠.٦	+٠.٣٥	-١.١٠	-١.٤	-٣.٠	-٠.٥	٠	+٠.٨	+٢.٢	-٠.٥	+١.١٠	٠	٣

Interference Effect %							**Conc. of Anion fold**
$MnO_{٤}^{-٢}$	**$CrO_{٤}^{-٢}$**	**$IO_{٣}^{-}$**	**$NO_{٣}^{-}$**	**Br^{-}**	**Cl^{-}**	**$SO_{٤}^{-٢}$**	
٠	+٠.٣	+٠.٥	٠	-٠.٢	٠	+٠.٥٠	١
+٠.١	-٠.٥	+٠.٧٥	٠	-١.٢	+١.٠	+٠.٧٥	٢
+٠.١	-٠.٩٨	+٠.٨	-٠.٣	-١.٣	٠	+٠.١٥	٣

٤A-٨: Study of the dead volume

To ensure accurate results obtained from this unit, we must be studied.

Wherever, the dead volume is small it means a best results.

Three experiments were done, in the first the iodine was formed from the system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$), the carrier solution was $H_{٣}O^{+}$ and injection I^{-} in ($L_{٢}$). $H_{٢}O$ was injected instead of ($ClO_{٣}^{-}$) in ($L_{١}$) and there was no response.

In the second experiment, ($ClO_{٣}^{-}$) was injected in ($L_{١}$) and injection ($H_{٢}O$) in ($L_{٢}$) instead of (I^{-}) and the carrier solution was ($H_{٣}O^{+}$), and there was no response obtained. From this experiment as well. In the third experiment, I^{-} was injected in loop (٢), and ($ClO_{٣}^{-}$) was injected in loop (١) and the carrier solution was ($H_{٢}O$) and there was also no response.

This means that there was no dead volume and the unit was well designed.

٤A-٩: Applications:

٤A-٩-١: Determination of chlorate ion in aqueous solution:

Procedure:

The carrier of (٢.٥ M) hydrochloric acid is pumped at a flow-rate of (١.٩٥ ml.min$^{-١}$). A (١٢٧ µl) aliquot of sample solution containing chlorate ion (٥×١٠$^{-٦}$, ٥×١٠$^{-٥}$, ٥×١٠$^{-٤}$, ٥×١٠$^{-٢}$ M) are injected in the first loop and (٣١.٤ µl) of potassium iodide concentration is injected in the second loop. Figure (٣-٤) shows that the carrier, sample and potassium iodide are mixed in the mixing coil at room temperature; the released iodine is measured spectrophotometrically at ٣٥٠ nm.

The results obtained by the reaction system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) using the homemade unit figure (٣-٩) of the standard samples are summarized in table (٤-١٥) from which it can be seen that a good agreement is achieved between the standard value and the found value.

Table (٤-١٥): Application in aqueous solutions.

Standard concentration of chlorate ion (M)	Found concentration of chlorate ion (M)
٥×١٠$^{-٦}$	٤.٩٩٥×١٠$^{-٦}$
٥×١٠$^{-٥}$	٥×١٠$^{-٥}$
٥×١٠$^{-٤}$	٥.٠٣×١٠$^{-٤}$
٥×١٠$^{-٢}$	٤.٩٩×١٠$^{-٢}$

٤A-٩-٢: Determination of chlorate ion in safety matches:

Due to the many uses and importance of matches in our life, which consists of material low kindling point, interesting phosphorus sesequisulfide ($P_٤S_٣$) with oxidant material such as potassium chlorate or barium chlorate that gives oxygen required to start the burning (Blaze) and mixing it with this materials soft glass powder with glue(١١٥), chlorate ion in match is determined by flow injection analysis technique figure (٣-٩), the response is found (٧.٩٦×١٠$^{-٤}$ M) which is(٠.٠٦٦ M) concentration of chlorate ion.

Procedure:

Taking five sticks, weighting them and dissolved in ٢٠ ml of distilled water. The sample is injected in loop (١) replace potassium chlorate and injected (٠.٥ mol.L$^{-١}$) of potassium iodide in loop (٢), (٢.٥ mol.L$^{-١}$) of hydrochloric acid used as a carrier stream at ١.٩٥ ml.min$^{-١}$ of flow-rate. The results shown in table (٤-١٦).

Table (٤-١٦): The chlorate concentration in one stick of match.

Sample No.	Conc. of chlorate ion in (M)	$\overline{Y}$	$\sigma_{n-١}$	%R.S.D.	$\bar{y} \pm t\frac{\sigma_{n-1}}{\sqrt{n}}$

١	٨×١٠^{-٤}	٧.٩×١٠^{-٤}	٥.٧×١٠^{-٦}	٠.٧٢٤	$٧.٩\times١٠^{-٤}\pm١.٤\times١٠^{-٥}$
٢	٨×١٠^{-٤}				
٣	٧.٩×١٠^{-٤}				

٤A-٩-٣: Determination of chlorate ion in hypochlorite solution:

The determination of chlorate in hypochlorite solution is done by using a sample of hypochlorate which is homemade by Babylon company for soap and detergent manufacturing limited-Baghdad, and taking a constant volume from it (١.٠ ml) and diluting it by distilled water (٥:١), then injecting in loop (١) figure (٣-٩) instead of potassium chlorate solution, and the results are shown in table (٤-١٧).

Table (٤-١٧): Determination of chlorate ion in hypochlorate solution.

Sample No.	Conc. of chlorate ion in (M)	$\overline{Y}$	$\sigma_{n-١}$	%R.S.D.	$\bar{y}\pm t\frac{\sigma_{n-1}}{\sqrt{n}}$
١	٩×١٠^{-٢}	٠.٠٨٩	٠.٠٠١٧	١.٩٤٦	٠.٠٨٩± ٠.٠٠٤٢
٢	٩×١٠^{-٢}				
٣	٨.٧×١٠^{-٢}				

٤B- Determination of chlorate ion by second unit:

٤B-١: Study the factors influencing on the absorbance in the determination of chlorate ion:

Study the influence of variables on absorbance of released iodine through the reaction of chlorate ion with potassium iodide in the presence of sulphuric acid for system ($ClO_{٣}^{-}-I^{-}-H_{٣}O^{+}$), which includes physical and chemical parameters for the home made unit which consists of three ways. The first way for sulphuric acid solution passes while the second way passes potassium iodide solution and the third is to transfer stream of sample injected through an injection valve and completing this reaction after passing through primary mixing coil, secondary mixing coil, and completion reaction coil then to cell reaction and to amplifier that is home made and finally to recorder for recording the signal.

٤B-١-١: Physical parameters optimization

٤B-١-١-١: Injection time:

Using experimental concentrations of sulphuric acid (١.٠ M) and potassium iodide (٠.١٢ M) by injecting sample volume (٦٠ µl) of chlorate ion and flow rate (٢ $ml.min^{-١}$), then study if the injection time has an effect on the absorbance of released iodine from system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$).

The time of injection applied was (١٠, ٢٠, ٣٠, ٤٠, ٥٠, ٦٠) count obtained from the results shown in table (٤-١٨) and figure (٤-١٥) explains the change in the intensity and shape of the response obtained when injection of chlorate ion at concentration (٣٠٠ $µg.ml^{-١}$), the changes were increase with an increasing the time period which allows the valve in the injection place to ensure from exit of sample section totally from injection valve as a result obtained from the response has intensity represent concentration of chlorate ion reaching to (٦٠ sec) (٤٠ count).

Table (٤-١٨): Effect of time of injection on the absorbance to system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) ٣٠٠ $µg.ml^{-١}$ of chlorate ion.

Time of injection (count)	Reaching time section of sample to cell (sec)	response $\overline{Y}$ in (mV)	$\sigma_{n-١}$ %RSD	$\overline{y} \pm t \frac{\sigma_{n-1}}{\sqrt{n}}$
١٠	٤٨.٠	١٠٢٠	١.٠٠ ٠.٠٩٨	١٠٢٠±٢.٤٨
٢٠	٥٤.٠	١٤٦٠	٠.٩٥ ٠.٠٦٥	١٤٦٠±٢.٣٦

١٩٢٠±٠.٥٧	٠.٢٣ ٠.٠١٢	١٩٢٠	٥٧.٦	٣٠
٢٠٧٠±٢.١١	٠.٨٥ ٠.٠٤١	٢٠٧٠	٦٠.٠	٤٠
٢٠٨٠±١.٣٧	٠.٥٥ ٠.٠٢٦	٢٠٨٠	٦٦.٠	٥٠
٢٠٩٠±١.٨٦	٠.٧٥ ٠.٠٣٤	٢٠٩٠	٧٢.٠	٦٠

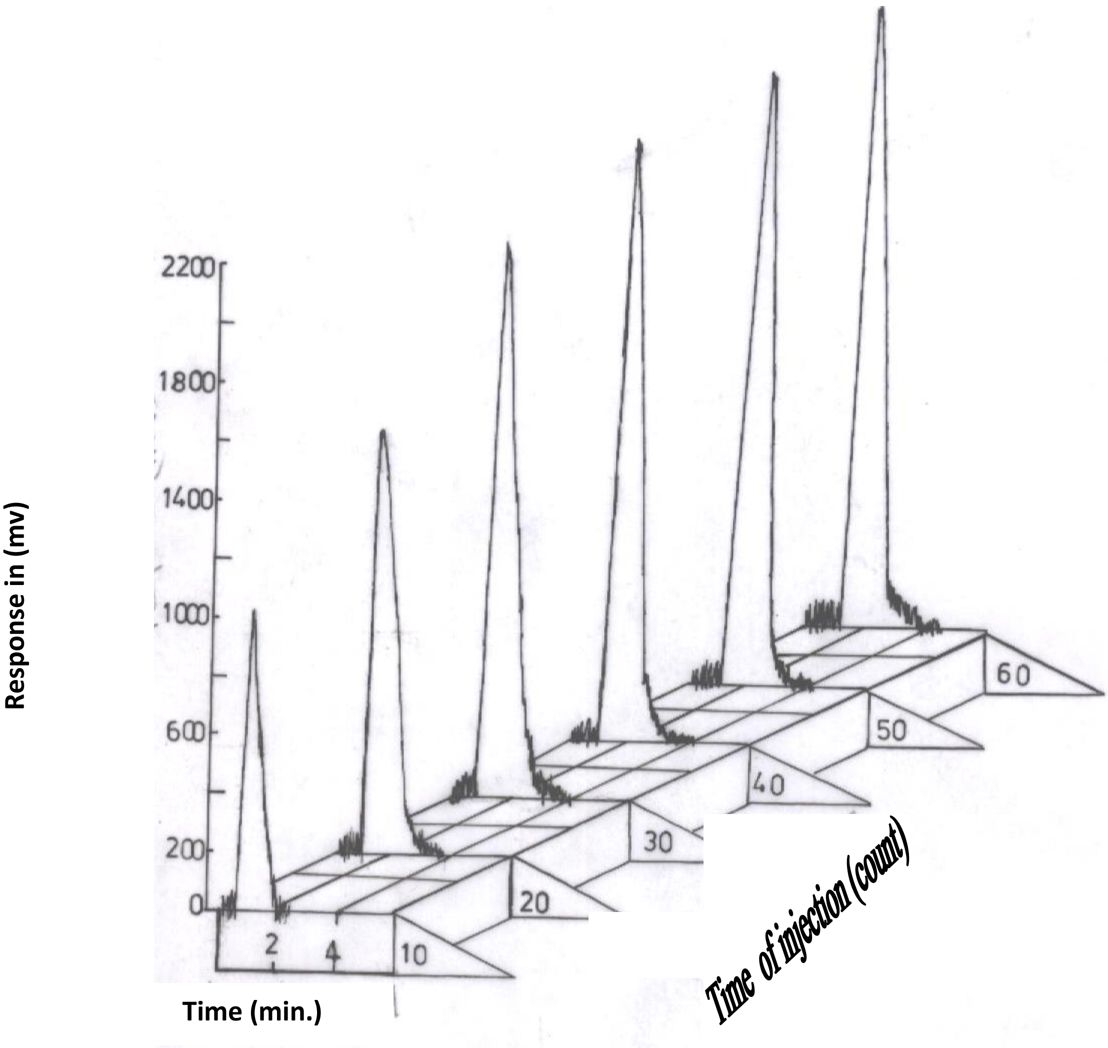


Figure (٤-١٥): Effect of changing in time of injection on the height and shape of the response by using (٣٠٠ $\mu g.ml^{-١}$) concentration of chlorate ion .

Although the increase of injection time caused a high intensity response, it causes an increase in width of the response peak by the effect of dispersion from diffusion, convection and process of dilution to coloured section. This increases of effect with increasing of path that passes for reaching to cell absorbance (at increasing time of injection), thus increasing the physical variables perhaps leads to low concentrations of chlorate ion (slump in detection limit).

The best time is (٦٠ sec) to assure the exit of section from injection valve, as shown in figure (٤-١٦) which shows minor differences of response intensity obtained from released iodine for system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) to reach injection time above (٦٠ sec.).

To obtain accurate details of response, the recorder paper chart speed must be increased to (٣ $cm.min^{-١}$) in comparison with speed of recorder paper (٠.٥ $cm.min^{-١}$), as shown in figure (٤-١٦).

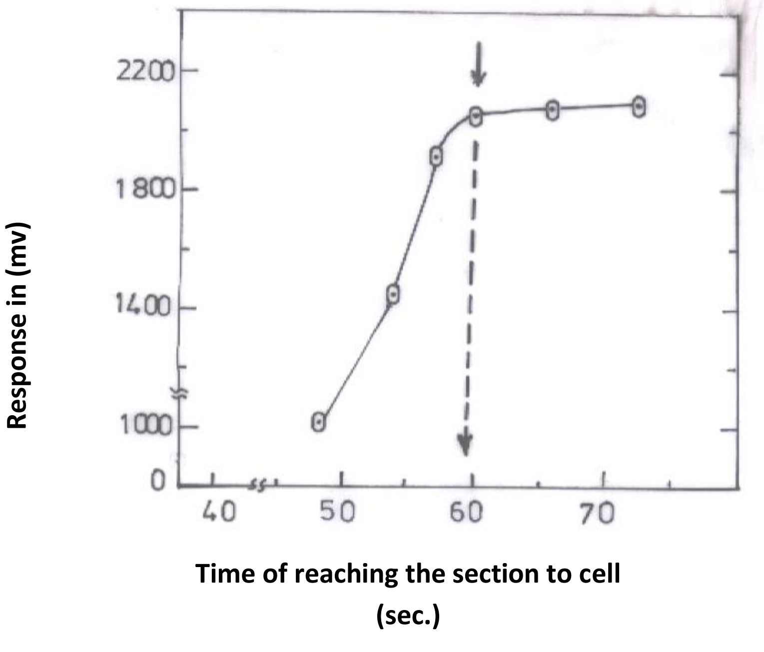


Figure (٤-١٦): The effect of changing in the time of injection on the height of response peak and choosing the optimum time which is (٦٠ sec.)

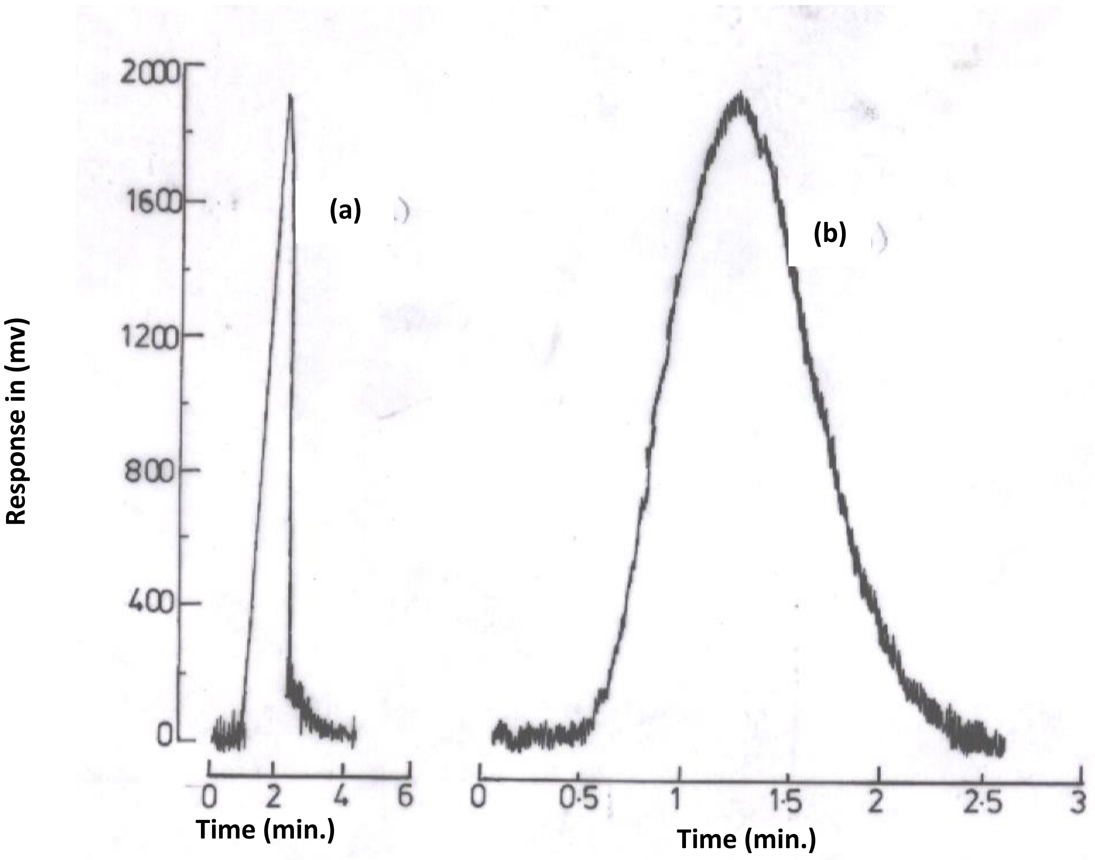


Figure (٤-١٧): Effect the increasing in chart speed of recorder on the shape of response

a- at speed ٠.٥ cm.min.$^{-١}$

b- at speed ٣ cm.min.$^{-١}$

٤B-١-١-٢: Flow-rate

The whole reaction consist of chlorate ion (٢٥٠ µg.ml$^{-١}$), (٠.١٢ M) of potassium iodide, and (١.٠ M) of sulphuric acid with volume of sample injection (٦٠ µl) and changing the flow rates (١, ١.٣, ١.٨, ٢, ٣, ٣.٥, ٤, ٤.٥ and ٥ ml.min$^{-١}$); this leads to obtain the results as shown in table (٤-١٩) by repeating the injection for each sample three times successively.

Table (٤-١٩): The changing in average of flow rate on the response of released iodine to system ($ClO_٣^-$-I^--$H_٣O^+$).

Flow-rate (ml.min$^{-١}$)	Reaching time the section coloured to cell (sec)	response $\overline{Y}$ in (mV)	$\sigma_{n-١}$ %RSD	$\overline{y} \pm t_{0.05} \frac{\sigma_{n-1}}{\sqrt{n}}$	Width of base response ΔtB (sec.)
١.٠	٩٦.٠٠	١٤٠٠	٢.٣٥ ٠.١٧	١٤٠٠±٥.٨٤	١٤٤
١.٣	٨٤.٠٠	١٤٦٠	١.٥٥ ٠.١١	١٤٦٠±٣.٨٥	١٣٢
١.٨	٧٢.٠٠	١٦٥٠	١.٠٣ ٠.٠٦٢	١٦٥٠±٢.٥٦	١٢٠
٢.٠	٦٠.٠٠	١٦٨٠	١.٩٧ ٠.١٢	١٦٨٠±٤.٨٩	٩٦
٣.٠	٥٥.٠٠	١٧٢٠	١.٣٣ ٠.٠٧٧	١٧٢٠±٣.٣٠	٨٤

٣.٥	٥٠.٠٠	١٨٦٠	٢.٠٥ ٠.١١	١٨٦٠±٥.٠٩	٧٢
٤.٠	٤٨.٠٠	١٩٠٠	١.٠١ ٠.٠٥٣	١٩٠٠±٢.٥١	٦٠
٤.٥	٤٢.٠٠	١٨٠٠	١.٩٢ ٠.١١	١٨٠٠±٤.٧٧	٥٨
٥.٠	٤٠.٠٠	١٧٠٠	١.٥٥ ٠.٠٩١	١٧٠٠±٣.٨٥	٥٨

The time which has been calculated from departuring valve of injection reaching to cell of absorption then the measurement.

The results from previous table indicated that in the low rates in which the effect of physical variables from dilution and dispersion is very high this lead to obtain on the response has low intensity and width in peaks by increasing volume of the section coloured comparison by increasing flow rate reaching to (٤ ml.min$^{-١}$) obtained from highly intensity to response and with sharp peaks and width in the basis of response is low figure (٤-١٨) show that.

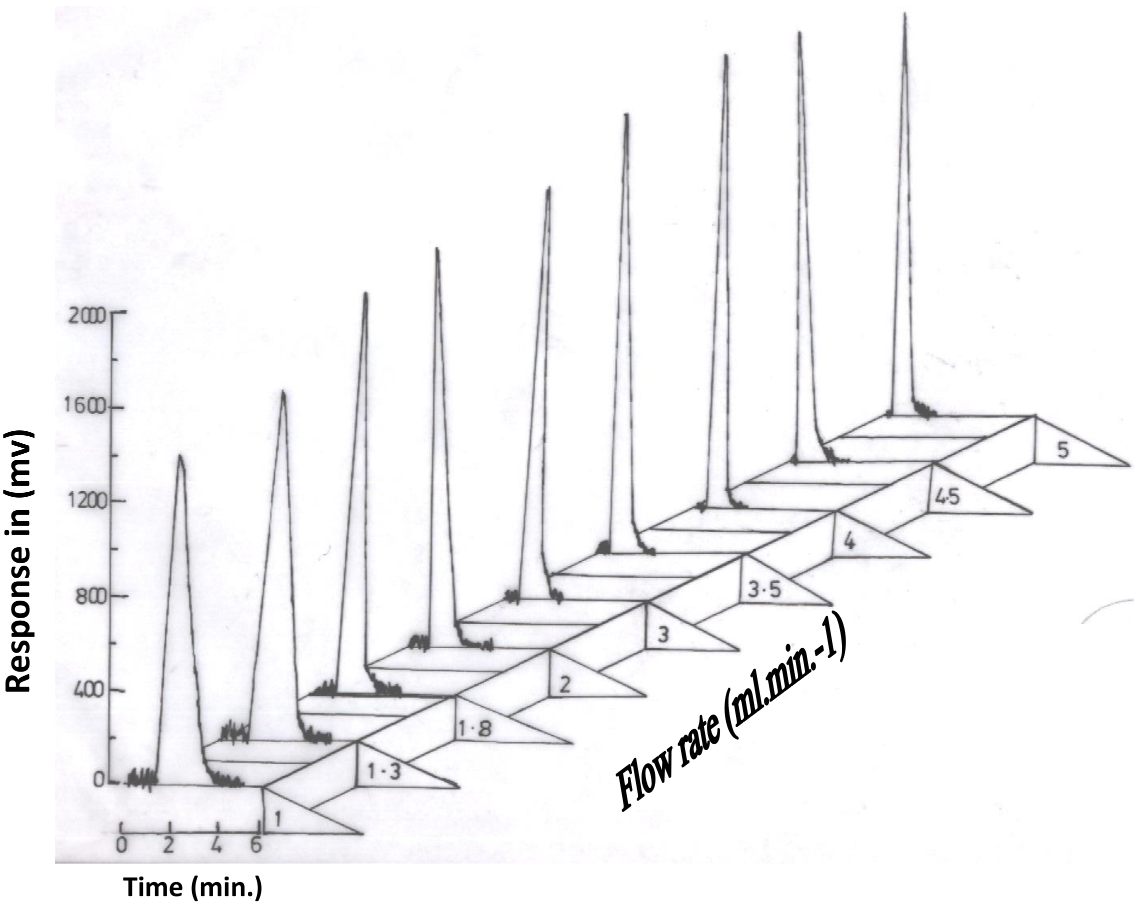


Figure (٤-١٨): Effect of the changing in flow-rate on the intensity and shape of the response by using conc. For injection sample of chlorate ion ٢٥٠ µg.ml$^{-١}$

In de [illegible] high rates, a sharp peaks of response were obtained, while in lov [illegible] because of the period of time needed to complete the reaction, ar [illegible] odine ($I_{٢}$) from the system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$), is little and not enough; this leads to obtain low intensity response as shown in figure (٤-١٩ a).

Therefore selection of flow rate (٤ ml.min$^{-١}$) is optimum to set sharp peaks responses, low to base width the response and high intensity; this leads to moving toward low concentrations and improvement of detection limit.

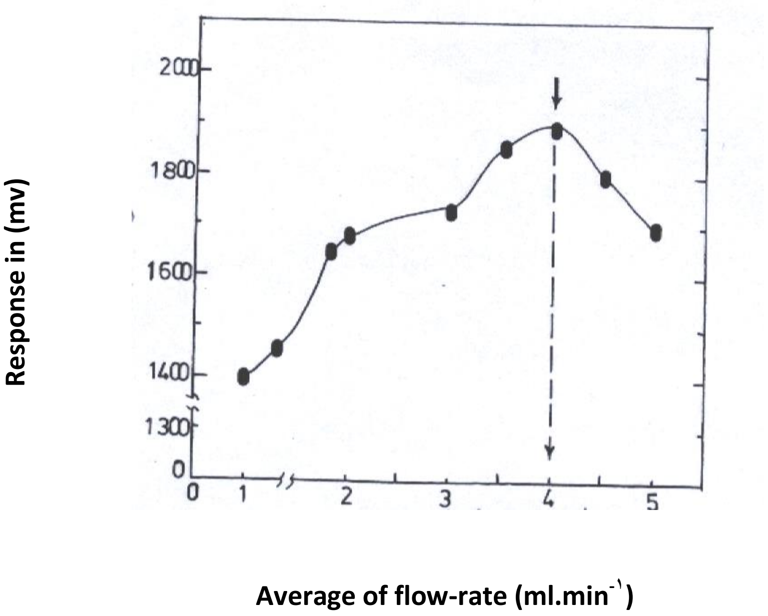


Figure (٤-١٩a): Effect the changing in average of flow-rate on the height of response optimum flow rate is (٤ ml.min$^{-١}$)

Also it has been noticed that by increasing the flow rate, a decrease in the time is required to reach the coloured section cell of absorption, and physical variables decrease too (dilution or dispersion); this leads to the reduction in volume of section coloured although effect of it on the decrease in the width base of response (ΔtB) figure (٤-١٩ b, c).

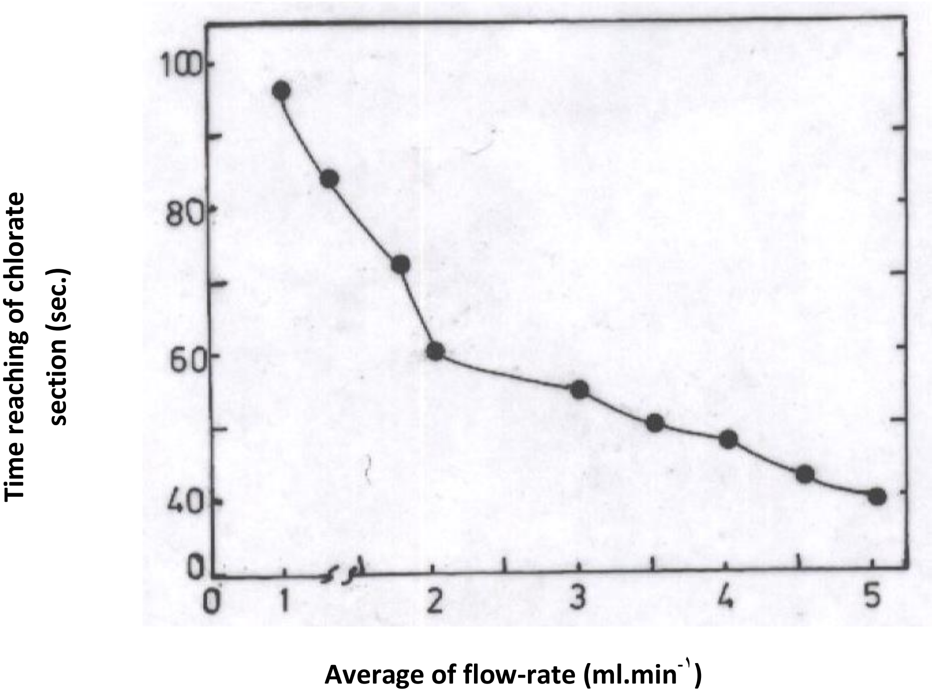


Figure (٤-١٩b): Effect of increasing in flow rate on decreasing of reaching time of colored section to cell of absorption

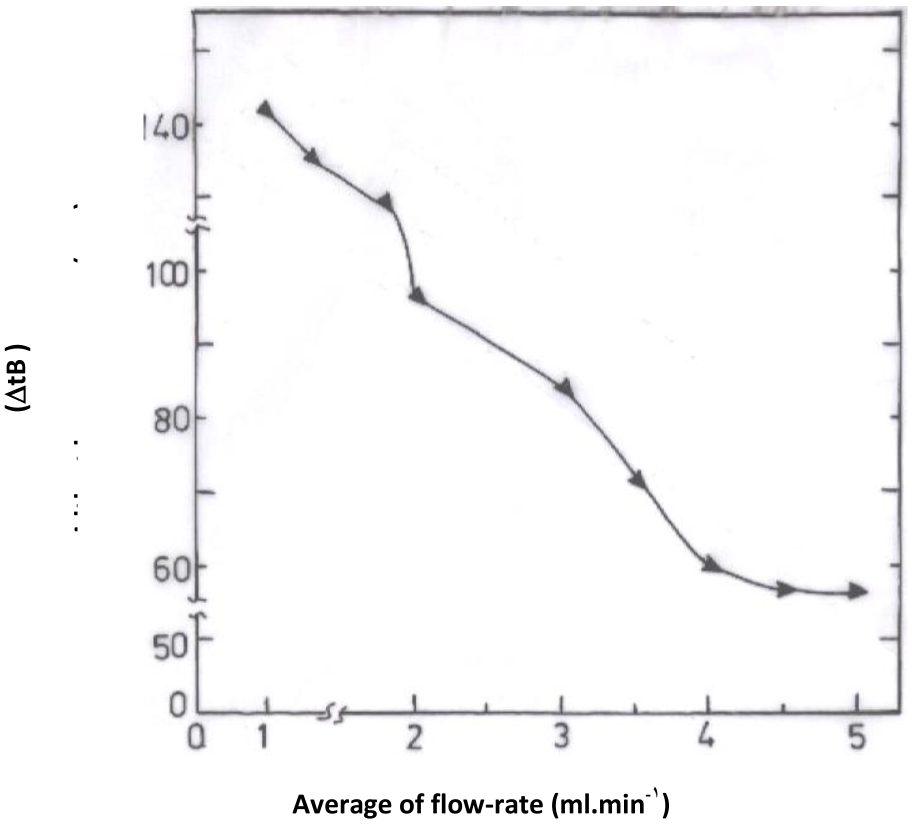


Figure (٤-١٩c): The increasing in flow rate on decreasing the width of base response (ΔtB) expressed by unit of time (sec.)

The results in table (٤-١٩) show the linear relationship between width of base response and required time from departuring section of sample for valve injection reaching to coloured section to cell of absorption such as shown in table (٤-٢٠). By repeating the measurement three times, with small percentage of relative standard deviation occurs.

Table (٤-٢٠): Results of relationship width of base response with the time.

Reaching time of the coloured section to cell (sec.)	Width base response ΔtB (sec.)	$\hat{Y}$ (sec.)
٤٢	٥٨	٥٩.٢٢
٤٨	٦٠	٦٩.٤٨
٥٠	٧٢	٧٢.٨٩
٥٥	٨٤	٨١.٤٤
٦٠	٩٦	٨٩.٩٨
٧٢	١٢٠	١١٠.٤٩
٨٤	١٣٢	١٣٠.٩٩
٩٦	١٤٤	١٥١.٥٠

٤B-١-١-٣: Sample volume

By using reaction unit (figure (٣-١٥)), the following materials are complementary to the reaction: chlorate ion (٢٥٠ µg.ml$^{-١}$), potassium iodide (٠.١٥ mol.L$^{-١}$), and sulphuric acid (١.٢ mol.L$^{-١}$), and using time of injection (٦٠ sec.) at flow rate (٤ ml.min$^{-١}$) with variable sections of sample by ٠.٧ mm diameter, to the result in table (٤-٢١) are obtained.

Table (٤-٢١): The changing in the volume of section sample on the response of released iodine to system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) .

Length of sample section (cm)	Volume of section sample (µl) experimentally	Reaching time of the section to cell (sec.)	Width of base response ΔtB (sec.)	response $\overline{Y}$ in (mV)	$\sigma_{n-١}$ %RSD	$\bar{y} \pm t_{0.05}\frac{\sigma_{n-1}}{\sqrt{n}}$
٥	٢٠	٤٧	٥٠	٢٧٠٠	١.٢٣ ٠.٠٤٦	٢٧٠٠±٣.٠٦
١٠	٤٠	٤٧	٥٥	٢٧٨٠	١.٥٨ ٠.٠٥٧	٢٧٨٠±٣.٩٣
١٥	٦٠	٤٨	٦٠	٣٠٠٠	٠.٩٥ ٠.٠٣٢	٣٠٠٠±٢.٣٦
٢٠	٨٠	٤٨	٧٢	٢٩٩٠	١.٣٣ ٠.٠٤٤	٢٩٩٠±٣.٣٠
٣٠	١١٥	٤٨	٧٥	٢٩٠٠	١.٥٥ ٠.٠٥٣	٢٩٠٠±٣.٨٥

From table (٤-٢١) we can conclude that with the increase of section volume the intensity of response for released iodine will increase reaching a volume of (٦٠ µl), then the response begins to decrease a little. This is due to the effect of internal filter that resulted from colour depth of released iodine that prevents sensitizer from accepting light intensity transmittance with high efficiency according to gradual decrease in response as shown in figure (٤-٢٠ a) that explains the intensity and shape of response. In addition figure (٤-٢٠ b) that shows the optimum section volume to obtain high intensity is (٦٠ µl).

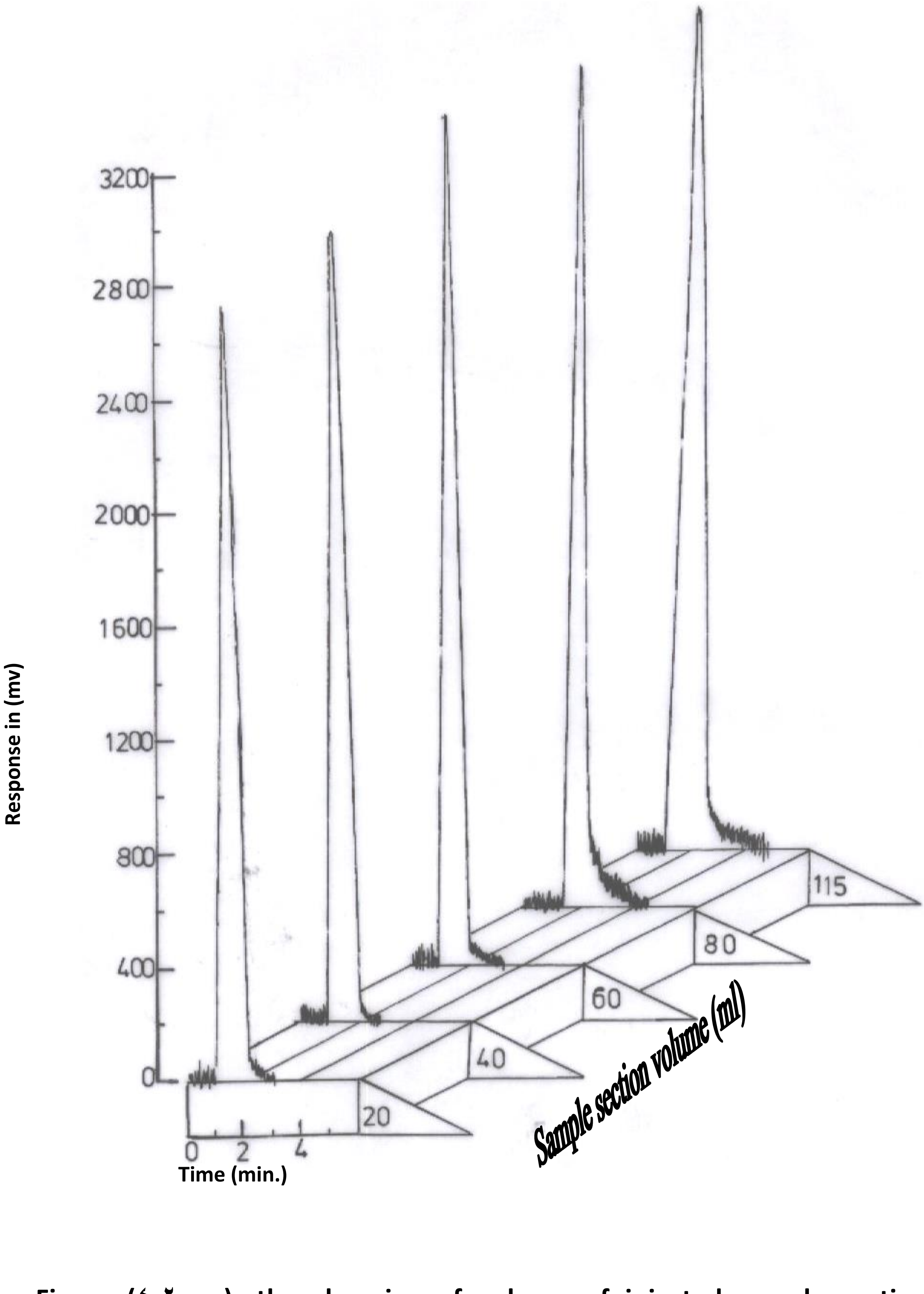


Figure (٤-٢٠ a): the changing of volume of injected sample section on intensity and shape of the response

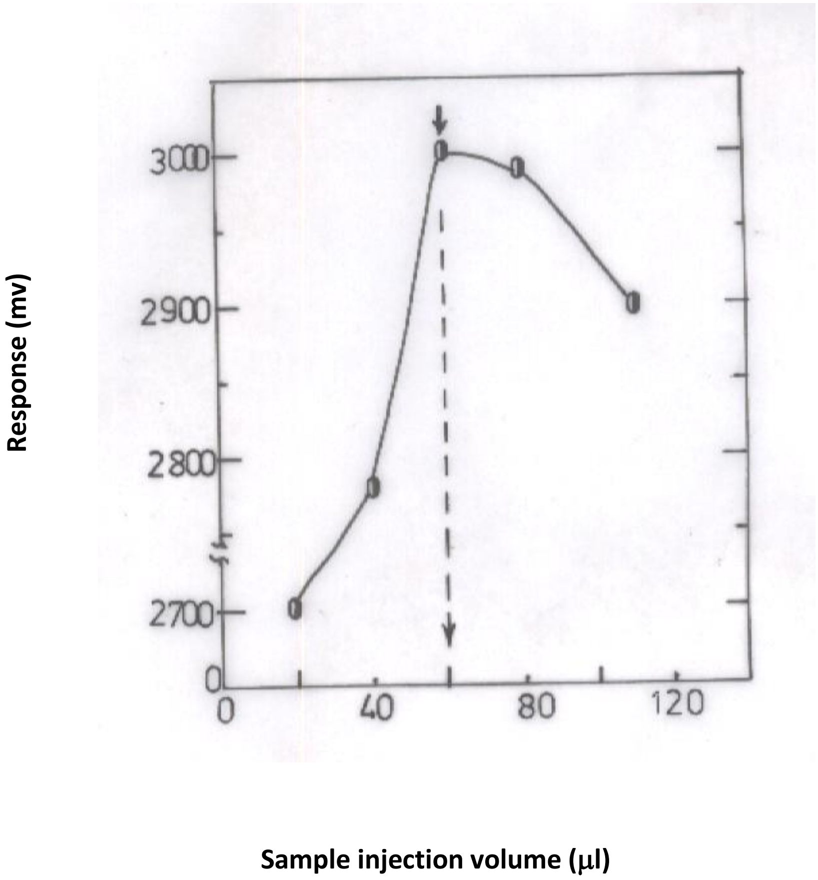


Figure (٤-٢٠ b): Effect of the changing in injected of sample volume on height of response and noticed the best volume of section is (٦٠µl)

٤B-١-٢: Chemical parameters

By using designed unit figure (٣-١٥) and fixed physical variables: injection time (٦٠ sec.), volume of injected sample (٦٠ µl), and flow rate (٤ ml.min$^{-١}$) and using changing percentage for each of sulphuric acid and potassium iodide with constant concentration of chlorate ion (٢٥٠ µg.ml$^{-١}$), the results indicates to the percentage of mixing in table (٤-٢٢) and by repeating all measurement three times.

Table (٤-٢٢): Effect the changing in conc.s of acid and potassium iodide on the response to system ($ClO_٣^-$-I^--$H_٣O^+$) .

Conc. KI mol.L$^{-١}$	Conc. acid $H_٣O^+$ mol.L$^{-١}$	response $(n = 3)\ \overline{Y}$ in (mV)	$\sigma_{n-١}$ / %RSD	$\bar{y} \pm t_{0.05} \frac{\sigma_{n-1}}{\sqrt{n}}$
٠	٠	٠	٠	٠
٠	٢.٠	٠	٠	٠
٠.١	١.٥	٣٠٦٠	٢.١٥ ٠.٠٧٠	٣٠٦٠±٥.٣٤
٠.١٥	١.٠	٢٨٤٠	١.٥٥ ٠.٠٥٥	٢٨٤٠±٣.٨٥
٠.٢٥	٠	٠	٠	٠
٠.٢٥	٢.٠	٢٨٠٠	١.٣٢ ٠.٠٤٧	٢٨٠٠±٣.٢٨

From results of the table, we can notice that on increasing the concentration of potassium iodide, the response will decrease compared with increasing of acidic media concentration, this lead to increasing intensity of response because of liberated Iodine.

While increasing of potassium iodide due to depth colour and the influence internal filter phenomena increased, which prevent reaching transmittance of light to sensitizer, therefore; we can conclude that high concentration of acid (١.٥ M) is the best and concentration of potassium iodide is more less (٠.١ M).

At the absence of any substance of completion reaction which leads to prevent releasing of iodine, thus did not obtain any response.

According to that fixed the percent mixing of acid with concentration (١.٥ M) with concentration of potassium iodide (٠.١ M) this is optimum percent lead to obtaining of the highest intensity of response and can indicated intensity and shape of this response in figure (٤-٢١).

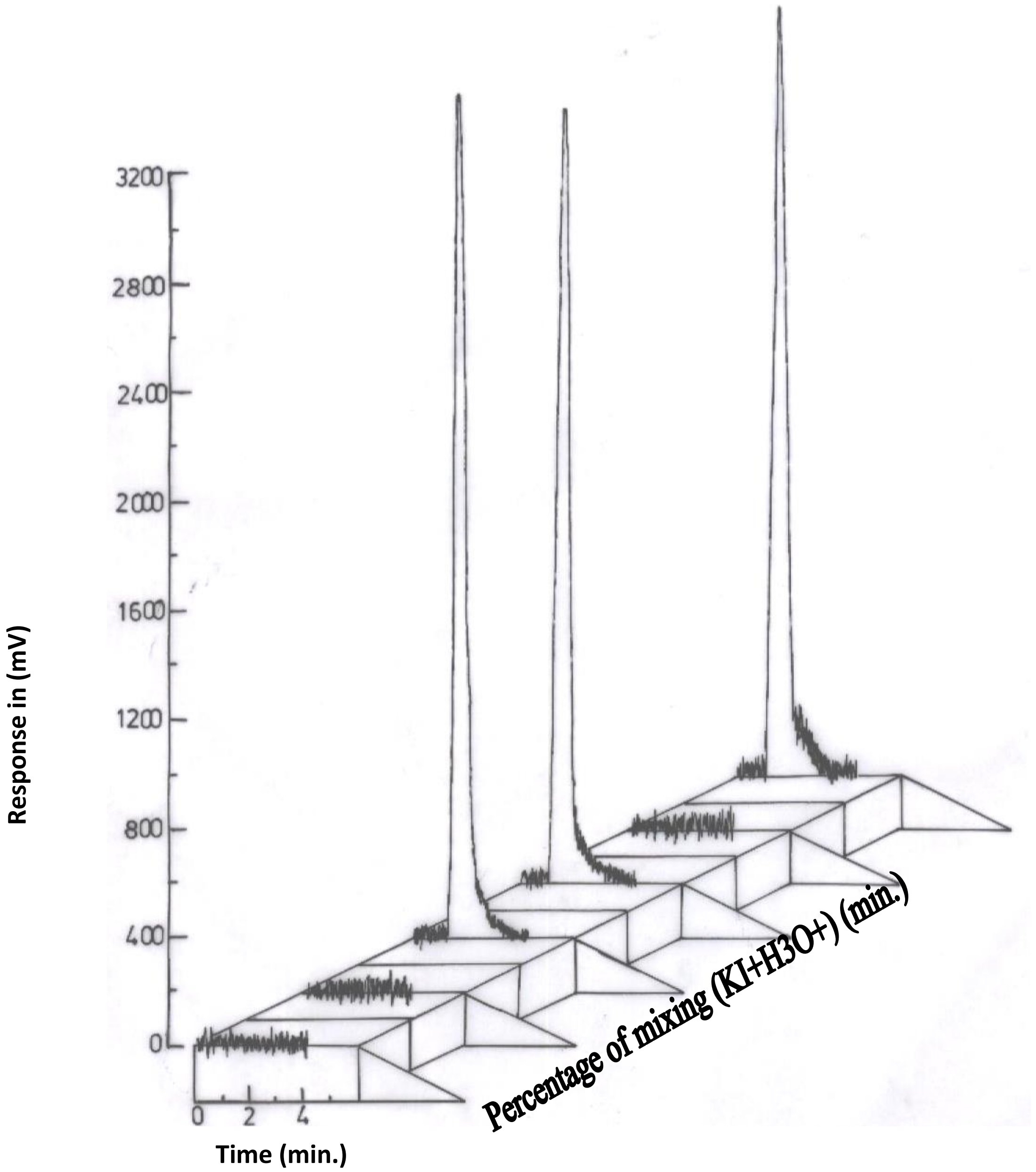


Figure (٤-٢١): Effect of the changing in the percent mixing to both of sulphuric acid and potassium iodide on the intensity and shape of the response and noticed the percent of mixing to $H_٣O^+$ (١.٥ M) + KI (٠.١ M) is the best.

٤B-٢: Variation of response versus concentration

٤B-٢-١: Preparation of calibration curve

By using the optimum conditions of physical and chemical variables, series of solutions were prepared by changing the concentrations of chlorate ion from (٥-٦٠٠ µg.ml$^{-١}$). The response of released iodine was measured for system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) and each concentration has been injected three times successively on the carrier stream of distilled water in unit figure (٣-١٥) and the obtained results were indicated in table (٤-٢٣) and figure (٤-٢٢).

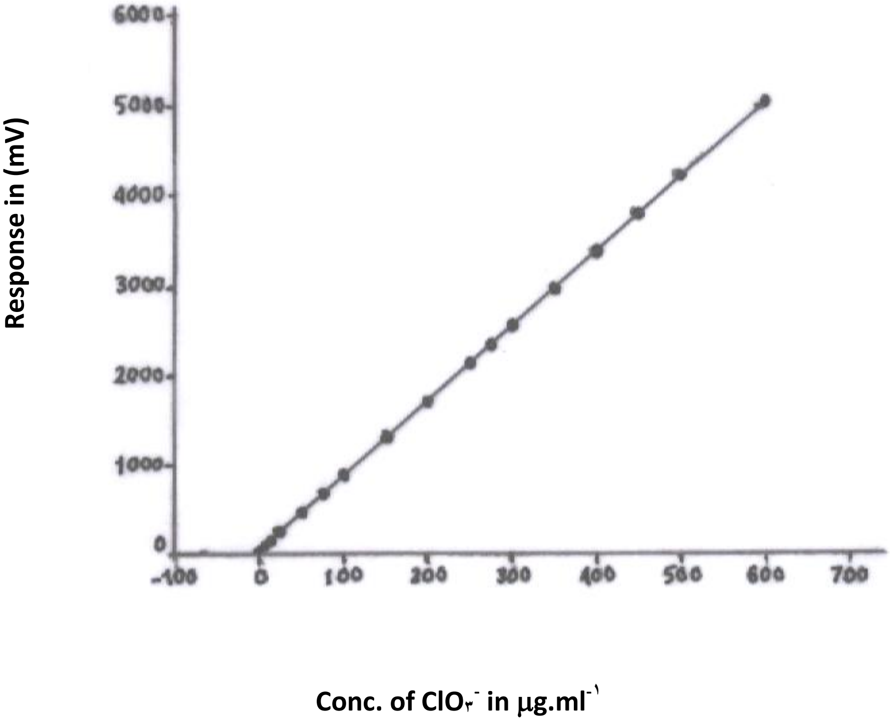


Figure (٤-٢٢): Changing the response with concentration for obtaining on calibration curve for system ($ClO_{٣}^{-}$- I^{-}-$H_{٣}O^{+}$)

Table (٤-٢٣): Results for the response obtained versus various concentration of chlorate; using the newly home made photometer.

$[ClO_{٣}^{-}]$ µg.ml$^{-١}$	Response to (n=٣) $\bar{y}$ in (mV)	$\sigma_{n-١}$ / %RSD	$\bar{y} \pm t_{0.05} \frac{\sigma_{n-1}}{\sqrt{n}}$	$\hat{y}$ predicted in (mV)
٠	٠	٠	٠	٥٥.٥٨
٥	٨٠	٠.٣٢ ٠.٤٠	٨٠±٠.٧٩	٩٧.٠٨
١٠	١١٢	٠.١١ ٠.٠٩٨	١١٢±٠.٢٧	١٣٨.٥٧
١٥	٢٠٠	٠.١٥ ٠.٠٧٥	٢٠٠±٠.٣٧	١٨٠.٠٦
٢٥	٢٤٠	٠.٣٣ ٠.١٣٨	٢٤٠±٠.٨٢	٢٦٣.٠٥
٥٠	٤٠٠	٢.١٥ ٠.٥٣٨	٤٠٠±٥.٣٤	٤٧٠.٥٣
٧٥	٦٠٠	١.٤٥ ٠.٢٤٢	٦٠٠±٣.٦٠	٦٧٨.٠٠
١٠٠	١٠٨٠	٢.٥٥ ٠.٢٣٦	١٠٨٠±٦.٣٤	٨٨٥.٤٨
١٥٠	١٤٦٠	١.٩٥ ٠.١٣٤	١٤٦٠±٤.٨٤	١٣٠٠.٤٢
٢٠٠	١٧٨٠	٢.٠٠ ٠.١١٢	١٧٨٠±٤.٩٧	١٧١٥.٣٧
٢٥٠	٢٠٤٠	٣.٠٥ ٠.١٤٩	٢٠٤٠±٧.٥٨	٢١٣٠.٣٢
٢٧٥	٢٣٤٩`	٢.٣٥ ٠.١٠٠	٢٣٤٩±٥.٨٤	٢٣٣٧.٧٩
٣٠٠	٢٤٦٠	٢.١١ ٠.٠٨٦	٢٤٦٠±٥.٢٤	٢٥٤٥.٢٧
٣٥٠	٢٩٥٧	٢.٠٩ ٠.٠٧١	٢٩٥٧±٥.١٩	٢٩٦٠.٢١
٤٠٠	٣٣٧٥	٣.٤٥ ٠.١٠٢	٣٣٧٥±٨.٥٧	٣٣٧٥.١٦
٤٥٠	٣٧٩٠	٢.١٩ ٠.٠٥٨	٣٧٩٠±٥.٤٤	٣٧٩٠.١١
٥٠٠	٤٢٠٥	١.٨٧ ٠.٠٤٤	٤٢٠٥±٤.٦٥	٤٢٠٥.٠٥
٦٠٠	٥٠٣٥	٢.٤٥ ٠.٠٤٩	٥٠٣٥±٦.٠٩	٥٠٣٤.٩٥

Table (٤-٢٤): The changing of response with concentration for obtaining on calibration curve

Lowest value theoretically can begin it calibration curve x=٥.DL		**٠.٢٧ ng**
Detection limit each ١٥µL	**Theoretically from linear equation y=L.O.D.=Y_B +٣S_B at confidence limit ٩٥٪**	**٢٩١.٧٠µg**
	Theoretically from equation D.L= $\frac{3S_D}{slope}$	**٥.٤٢٥ pg**
	practically from dilution to low conc. In calibration curve	**١ µg.ml$^{-١}$**
Conc. Allowed to reach it calibration curve (١٠٪r→r)		**٠.٩٩٨٨٤→٠.٨٩٨٩٥**
t calculate from $t=\frac{\lvert t\rvert\sqrt{n-2}}{\sqrt{1-r^2}}$		**٣٥١.٩٨**
t from table at confidence limit ٩٥٪ for (n-٢)		**٤.٣٠٣**
Correlation coefficient and percentage of linearity %r^{٢}		**٠.٩٩٨٨٤** **٪٩٩.٧٧**
No. of [ClO$_٣^-$] measured		**١٨**
Linear equation at confidence limit ٩٥٪ Abs.I. (mV)=(a±Sat)+(b±Sbt) [ClO$_٣^-$] µg.ml$^{-١}$		**٥٥.٥٨±٣١.٥٤٥*٤.٣٠٣+٨.٢٩٨±٠.١١٢*٤.٣٠٣**
Range of [ClO$_٣^-$] µg.ml$^{-١}$ in calibration curve		**٥→٦٠٠**

$[ClO_٣^-]$ in $\mu g.L^{-١}$ measured	٥→٦٠٠

٤B-٢-٢: The standard deviation for the relationship response with concentration and normal distribution of results:

According to the results for changing the response with concentration in (٤B-٢-١) and taking δ, ٢ δ, ٣ δ from value $\hat{Y}_i$ predicted, the results are shown in table (٤-٢٥); there results showed approximately obey to the normal distribution behaviour .

٦٨٪ falling within ±δn-١ from value $\hat{Y}_i$ predicted, ٩٥٪ falling within ±٢δn-١ from value $\hat{Y}_i$ and predicted ٩٩٪ falling within ±٣δn-١ from value $\hat{Y}_i$ predicted.

And from the results in table (٤-٢٥) and figure (٤-٢٣) we can notice the practical values.

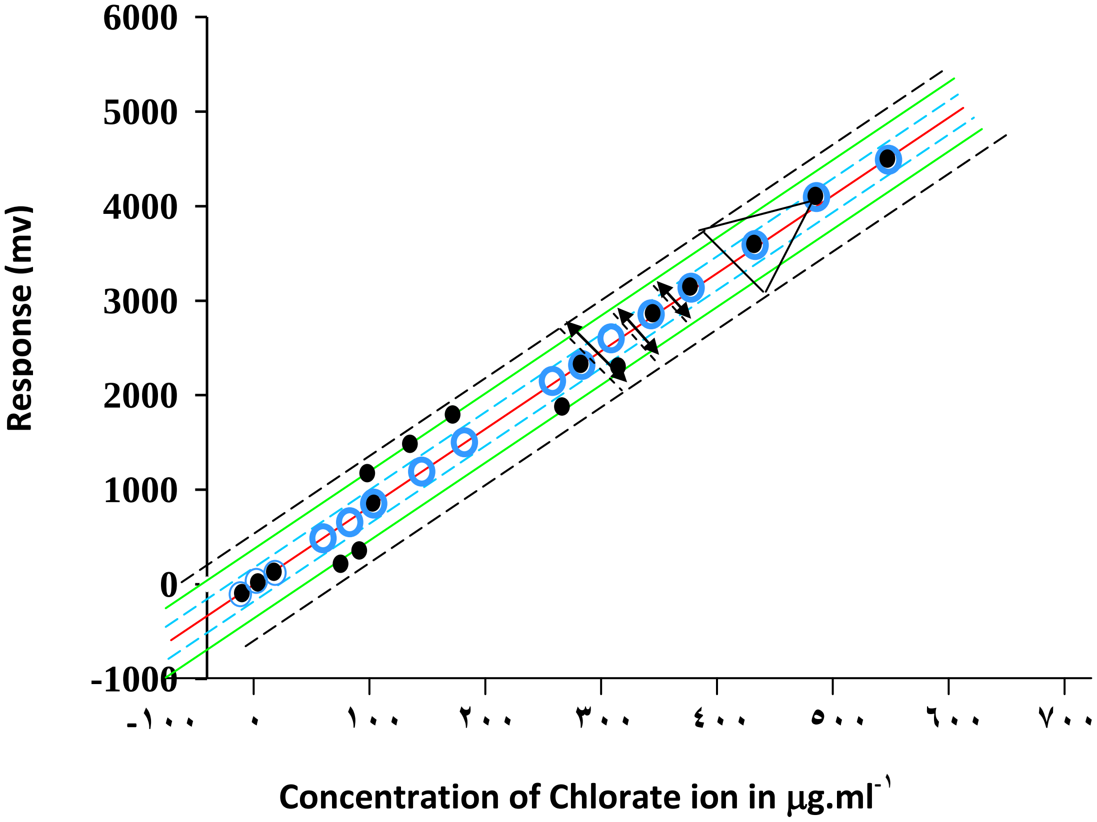


Figure (٤-٢٣): Calibration curve for determination of chlorate ion expressed by (mv) against concentration (µg.ml-١) shown standard deviation and ranges of satisfy ±١ σŷ represented ٦٨٪, ±٢σŷ represented ٩٥٪ and ±٣σŷ represented ٩٩.٧٪ according to Guass curve of normal distribution. The curve shows at ±١σŷ there is ٢٥ of ٣٦ measurement fall in range that act ٦٩.٤٪ while in ±٢σŷ its follows ٣٤ of ٣٦ measurement in the range at ٩٤.٤٪ and at ±٣σŷ all points fall in normal distribution curve.

While the calculation of residual of $(y_i - \hat{y}_i)$ and the percentage can be shown in table (٤-٢٦) and figure (٤-٢٤).

Table (٤-٢٦): The results of changing the response with concentration to calculating residual (y_i) practical from $(\hat{y}_i)$ predicted and the percentage.

[ClO$_{٣}^{-}$] µg.ml$^{-١}$	Practical y_i mv	Predicted $\hat{y}_i$ mv	Residual $(y_i - \hat{y}_i)$ mV	% Residual $\frac{y_i - \hat{y}_i}{y_i} \times 100$
٠	٠	٥٥.٥٨	-٥٥.٥٨	٠.٠٠
٥	٨٠	٩٧.٠٧	-١٧.٠٨	-٢١.٣٤
١٠	١١٢	١٣٨.٥٧	-٢٦.٥٧	-٢٣.٧٢
١٥	٢٠٠	١٨٠.٠٦	١٩.٩٤	٩.٩٧
٢٥	٢٤٠	٢٦٣.٠٥	-٢٣.٠٥	-٩.٦١
٥٠	٤٠٠	٤٧٠.٥٢	-٧٠.٥٣	-١٧.٦٣
٧٥	٦٠٠	٦٧٨.٠٠	-٧٨.٠٠	-١٣.٠٠
١٠٠	١٠٨٠	٨٨٥.٤٨	١٩٤.٥٢	١٨.٠١
١٥٠	١٤٦٠	١٣٠٠.٤٢	١٥٩.٥٨	١٠.٩٣
٢٠٠	١٧٨٠	١٧١٥.٣٧	٦٤.٦٣	٣.٦٣
٢٥٠	٢٠٤٠	٢١٣٠.٣٢	-٩٠.٣٢	-٤.٤٣
٢٧٥	٢٣٤٩	٢٣٣٧.٧٩	١١.٢١	٠.٤٨
٣٠٠	٢٤٦٠	٢٥٤٥.٢٧	-٨٥.٢٧	-٣.٤٧
٣٥٠	٢٩٥٧	٢٩٦٠.٢١	-٣.٢١٢	-٠.١١
٤٠٠	٣٣٧٥	٣٣٧٥.١٦	-٠.١٥٩	-٠.٠٠٤٧
٤٥٠	٣٧٩٠	٣٧٩٠.١١	-٠.١٠٧	-٠.٠٠٢٨
٥٠٠	٤٢٠٥	٤٢٠٥.٠٥	-٠.٠٥٥	-٠.٠٠١٣
٦٠٠	٥٠٣٥	٥٠٣٤.٩٥	-٠.٠٥٠٥	٠.٠٠١٠٠

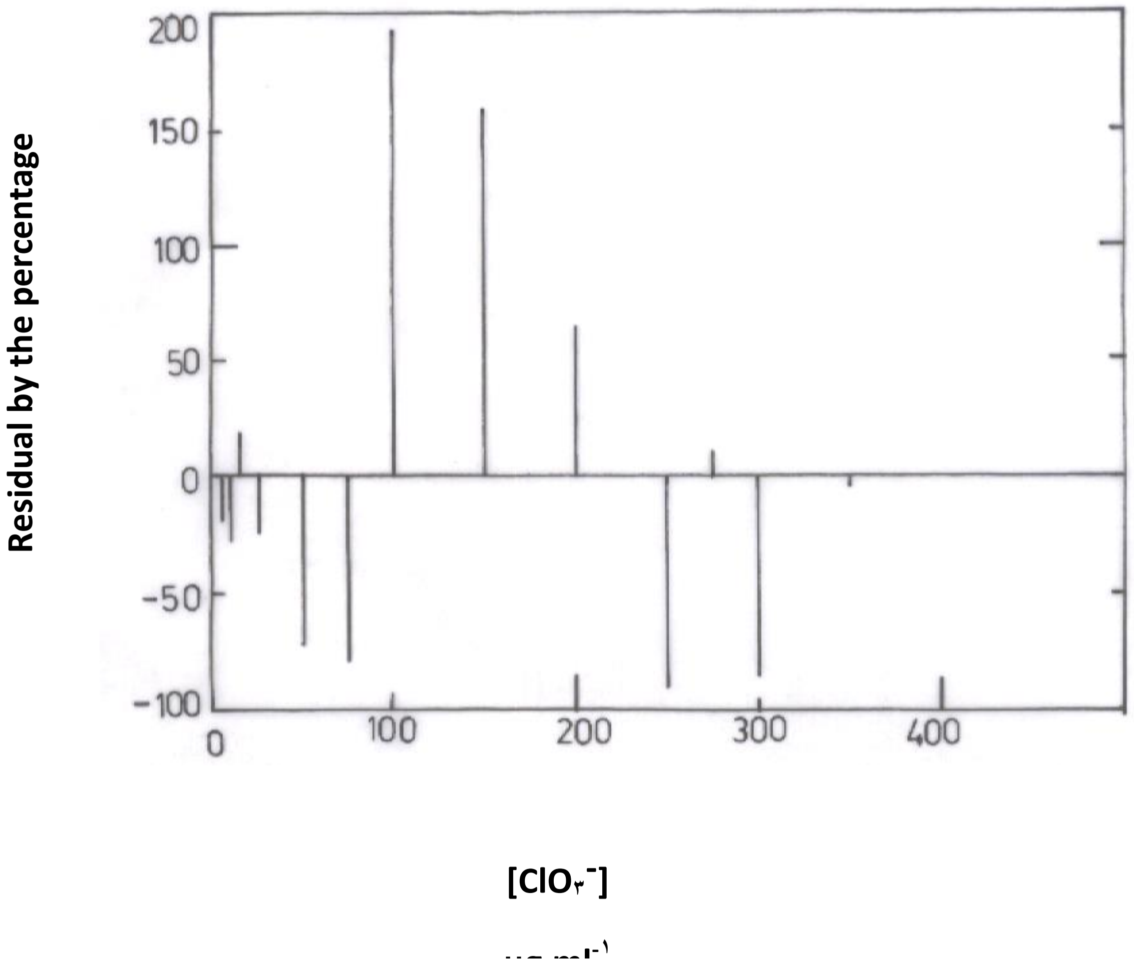


Figure (٤-٢٤): Indicating value of residual response that obtained practically (y_i) from predicated response (obtained on it from linear equation (y_i)) by percentage

٤B-٢-٣: Detection limit:

Whereas detection limit is less concentration and the given response is higher than response of blank solution with amount (٣S_B), therefore there are three ways to determine detection limit:

١. From gradually dilution for less concentration has been obtained from calibration curve is (٥.٠ μg.ml$^{-١}$) this dilution lead to moving toward low concentrations (١.٠ μg.ml$^{-١}$) by using the volume of sample injection (٦٠ μl).

$\because \chi = 1\mu\text{g.ml}^{-1}$

$\because \chi = 0.06\,\mu\text{g}/60\,\mu\text{l}$

=٦٠ ng/٦٠ μl= D.L

This given response can be sensed and higher than response of distilled water by amount (٣S_B) and with intensity (٥٢ mV) as indicated in figure

(٤-٢٥).

٢. By depending on the value of slope::

$$\mathrm{D.L} = \frac{3S_B}{\mathrm{slope}} \Rightarrow \frac{3\times 0.001\,\mathrm{mV}}{8.299\,\dfrac{\mathrm{mV}}{\mu\mathrm{g.ml}^{-1}}}$$

$$\Rightarrow \mathrm{D.L.} = 3.615\,\mu\mathrm{g.ml}^{-1}$$

$$= 21.7\ \mathrm{pg}/60\ \mu\mathrm{l}$$

٣. From linear equation

$Y=L.O.D=y_B+٣S_B$

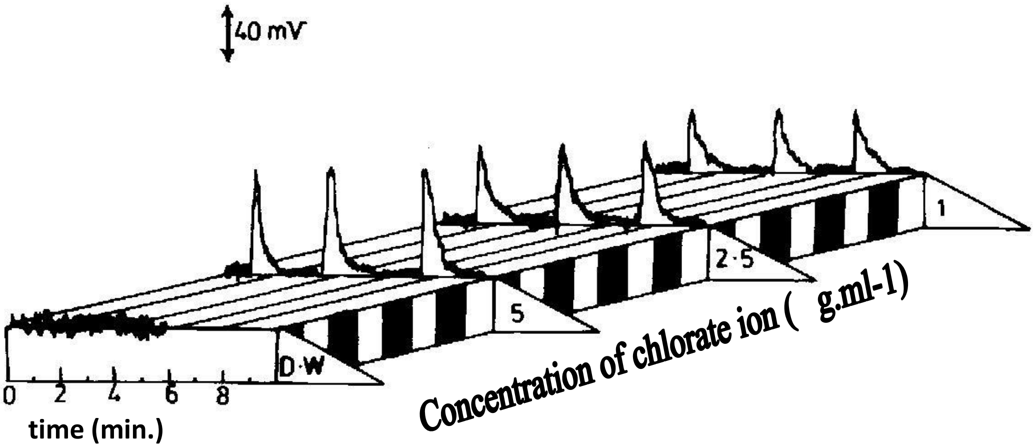


Figure (٤-٢٥) Detection limit for determination of chlorate ion for system ($ClO_٣^{-}$-I^{-}-$H_٣O^{+}$) and from dilution moving toward low concentration b y amount ٦٠ ng for ٦٠ µl.

٤B-٢-٤: The reproducibility:

The study in this unit is distinguished with high reproducibility, whereas the values of percentage for relative standard deviation was very small after fixing the optimum conditions of chemical variables: concentrations of sulphuric acid (١.٥ M) and potassium iodide (٠.١ M), and for changing concentration of injection sample and physical variables: volume of sample (٦٠ µl), injection time (٦٠ sec.) and flow rate (٤ $ml.min^{-١}$), and results are shown in table (٤-٢٥) and figure (٤-٢٦).

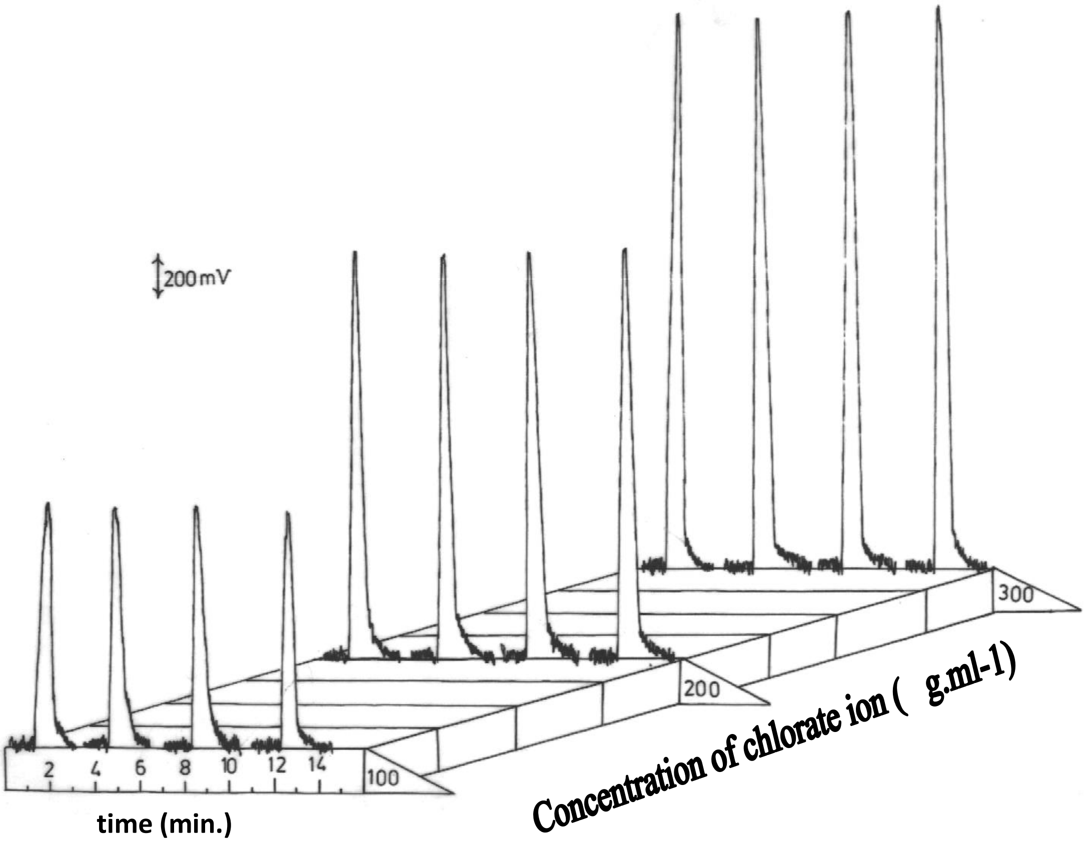


Figure (٤-٢٦): Study of reproducibility through determination of chlorate ion for system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$)

Table (٤-٢٧): The results of reproducibility to measurement intensity of response for releasing iodine from system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$).

$[ClO_{٣}^{-}]$ µg.ml$^{-١}$	$\bar{y}$ (mV)	Standard deviation $\sigma_{n-١}$	Reproducibility RSD%= $\frac{\sigma_{n-1}}{7}\times 100$	Injection No.	$\bar{y} \pm t_{0.05} \frac{\sigma_{n-1}}{\sqrt{n}}$ to n -1 and confidence limit ٩٥٪
١٠٠	١٠٨٠	٠.٩٨	٠.٠٩١	٤	١٠٨٠ ± ١.٥٥٨
٢٠٠	١٧٨٠	١.٣٢	٠.٠٧٤	٤	١٧٨٠ ± ٢.٠٩٨
٣٠٠	٢٤٦٠	٢.٥٥	٠.١٠٤	٤	٢٤٦٠ ± ٤.٠٥٤

٤B-٣: Effect of interferences

Although methods of continuous flow injection are sensitive methods and through it moving toward low concentrations but exposed to interfering for many of positive and negative ions and in this study chlorate ion was determined and it's oxidant material and influenced with finding many of interference ions and this effect on the shape and intensity of the response, therefore should after fixed all variables study effect other of cations, such as

Fe (II), Ni (II), Zn (II), Cr (II), Co (II)

And anions, such as

$NO_{٣}^{-}$, $Cr_{٢}O_{٧}^{-٢}$, $CrO_{٤}^{-}$, Br^{-}, $C١^{-}$, …..

And this study was done by using constant concentration of chlorate ion (١٠٠ µg.ml$^{-١}$) in three bottles which have capacity (١٠٠ ml) contain changing of concentration for interferences ions (٢٥, ٥٠ µg.ml$^{-١}$) in bottles (٢, ٣) and first bottle was prepared that contain chlorate ion is reference to compare with variable concentration of interference ion by finding chlorate ion in bottles ٢, ٣, injected of reference solution and other solutions for three times sequencely caused increasing in response of reference that compare with responses obtained from solutions contain interference ion to calculate percentage for interference or response of chlorate ion of unit ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) in tables (٤-٢٨), (٤-٢٩).

That show percentage of interference effect for positive and negative ions with small value of relative standard deviation.

Table (٤-٢٨): Effect of cation interferences on height response for system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) by percentage of interfering effect.

Conc. of interference ion (µg.ml$^{-١}$)	Percentage of interfering effect (%)				
	$CO^{+٢}$	$Zn^{+٢}$	$Cr^{+٣}$	$Ni^{+٢}$	$Fe^{+٢}$
٢٥	-١.٥٨	+١.٣٥	-٦.٢٥	+١.٥٦	-٦٥.٨٢
٥٠	-١٢.٦٩	+٢.٩٨	-٦.٥٣	+٣.١٣	-٧٠.٨٩

Table (٤-٢٩): Effect of Anion interferences on height response for system ($ClO_{٣}^{-}$-I^{-}-$H_{٣}O^{+}$) by percentage of interfering effect.

Conc. of interference ion (µg.ml$^{-١}$)	Percentage of interfering effect (%)					
	$IO_{٣}^{-}$	$Cr_{٢}O_{٧}^{-٢}$	$NO_{٣}^{-}$	$CrO_{٤}^{-٢}$	Cl^{-}	Br^{-}
٢٥	+٣.١٧	+١١.١١	+٨٥.٧١	+٤.٧٦	-٢.٥٣	-٤٠.٥١
٥٠	+١١.١١	+٣٤.٩٢	+١١٤.٢٩	+٢٠.٦٣	-٣٢.٩١	-٤٣.٠٤

The cation interferences can be removed by putting small column before entering the loop or by putting resin to solution before entering the unit of flow injection analysis, while anion interferences can not remove the interference.

٤B-٤: Standard addition method and applications:

After fixing optimum condition, the sample of hypochlorate which is used is homemade from Babylon company of soap and detergent for limited industry-Baghdad, and pull a constant volume from it (٠.١ ml) in five volumetric flasks, the first flask was prepared and contains enough sample solution, while the rest of the flasks are added to each one gradually, increasing of volume chlorate ion for obtaining finally on changing concentrations of chlorate ion (٢٥, ٥٠, ٧٥, ١٠٠ µg.ml$^{-١}$). In addition it contains constant volume of sample solution as shown in table (٤-٣٠).

Table (٤-٣٠): Results of additions by standard addition method

No. of Bottles	١	٢	٣	٤	٥
Volume of sample (ml)	٠.١	٠.١	٠.١	٠.١	٠.١
$[ClO_{٣}^{-}]$ μg.ml$^{-١}$	-	٢٥	٥٠	٧٥	١٠٠
Type of solution	Sample solution	Standard solutions + sample solution			

The complete flask to (٥٠ ml) by distilled water after that measured the sample and obtained results in table (٤-٣١); the measurement was repeated for three times.

Table (٤-٣١): Changing the response with concentration by standard addition method.

$[ClO_{٣}^{-}]$ μg.ml$^{-١}$	**Response height** (ȳ) mV	**$\sigma_{n-١}$** **%RSD**	$\bar{Y} \pm t_{0.05}\frac{\sigma_{n-1}}{\sqrt{n}}$
Sample solution	١٧٠٠	١.٢٣ ٠.٠٧٢	١٧٠٠ ±٣.٠٥٥٨
٢٥	١٩٠٠	٢.٣٣	١٩٠٠±٥.٧٨٨٦

		٠.١٢٢	
٥٠	٢١٠٠	٥.٠٠ ٠.٢٣	٢١٠٠±١٢.٤٢٢٠
٧٥	٢٣٠٠	٣.١٢ ٠.١٣٥	٢٣٠٠±٧.٧٥١٣
١٠٠	٢٤٦٠	٢.٥٥ ٠.١٠٤	٢٤٦٠±٦.٣٣٥٢

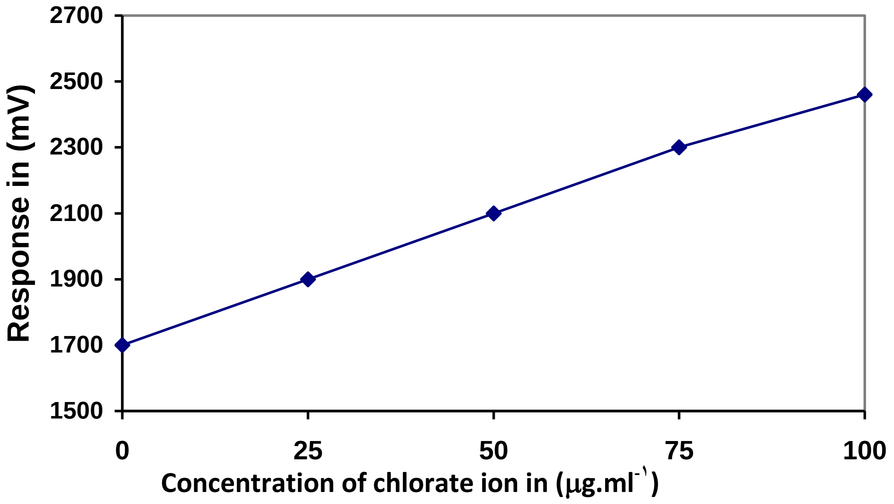


Figure (٤-٢٧): Determination the concentration of chlorate ion in hypochlorite solution.

٤B-٥- Comparison between the first unit and the second unit

From the results of two units, figure (٤-٢٧ a) shows that unit A is good sensitive and correlation coefficient of it (٠.٩٩٩٨).

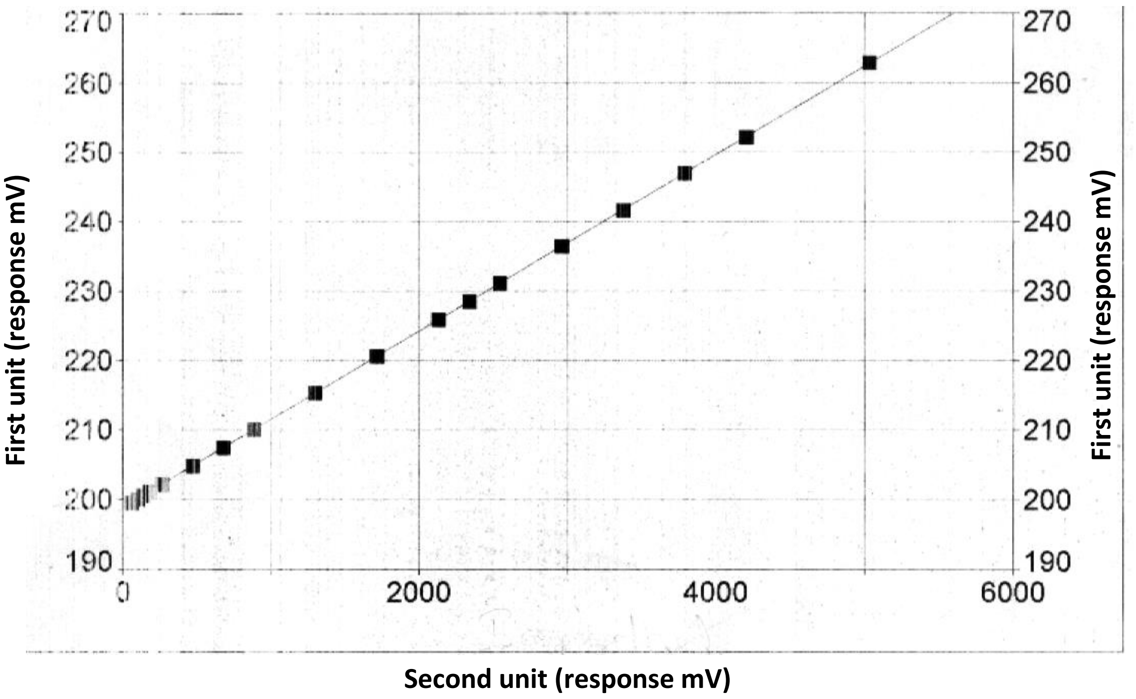


Figure (٤-٢٨ a): The unit is good sensitive

While figure (٤-٢٨ b) shows that unit B is more sensitive and high linearity because of negative intersection and correlation coefficient of it (٠.٩٩٨٨).

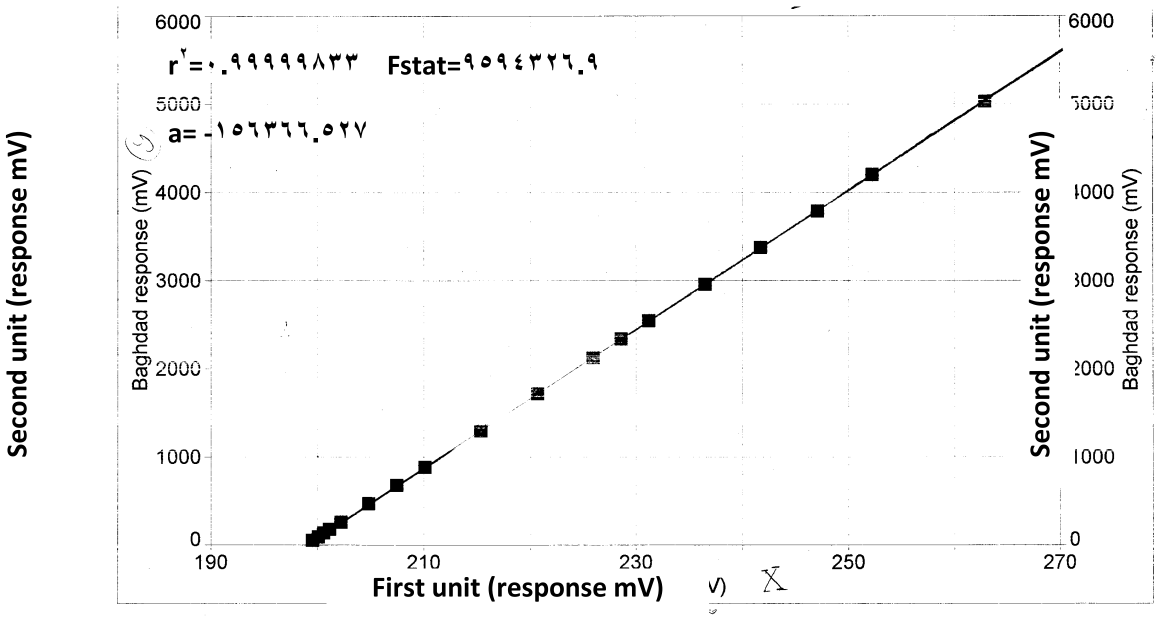


Figure (٤-٢٨ b): Show the first and second unit

Figure (٤-٢٨ c) shows that calibration curve form both units which explain the high sensitivity of unit b compared with unit a.

The sensitivity of unit b is larger than ٧٩ time of unit a and the linearity of unit b is best for same range of concentration.

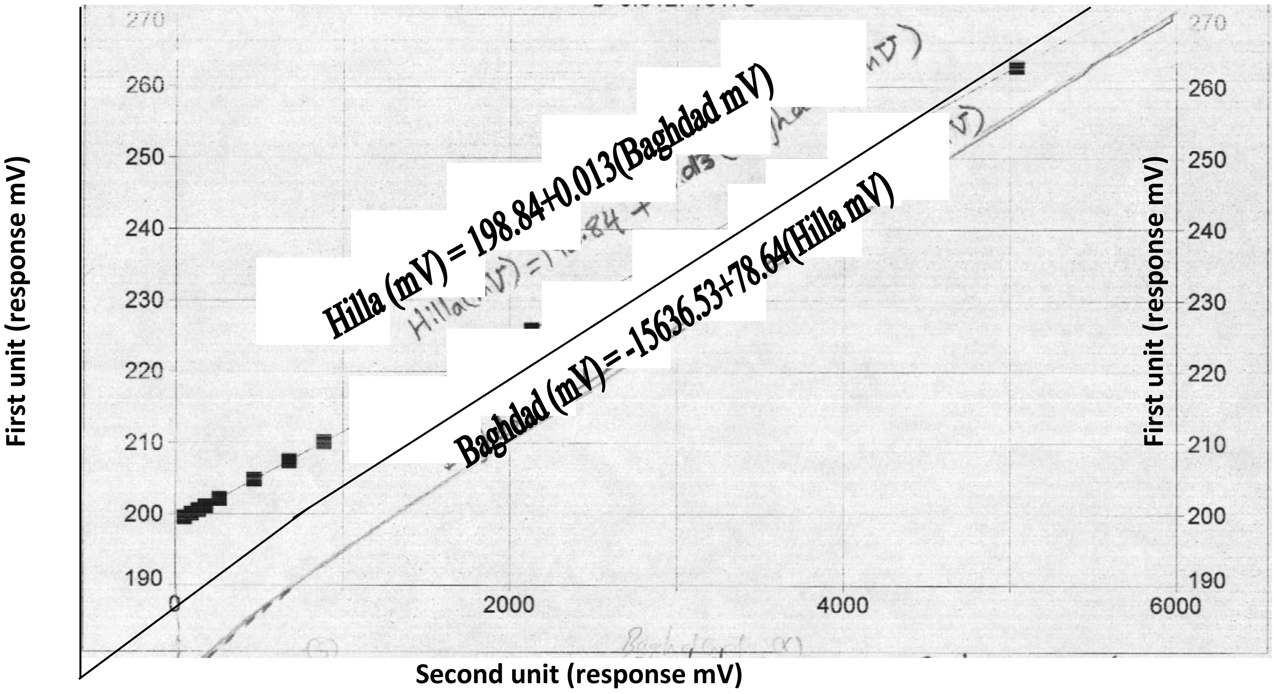
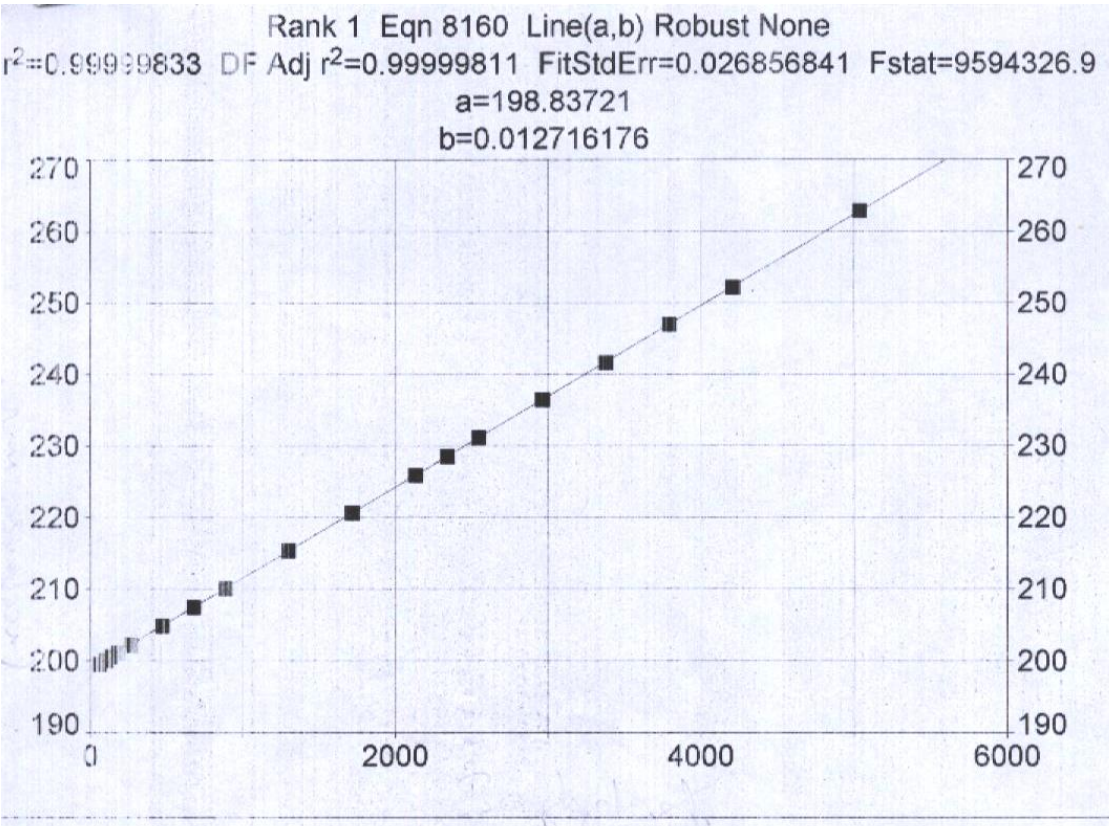


Figure (٤-٢٨ c)

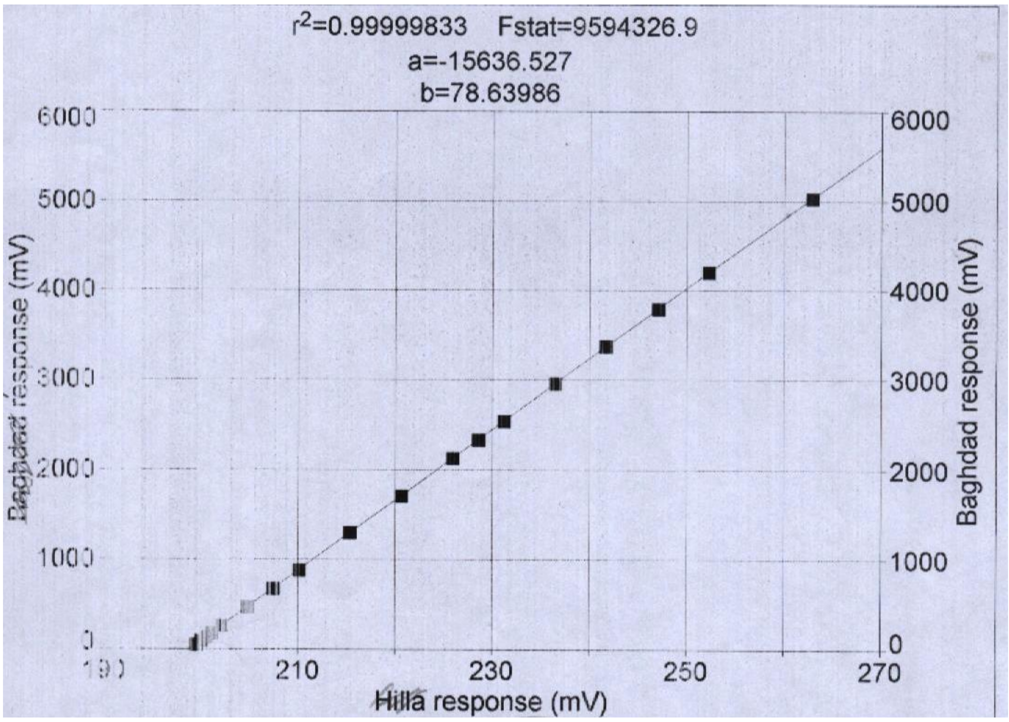
Figure (٤-٢٨ a,b,c) Comparison between two units of the rule of response

Figure (٤-٢٩ a,b,c) shows the value of y (y predicted) for the two units which indicate the sensitivity of the both units



Second unit (response mV)

Figure (٤-٢٩ a): Comparison between tow units of y (y predicted)



Second unit (response mV)

First unit (response Mv)

Figure (٤-٢٩ b)

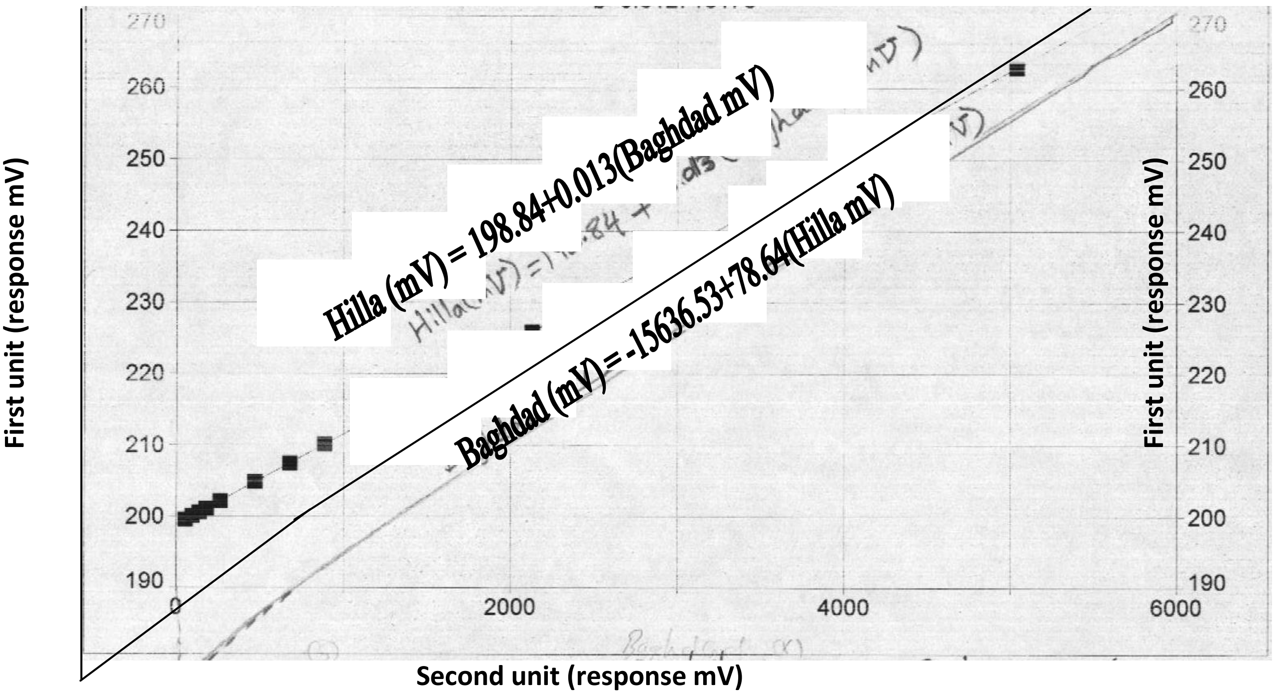


Figure (٤-٢٩ c)

Figure (٤-٢٩ a,b,c) Comparison between two units of $\bar{y}$ (y predicted)

References

References

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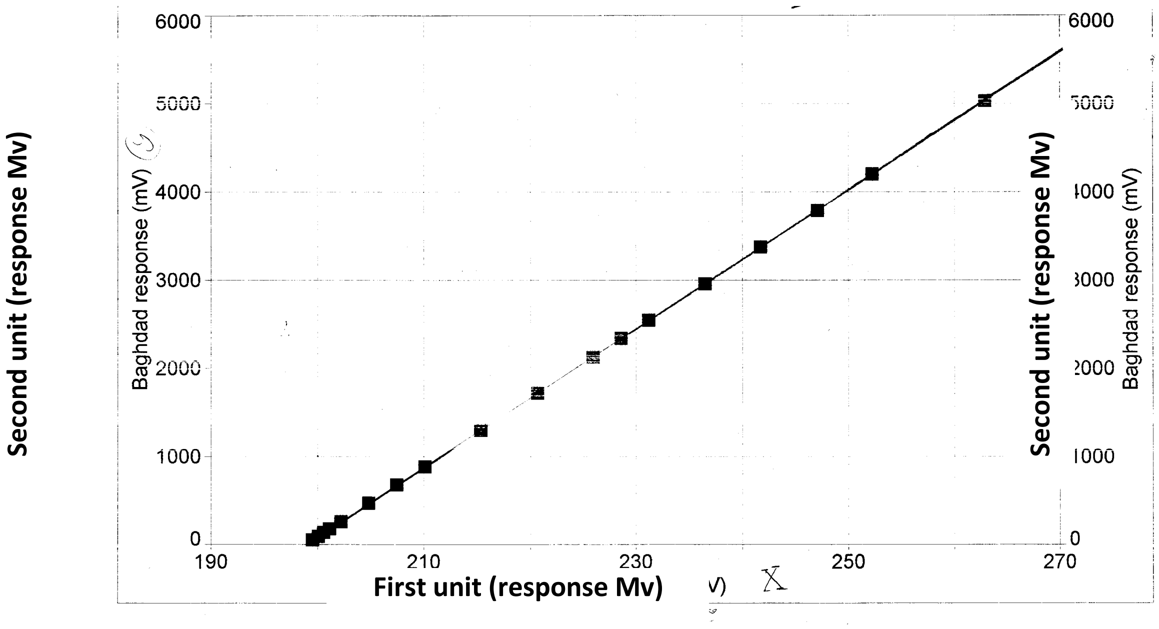
$r^{٢}$=٠.٩٩٩٩٩٨٣٣ Fstat=٩٥٩٤٣٢٦.٩

a= -١٥٦٣٦٦.٥٢٧


Second unit (response Mv)
Baghdad response (mV)
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5000
4000
3000
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X
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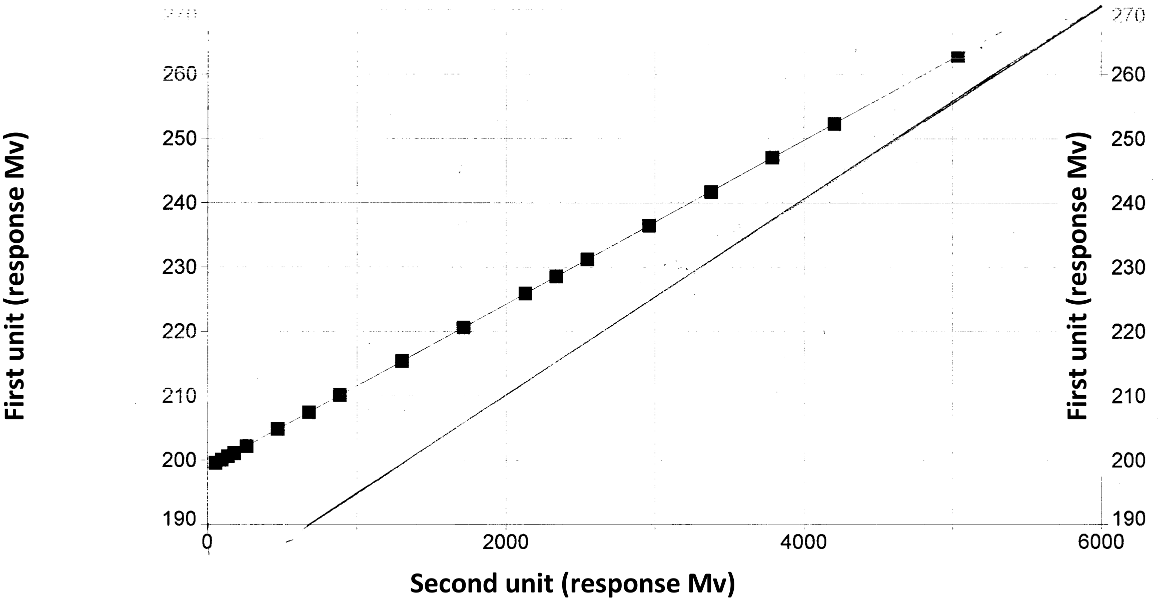
Baghdad response (mV)

(٤-b)


First unit (response Mv)
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240
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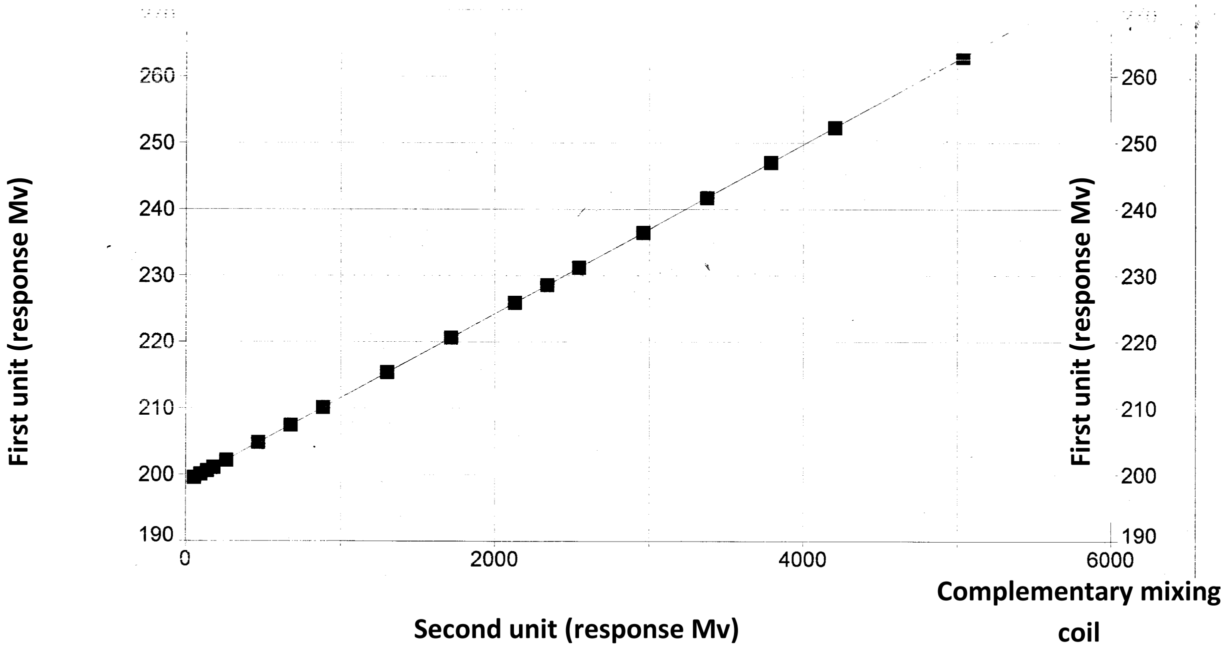
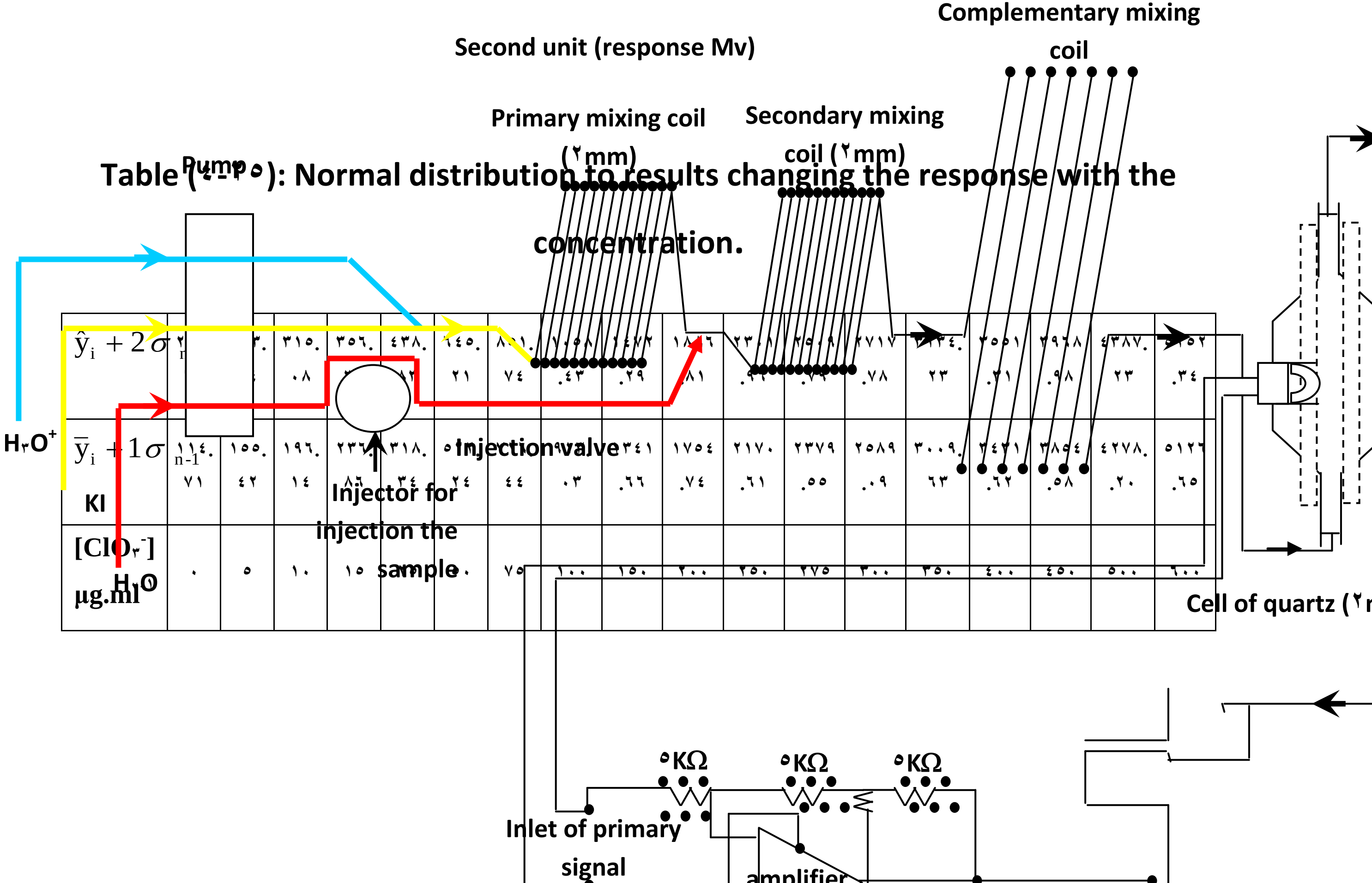


Table (٤-٣٥): Normal distribution to results changing the response with the concentration.

$\hat{y}_i + 2\sigma_{n-1}$	[illegible]	[illegible]	٣١٥.٠٨	[illegible]	[illegible]	٦٤٥.٢١	[illegible]	١٠٥٨.٤٣	١٤٧٢.٢٩	[illegible]	[illegible]	[illegible]	٢٧١٧.٧٨	[illegible]	٣٥٥١.٣١	٣٩٦٨.٩٨	٤٣٨٧.٢٣	[illegible]
$\bar{y}_i + 1\sigma_{n-1}$	١١٤.٧١	١٥٥.٤٢	١٩٦.١٤	٢٣٦.٨٦	٣١٨.٣٤	[illegible]	[illegible]	[illegible]	١٣٤١.٦٦	١٧٥٤.٧٤	٢١٧٠.٦١	٢٣٧٩.٥٥	٢٥٨٩.٠٩	٣٠٠٩.٦٣	٣٤٢١.٦٢	٣٨٥٤.٥٨	٤٢٧٨.٢٠	٥١٢٦.٦٥
[ClO٣⁻] µg.ml	٠	٥	١٠	١٥	[illegible]	[illegible]	٧٥	١٠٠	١٥٠	٢٠٠	٢٥٠	٢٧٥	٣٠٠	٣٥٠	٤٠٠	٤٥٠	٥٠٠	٦٠٠



Y_i practically (mV)	٠	٨٠	١١٢	٢٠٠	٢٤٠	٤٠٠	٦٠٠	١٠٨٠	١٤٦٠	١٧٨٠	٢٠٤٠	٢٣٤٩	٢٤٦٠	٢٩٥٧	٣٣٧٥	٣٧٩٠	٤٢٠٥	٥٠٣٥
$\hat{y}$ **predicted (mV)**	٥٥.٥٨	٩٧.٠٨	١٣٨.٥٧	١٨٠.٠٦	٢٦٣.٠٥	٤٧٠.٥٣	٦٧٨.٠٠	٨٨٥.٤٨	١٣٠٠.٤٢	١٧١٥.٣٧	٢١٣٠.٣٢	٢٣٣٧.٧٩	٢٥٤٥.٢٦	٢٩٦٠.٢١	٣٣٧٥.١٥	٣٧٩٠.١٠	٤٢٠٥.٠٥	٥٠٣٤.٩٤
$\bar{y}_i - 1\sigma_{n-1}$	-٣.٥٥	٣٨.٧٣	٨١.٠٠	١٢٣.٢٧	٢٠٧.٧٦	٤١٨.٨٢	٦٢٩.٥٦	٨٣٩.٩٢	١٢٥٩.١٨	١٦٧٦.٠٠	٢٠٩٠.٠٣	٢٢٩٦.٠٣	٢٥٠١.٤٤	٢٩١٠.٧٩	٣٣١٨.٦٩	٣٧٢٥.٦٣	٤١٣١.٩١	٤٩٤٣.٢٤
$\bar{y}_i - 2\sigma_{n-1}$	-١٢١.٤٤	-٧٩.٦٩	-٣٧.٩٤	٣.٨٠٩	٨٧.٢٨	٢٩٥.٨٥	٥٠٤.٢٥	٧١٢.٥١	١١٢٨.٥٤	١٥٤٣.٩٣	١٩٥٨.٦٧	٢١٦٥.٧٩	٢٣٧٢.٧٥	٢٧٨٦.١٩	٣١٩٩.٠١	٣٦١١.٢٣	٤٠٢٢.٨٧	٤٨٤٤.٥٦
$\sigma_{n-١}$	٠	٠.٣٢	٠.١١	٠.١٥	٠.٣٣	٢.١٥	١.٤٥	٢.٥٥	١.٩٥	٢.٠٠	٣.٠٥	٢.٣٥	٢.١١	٢.٠٩	٣.٤٥	٢.١٩	١.٨٧	٢.٤٥