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Determination of Bismuth (III) ion by continuous flow injection analysis via turbidimetric (T_{180}^{o}) and scattered light effect at two opposite position ($2N_{90}^{o}$) using Ayah $4S_W$-3D-T_{180}^{o} -$2N_{90}^{o}$ -Solar - CFI Analyser

تقدير آيون البزموث باستخدام تحليل الحقن الجرياني المستمر عن طريق قياس التعكريه (T_{180o}) وتأثير استطاره الضوء عند اتجاهين متعاكسين ($2N_{90o}$) باستخدام المحلل Ayah $4S_W$-3D-T_{180}^{o} -$2N_{90}^{o}$ -Solar - CFI

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Abstract

A simple and highly sensitive method for the determination of Bi(III) ion was developed by continuous flow injection analysis via turbidimetric (T_{180}^{o}) and scattered light effect at two opposite position ($2N_{90}^{o}$). The formation of a black precipitate is based upon the reaction between Bi(III) with SnO_2^{2-} in basic medium. The precipitate is measured via the attenuation of incident light and it's scattering in two opposite directions. Chemical and physical parameters were studied to obtain the best condition . The linearity of Bi(III) ion is ranged from 0.08 to50mmol.L^{-1}, with correlation coefficient r=0.9973, limit of detection (LOD) 0.06 mmol.L^{-1}($3S_B$)(S/N=3) and the percentage relative standard deviation for 45 mmol.L^{-1} Bi(III) solution is lower than 3% (n=6). This method has been applied successfully to determine a bismuth ion in drug. Also provided a comparison between the new method with the classical method (spectrophotometric method) of analysis using the standard addition method. It shows that there was no significant difference via the use of paired t- test at α=0.05(95% confidence) between the two methods and could be using the develop method as an alternative method.

Key word: Bismuth(III), Spectrophotometry, Turbidity & Nephelometry, Flow injection analysis

الخلاصة

طورت طريقة بسيطه و عالية الحساسية لتقدير ايون البزموث(III) بواسطة الحقن الجرياني المستمر مع قياس التعكريه والبعثره باتجاهين متعاكسين. أستندت على تكوين الراسب الأسود على تفاعل ايون البزموث(III) مع ايون القصديريت SnO_2^{2-} في الوسط القاعدي . تم قياس التعكريه بواسطة توهين الضوء الساقط وكذلك بعثرته عند زاوية قائمه وباأتجاهين متعاكسين. تم دراسة المتغيرات الكيميائية والفيزيائية للحصول على الضروف الفضلى، المدى الخطي لايون البزموث يمتد بين(0.08- 50) مللي مول.لتر$^{-1}$ مع معامل الارتباط r=0.9973 و تم الحصول على حدود كشف (L.O.D) 0.06 ملي مول.لتر$^{-1}$ ($3S_B$) (3 = S/N) و الانحراف القياسي النسبي المئوي لتركيز 45 مللي مول.لتر$^{-1}$ لايون البزموث اقل من 3% (6 = n). طبقت هذه الطريقة بنجاح لتقدير البزموث (III) في احدى المستحضرات الصيدلانيه. تم اجراء مقارنة بين الطريقة الجديده مع الطريقة التقليديه باستخدام طريقة الاضافات القياسية ولوحظ عدم وجود فرق جوهري بين الطريقتين باستخدام اختبار- t الزدوج عند α =0.05 وحدود ثقه 95% وبالامكان استخدام الطريقه المستحدثه كطريقة بديلة في التقدير.

Introduction

Bismuth is found in the earth's crust up to 0. 0002%, which is the least toxic among the heavy metals. A number of toxic effects in humans have been attributed to bismuth compounds, such as nephrotoxic, neurotoxic, kidney damage symptoms nephropathy, osteoarthrapathy, hepatitis and

neuropathology. Bismuth is a strategic element, thus its identification and determination are very important [1]. Bismuth has been widely used for various industrial purposes, for instance, as a pigment for coloring plastics and paints [2], batteries [3] and ceramics [4]. Bismuth and its compound are also used in semiconductors cosmetic preparations, alloys and metallurgical additives and in the preparation and recycling of uranium nuclear fuels [5]. Bismuth has been used in peptic ulcer treatment and tropical dermatological cream. As the use of bismuth in medicine increased, it has spread in the environment and the chance of exposure of organisms to bismuth has been increased. A number of toxic effects in humans have been attributed to bismuth compounds, such as nephrotoxic, neurotoxic, kindeydamhage symptoms nephropthy, osteoarthrapathy, hepatitis and neuropathology [6]. Bismuth salts have emerged as efficient lewis acids due to their relatively low toxicity, therefore, it used a catalyzed route for the synthesis of α-aminophosphonates from aldehydes [7]. Bismuth salt is used for synthesis and characterization of compounds, using bismuth nitrate pentahydrate in Tetrahydrofuran (THF) adsorbed silica gel/fly ash under microwave method[8].Although bismuth was not known as a metal, it was used as a beauty treatment during antiquity. For nearly 150 years, low doses of bismuth compounds have been excellent remedies against gastric disorders, especially for colitis, diarrhea and peptic ulcers. They were and still are used for burn bandage dressings, antiseptic powders, salves or ointments and in the treatment of venereal diseases [9].The exact mechanism of its action is yet unknown, but its therapeutic activity might result from mucosa-protective properties, and from inhibition of colonic bacteria acting on fermentable food residues. Although the absorption of Bi(III) in the human organism is generally low, several cases of nephrotoxic, neurotoxic and kidney damage symptoms attributable to the use of Bi(III)-containing pharmaceutical formulations have been reported [10,5].

The development of analytical techniques for the determination of bismuth at low levels in aquatic sample is significant. So, analytical techniques such as spectrophotometry, flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) have been used for its measurement [11]. The determination of bismuth in human plasma by ICP-MS and its use in bioequivalence studies has been reported [12]. Gallacetophenone phenyl hydrazone (GPPH) has been used as an analytical reagent for amperometric determination of bismuth in wood and alloy [13]. Several reagents have been used for the spectrophotometric determination of bismuth such as,dithiozone,

diethyldithiocarbamate, xylenol orange, iodide, thiourea and azo reagents [14]. Kinetic spectrophotometric determination of Bi (III) has been employed, the method is based on using its catalytic effect on the oxidation of phenylfluorone by hydrogen peroxide in ammonia buffer, the method was confirmed by determining Bi (III) in a stomach ulcer drug [15]. Extractive spectrophotometric determination of bismuth (III) in alloy samples using 1-amino-4, 4, 6-trimethyl (1H, 4H) pyrimidine-2-thiol as an analytical reagent has also been reported [1].

This paper describes aflow injection-turbidimetric and nephelometric method for determination of Bi(III) ion by using Ayah $4S_W$-3D-$T_{180}{}^o$-$2N_{90}{}^o$ -Solar - CFI Analyser. The purposed method can be determined three characteristic properties of formed precipitate i.e. attenuation and reflection of light at two opposite reverse direction also the algebraic sum of them . The output signal was recorded as an analytical response via time for each concentration level.

Experimental

Chemicals

All chemicals were used of analytical-reagent grade while distilled water was used to prepare the solutions. A standard solution of Bi(III) ion ($Bi(NO_3)_3.5H_2O$,484.98, BDH, 0.083mol.L^{-1}) was prepared by dissolving 10.0633g in 250ml (dissolving and diluting in 1:5HNO_3). A stock solution Tin(II) chloride ($SnCl_2.2H_2O$, 225.65,BDH, 0.5 mol.L^{-1}) was prepared by dissolving 28.2063g in 250ml of distilled water(dissolve in 42.5ml concentrated HCl). Potassium iodide solution (KI, 166.0028,BDH, 20%wt/v) was prepared by dissolving 20.00g in 100ml distilled water and 1:5 sulfuric acid solution was prepared. Sodium hydroxide solution (NaOH, 40, Fluka,1mol.L^{-1}) was prepared by dissolving 40g in 1L (Standardized with HCl solution). A sample solution of Bi(III) ion

($(BiO)_2CO_3$, 509.92g/mol, SDI, 0.1mol.L^{-1}) was prepared from pure powder drug by dissolving 5.0992g in 100ml.

Cleaning Solution (washing buffer)

A washing buffer solution containing 40g EDTA(disodium salt), 7g of Ammonium chloride and 57ml of 25%(wt/wt) ammonia ,was prepared by dissolving the chemicals in succession in 500ml of distilled water followed by dilution to 1L in a volumetric flask[16].

Apparatus

Peristaltic pump – 4 channels (Switzerland) an Ismatic type ISM796. A rotary 6- port injection valve (Teflon) ,(IDEX corporation, USA).The response was measured by a homemade Ayah $4S_W$-3D-T_{180} - $2N_{90}$ - Solar - CFI Analyser [17] ,which uses four white snow LED for irradiation of the flow cell at 2mm path length. Three solar cell were used as a detector for collecting signals via travelling of sample for 40mm length . The readout of the system composed of x-t potentiometric recorder (KOMPENSO GRAPH C-1032) SIEMENS (Germany) or digital AVO-meter (auto range)(0.00-2000mV) (China). Spectrophotometric readings under batch conditions were made by means of a Shimadzu (Japan) UV-1800 double-beam spectrophotometer and quartz cuvette with an optical path length of 10 mm.

Methodology

Three line manifold system was used. Distilled water was passed in the first line as a carrier stream (2.8ml.min^{-1} flow rate) ,the same line leading to the injection valve which allows the use of 100 µl sample volume from Bi(III); while the second line supply hydroxide ion from sodium hydroxide(1mol.L^{-1}) (2.9ml.min^{-1} flow rate); while the third line supply Sn(II) from tin chloride solution (50mmol.L^{-1}) (2.9ml.min^{-1} flow rate). Both line meet at a junction (methyl methacrylate – Y-junction); with an outlet for reactant product (form the precipitating agent as SnO_2^{2-}) followed by a mixing coil to complete the reaction. The output is connected with the injected sample (Bi(III) ion) via Y-junction to form the precipitate (Black precipitate bismuth) . Figure no. 1 shows flow diagram that have been used throughout this work. The mechanism of reaction shows as equation as following [18].

$$Sn^{2+} + 2OH^- \rightleftharpoons Sn(OH)_2 \quad \text{----------(1)}$$

$$Sn(OH)_2 + 2OH^- \rightleftharpoons SnO_2^{2-} + 2H_2O \quad \text{----------(2)}$$

$$2Bi^{3+} + 3SnO_2^{2-} + 6OH^- \rightleftharpoons 2Bi\downarrow + 3SnO_3^{2-} + 3H_2O \quad \text{----------(3)}$$

Black precipitate

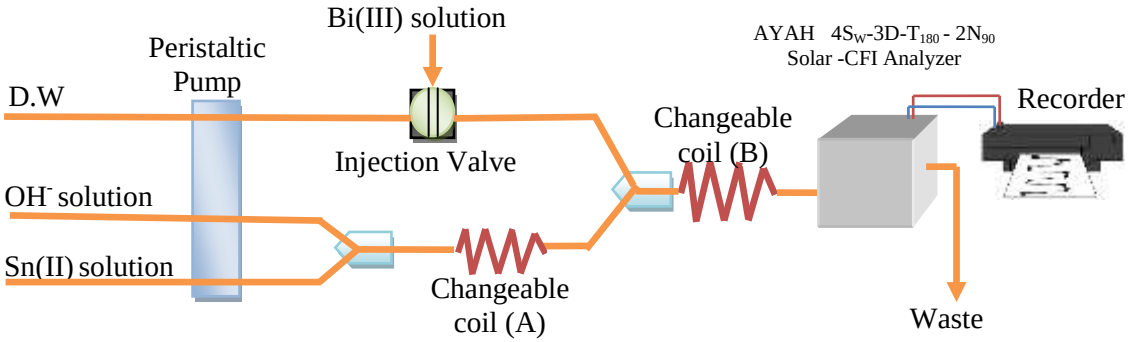


Fig. 1: Flow gram for Bi(III) ion determination using three lines system.

Optimization of Variables

Chemical parameters (mainly concentration) as well as physical parameters (intensity of incident light (p^o), volume of coil, flow rate, sample volume and purge time) were studied.

Chemical Variables

Tin (II) Concentration

A series of the Tin chloride solutions (10- 100 mmol.L^{-1}) were prepared.1mol.L^{-1} sodium hydroxide and 20 mmol.L^{-1} of bismuth (III) ion solution were used with 100 µl sample volume using 2.9 ml.min^{-1} flow rate and the intensity of incident light of total four LEDs of 1000 mV. The total obtained results were tabulated in table no. 1. It can be seen that an increase in Sn(II) ion concentration causes an increase in the attenuation of incident light as well as in the reflections of the light on particles surfaces. After 50mmol.L^{-1} there is a decrease in the attenuation of incident light but an increase at N_L and N_R; followed by a nearly constant response as shown in figure no.2A.i.e, 50mmol.L^{-1} Sn(II) ion concentration was chosen as the optimum concentration to formation SnO_2^{2-} precipitating agent as shown in figure no.2B that used for further experiments.

Table 1: Effect of Sn(II) concentration on the measurement of attenuation of incident light as well as reflection of light at two opposite position and algebraic sum of them.

[Sn(II)] mmol.L^{-1}	Type of measurement $\bar{y}_i \pm t_{0.05/2}\ \sigma_{n-1}/\sqrt{n}$ (n=3) (mV)			
	Attenuation of incident light $T_{(0\text{-}180)}$	Scattering of light (L) N_L (+90)	Scattering of light (R) N_R (-90)	Algebraic sum of the scattering of light $N_{(L+R)}$ (±90)
10	412±2.234	8±1.203	8±0.000	2±0.000
30	512±2.452	32±0.000	10±1.418	16±0.000
50	660±1.347	52±1.004	16±1.632	36±0.993
70	580±1.042	78±1.624	20±1.729	48±1.548
100	560±2.732	88±1.663	24±1.522	58±1.279

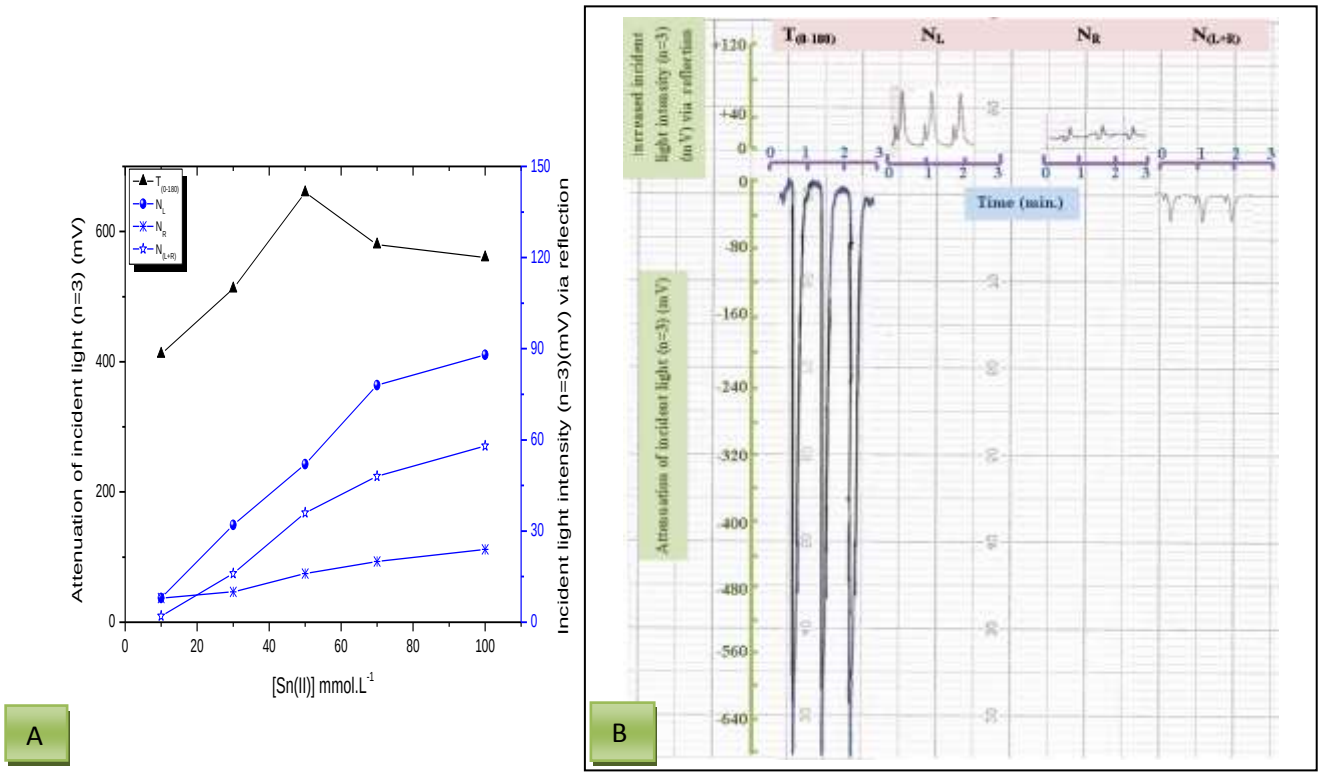


Fig. 2: Effect of Sn (II) concentration on : (A)Attenuation of incident Light, scattering of light at two opposite directions and the algebraic sum of them, (B)Response profile at optimum Sn (II) concentration for three successive measurements.

Sodium Hydroxide Concentration

Effect of NaOH concentration was studied using 50mmol.L^{-1} of Sn(II); while maintaining other variable as in previous experiment. Variable NaOH concentration 0.025-1.2 mol.L^{-1} was used. The results tabulated in table no. 2 which shows that an increase on the attenuation of incident light, scattering of light in two way and outcome of scattering light (±90) with increased concentration of NaOH. 1mmol.$L^{-1}$was selected as the optimum concentration that can be used to give a better reproducible outcome. It might be attributed that at low concentration (i.e., less than 1mmol.L^{-1}) leading to formation $Sn(OH)_2$ more than SnO_2^{2-} up to 1mmol.L^{-1} gave the best concentration of precipitating agent (SnO_2^{2-}). Figure no.3A shows the effect of NaOH concentration on attenuation of light, scattering light (±90) and the algebraic sum of them, figure no. 3B shows the response profile at optimum OH^- concentration for three successive measurements.

Table 2: Effect of OH^- concentration on the measurement of attenuation of incident light as well as reflection of light at two opposite position and the algebraic sum of them.

$[OH^-]$ mol.L^{-1}	Type of measurement $\bar{y}_i \pm t_{0.05/2}\ \sigma_{n-1}/\sqrt{n}$ (n=3) (mV)			
	Attenuation of incident light $T_{(0-180)}$	Scattering of light (L) N_L (+90)	Scattering of light (R) N_R (-90)	Algebraic sum of the scattering of light $N_{(L+R)}$ (±90)
0.025	230±2.652	20±1.643	4±0.000	4±0.000
0.500	345±3.539	24±1.754	8±0.000	10±0.000
0.700	400±2.233	38±2.492	12±0.000	20±0.985
1.000	612±1.087	102±1.004	32±0.931	52±1.348
1.200	527±2.433	108±1.394	36±0.870	68±1.073

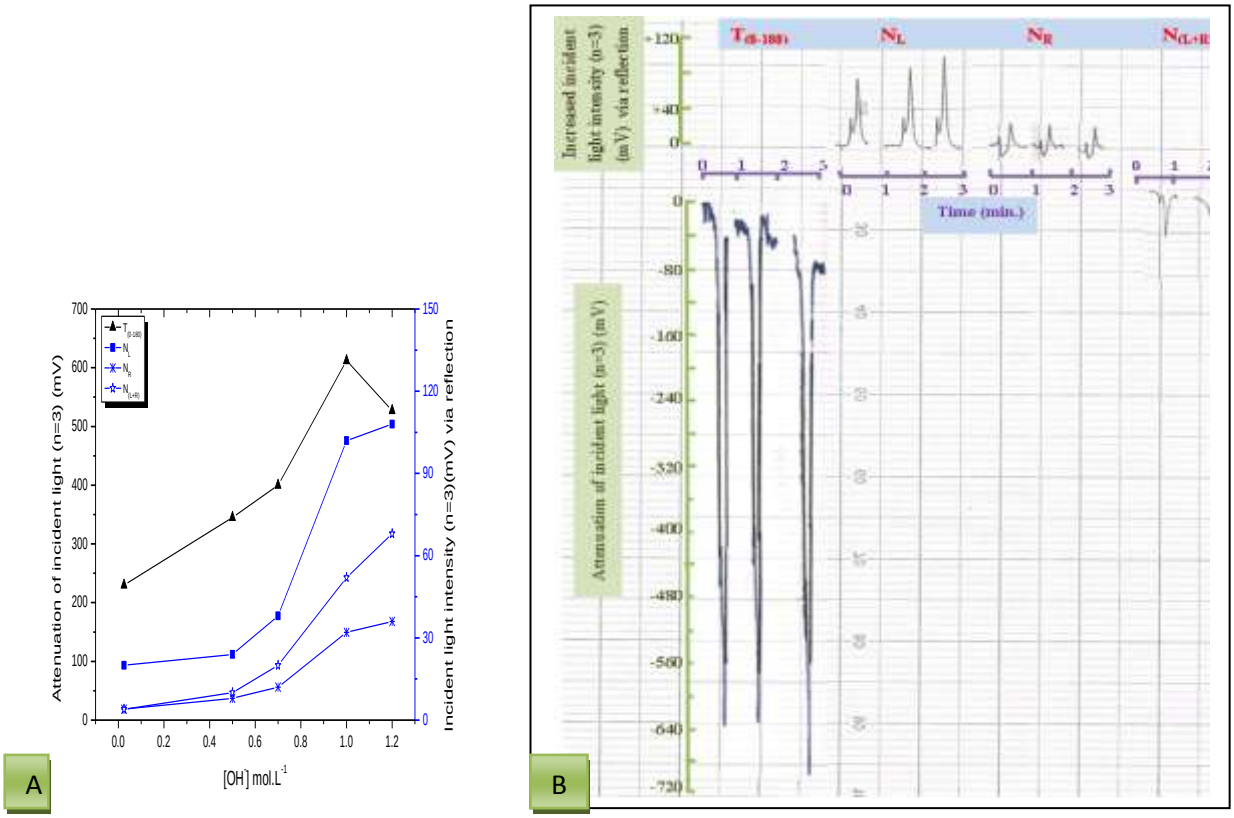


Fig.3: Effect of OH^- concentration on : (A)Attenuation of incident Light, scattering of light at two opposite directions and the algebraic sum of them, (B)Response profile at optimum OH^- concentration for three successive measurements.

Physical Variables

Incident Light Intensity

Intensity of light source was studied while maintaining other chemical parameters fixed. Variable intensity of light source was used 770 -1800mV by variation of light intensity channel in AYAH $4S_W$-3D-T_{180} -$2N_{90}$-Solar CFI Analyzer operation where read by AVO-meter. The results tabulated in table no.3 shows that an increase on turbidity and the reflection of light at two opposite direction with the algebraic sum of both opposite signals with increased intensity of source light. The intensity of (1400 mV) was selected as the voltage that can be supplied to give a better reproducible outcome. Figure no.4A shows the effect of variation of light intensity on attenuation of light, scattering light (±90) and the algebraic sum of them, figure no.4B shows the response profile at optimum incident light intensity for three successive measurements.

Table 3: Effect of incident light intensity on the measurement of attenuation of incident light as well as reflection of light at two opposite position also algebraic sum of them.

Intensity of source light(p^o) (mV)	Type of measurement $\bar{y}_i \pm t_{0.05/2}\ \sigma_{n-1}/\sqrt{n}$ (n=3) (mV)			
	Attenuation of incident light $T_{(0-180)}$	Scattering of light (L) N_L (+90)	Scattering of light (R) N_R (-90)	Algebraic sum of the scattering of light $N_{(L+R)}$ (±90)
770	480±2.463	16±1.324	2±0.000	6±0.000
1020	541±3.486	16±0.000	2±0.000	8±0.000
1230	504±4.653	24±0.000	3±0.000	18±0.000
1400	500±2.364	52±0.000	4±0.000	36±0.000
1650	508±4.356	76±0.938	8±0.663	48±1.893
1800	520±1.976	100±0.891	16±0.543	64±1.478

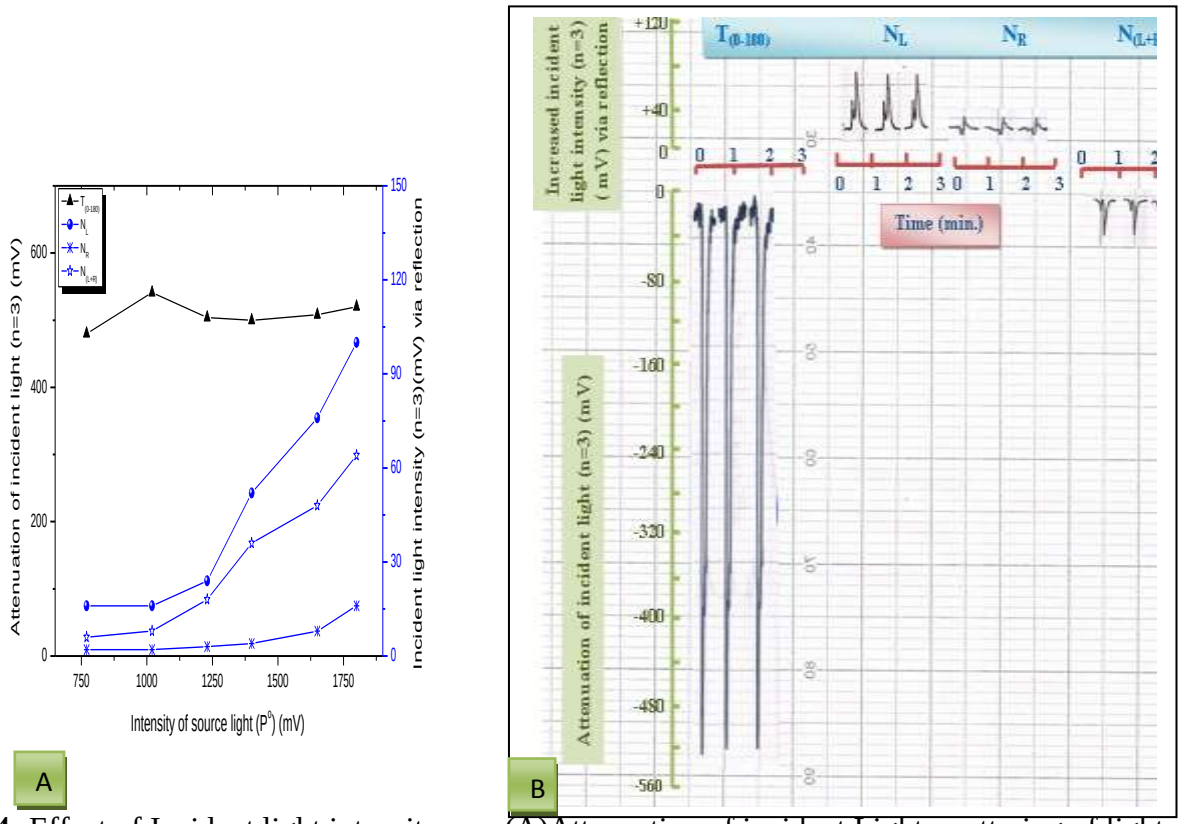


Fig. 4: Effect of Incident light intensity on : (A)Attenuation of incident Light, scattering of light at two opposite directions and the algebraic sum of them, (B)Response profile at optimum incident light intensity for three successive measurements.

Reaction Coil Length

Variable coil(A) length 0 - 50cm was studied this range of length comprises a volume of 0 - 1572 µl which is connected after Y-junction no.1 directly in manifold system as shown in figure no.1. Optimum chemical parameter, and light intensity of 1400mV were used. Table no. 4 summarized all the results obtained. The table shows clearly that 30cm reaction coil which was suitable for the formation a precipitation agent (SnO_2^{2-}) and will serve as a more reproducible and more sensitive measurements. Figure no.5A shows the effect of reaction coil length on attenuation of incident light, scattering of light at two opposite directions and the algebraic sum of them. While the arrival time of injected sample to nibble of the measure 12Secend.

Variable coil(B) length 0 - 70cm was studied, this range of length comprises a volume of 0 - 2199µl which connected after Y-junction no. 2 directly in manifold system figure no.1 .Table no.4 shows all the results obtained for turbidity and the reflection of light at two opposite direction with the algebraic sum of both opposite signals. The table shows clearly that 40cm reaction coil will serve as a more reproducible and more sensitive measurements to complete precipitation of Bi(III) as a black bismuth metal and more than 40cm leading to obtain a broad response maxima. Figure no.5B shows the effect of reaction coil length on attenuation of incident light, scattering of light at two opposite directions and the algebraic sum of them.

Table 4: Effect of Volume of coil on the measurement of attenuation of incident light as well as reflection of light at two opposite position and the algebraic sum of them.

No. of coil	(cm) Diameter (2mm)	Volume of coil (µl)	Type of measurement $\bar{y}_i \pm t_{0.05/2}\, \sigma_{n-1}/\sqrt{n}$ (n=3) (mV)			
			Attenuation of incident light $T_{(0-180)}$	Scattering of light (L)N_L (+90)	Scattering of light (R)N_R (-90)	Algebraic sum of the scattering of light $N_{(L+R)}$ (±90)
Coil A	0	0	396±1.984	38±1.333	6±0.000	32±1.462
	10	314	412±1.051	36±1.092	8±0.000	24±1.543
	20	628	416±1.802	40±1.471	8±1.341	26±0.000
	30	942	468±2.711	44±1.924	16±0.847	24±0.887
	40	1252	417±3.039	38±1.119	14±0.811	28±0.342
	50	1570	424±2.873	44±1.023	14±1.033	26±0.945
Coil B	0	0	384±2.449	40±1.205	8±0.525	24±1.453
	10	314	400±2.018	32±2.392	6±0.000	16±0.000
	20	628	440±1.930	26±1.561	8±0.000	20±1.459
	40	1252	476±1.325	48±1.008	16±1.045	34±1.118
	50	1570	480±1.739	36±1.923	14±1.342	28±2.016
	70	2199	500±1.038	60±1.562	16±1.466	40±1.992

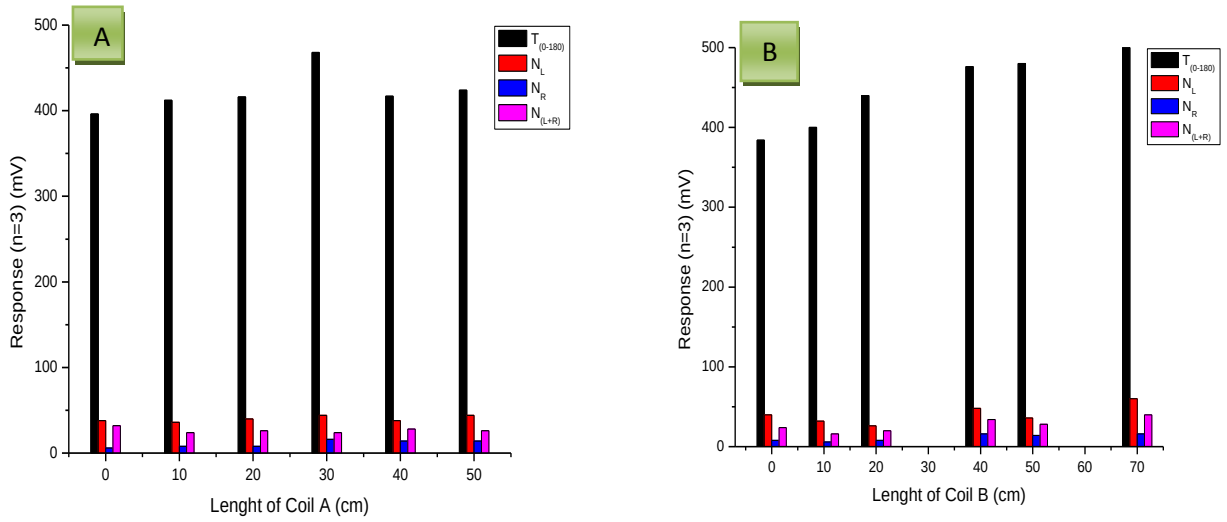


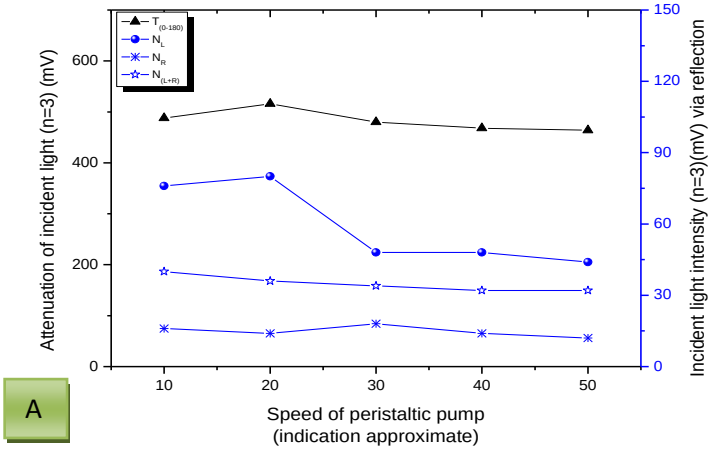
Fig. 5: Effect of volume of coil on the measurement of attenuation of incident light as well as reflection of light at two opposite position also algebraic sum of them, (A) Variable volume of coil A, (B) Variable volume of coil B.

Flow rat

The influences of the flow rate on the measurement were studied. Flow rates ranging from 0.7 to 3.5 ml.min^{-1} for carrier stream were assayed with the aim to evaluate their effect on the peak height and repeatability of the analytical data. Figure no.6A,B shows that at low flow rate there is an increase in dispersion and dilution . While at a higher speed (>30 speed of pump), although the effect of physical parameter was very crucial on the response for obtaining regular response and very sharp maxima attenuation of incident light , reflection of incident light at two way ($N_{\pm 90^0}$) and algebraic sum of them , therefore a flow rate 2.1, 2.2, 2.1ml.min^{-1} for carrier stream , Sn(II) line & OH^- line respectively was used as a compromise to obtain regular response , narrower Δt_B, minimize the consumption of reactions solutions and to complete precipitation of Bi(III) as Bi metal by course of the reaction with SnO_2^{2-} as shown in table no.5.

Table 5: Effect of flow rate on the measurement of attenuation of incident light as well as reflection of light at two opposite position and algebraic sum of them.

Speed of peristaltic pump (indication approximate)	Flow rat of carrier stream (ml.min^{-1}) (D.W)	Flow rat of Sn(II) solution stream (ml.min^{-1})	Flow rat of OH^- solution stream (ml.min^{-1})	Type of measurement $\bar{y}_i \pm t_{0.05/2}\ \sigma_{n-1}/\sqrt{n}$ (n=3) (mV)			
				Attenuation of incident light $T_{(0-180)}$	Scattering of light (L) N_L (+90)	Scattering of light (R) N_R (-90)	Algebraic sum of the scattering of light $N_{(L+R)}$ (±90)
10	0.7	0.75	0.75	488±1.772	76±1.341	16±0.984	40±1.002
20	1.4	1.5	1.5	516±2.563	80±1.009	14±0.000	36±1.314
30	2.1	2.2	2.1	480±1.452	48±1.561	18±0.000	34±0.905
40	2.9	3.0	3.1	468±2.783	48±1.342	14±1.251	32±0.935
50	3.5	3.7	3.6	464±2.494	44±1.023	12±0.000	32±0.000



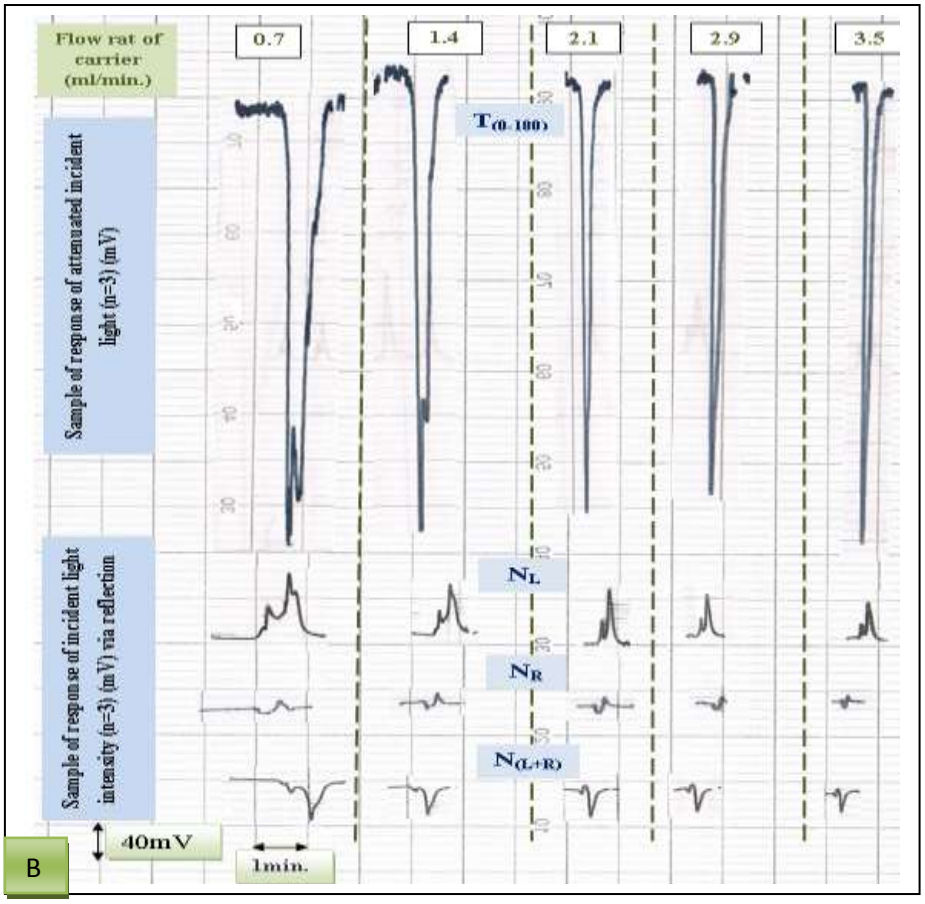


Fig. 6: Effect of flow rate on: (B)Attenuation of incident light, scattering of light at two opposite directions and the algebraic sum of them, (A)Response profiles.

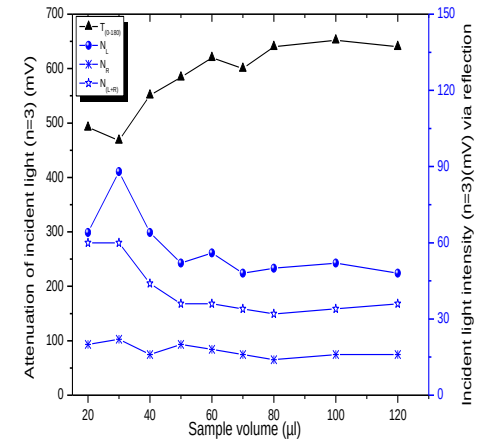
Sample Volume

Using the optimum flow rate (2.1, 2.2 and 2.1) ml.min^{-1} for carrier stream , Sn(II) line and OH^- line respectively .The injected volume of sample was varied in the range 20 – 120 µl by changing the length of the sample loop in the injection valve, while the other variable remained fixed. An increase in the volume led to a significant increase in sensitivity, more perceptible than low volumes as shown in figure no.7A,B, which shows that the optimum sample volume of 40 µl gave regular responses for the attenuation of incident light and scattering of light (±90). Using sample volume > 40µl even though it gave a slight higher response, but it was characterized by

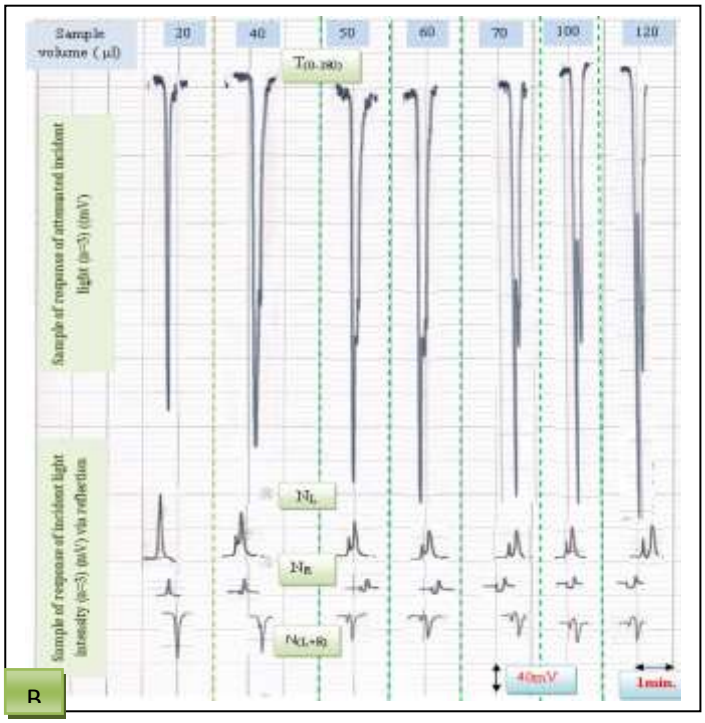
increase Δt_B which might be probably attributed to the relatively longer duration of the precipitate particle segment in front of the detector as illustrated in figure no.8B, while all the results tabulated in table no.6.

Table 6: Effect of sample volume on the measurement of attenuation of incident light as well as reflection of light at two opposite position and algebraic sum of them. (Arrival time of sample segment from injected valve reaching to the measuring flow cell 12sec.)

length of sample loop(cm) diameter (0.5mm)	Sample volume (µl)	Type of measurement $\bar{y}_i \pm t_{0.05/2}\ \sigma_{n-1}/\sqrt{n}$ (n=3) (mV) / Δt_B (Sec.)			
		Attenuation of incident light $T_{(0-180)}$	Scattering of light (L) N_L (+90)	Scattering of light (R) N_R (-90)	Algebraic sum of the scattering of light $N_{(L+R)}$ (±90)
10	20	492±0.993 / 15	64±1.004 / 12	20±0.000 / 10	60±1.654 / 12
15	30	468±2.342 / 20	88±2.043 / 13	22±1.027 / 12	60±1.875 / 15
20.4	40	551±1.342 / 35	64±2.652 / 16	16±0.000 / 12	44±1.543 / 18
25	50	584 ± 0.976 / 30	52±1.092 / 18	20±0.982 / 10	36±1.001 / 15
30	60	620±2.309 / 32	56±0.986 / 15	18±1.527 / 10	36±0.000 / 12
35	70	600±2.666 / 26	48±1.333 / 12	16±1.477 / 9	34±1.987 / 12
41	80	640±3.109 / 28	50±2.985 / 12	14±1.306 / 8	32±1.073 / 10
51	100	652±3.201 / 24	52±2.342 / 10	16±1.002 / 6	34±0.988 / 10
60	120	640±2.981 / 20	48±1.932 / 10	16±1.542 / 6	36±1.087 / 9



A



B

Fig. 7: Effect of sample volume on; (A) Attenuation of incident light, scattering of light at two opposite directions and the algebraic sum of them, (B) Response profiles.

Purge Time

Allowed permissible time for the sample to be injected via the carrier stream was studied. The effect on the response and it is sensitivity was followed using the optimum physical and chemical parameters achieved in previous sections. Allowed time of 10, 15, 20 and 25 seconds and open valve mode were used for this study. It can be seen from the figure no. 8A,B , an increase of the response with increasing the allowed permissible time , so that open valve was found to be the best purge time where it gave the highest response for the attenuation of incident light as well as the scattering of incident light at $\pm 90^{o}$ (N_L and N_R) and the algebraic sum of them.

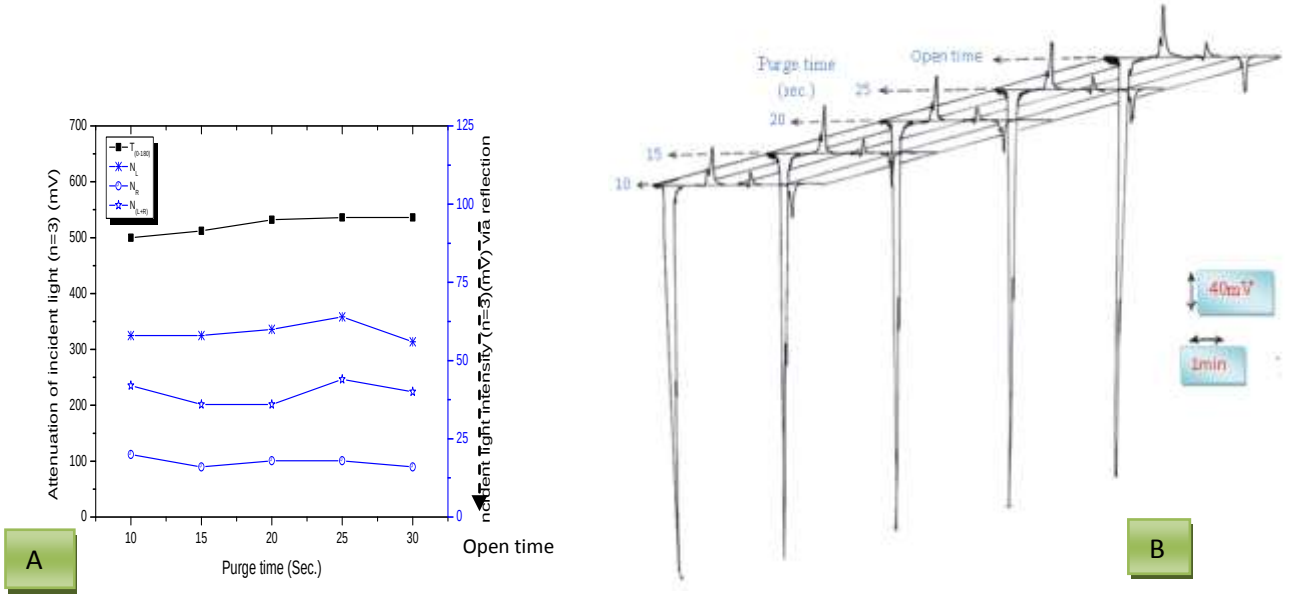


Fig. 8: Effect of purge time on; (A) Attenuation of incident light, scattering of light at two opposite directions and the algebraic sum of them, (B) Response profiles.

Calibration Curves and Statistical Parameters

When chemical and physical parameters were studied, the calibration curves of continuous flow injection analysis via attenuation of incident light, scattering of light at two opposite position method were estimated. All results tabulated in table no.7. Figure no. 9A shows an increasing of attenuation of incident light with concentration of Bi(III) which might be attributed to increase the dense black Bismuth particles and accumulation it in front of the detector causing obscure and attenuation of light (increase $T_{0\text{-}180}{}^{o}$); while increase of scattering light at low concentration due to the increase of amount of transmitted light by precipitate light by precipitate particulate & increase interstitial spaces causing an increase of scattered light at $\pm 90^{o}$ as shown in figure no. 9B.

Table 7: Summary of linear regression equation for estimate of Bi(III) ion by Sn(II)-OH^- - Bi(III) system (direct method)[19, 20].

Type of measured	No. of measurement	Range of [Bi(III)] $mmol.L^{-1}$	$y^{\cdot}(mV)=a\pm S_a t+ b\pm S_b t[x]$ at confidence level 95%, n-2	r $r^2\%$	t_{tab} at 95% confidence level, n-2	$t_{cal}=\frac{\lvert r\rvert\sqrt{n-2}}{\sqrt{1-r^2}}$.
$T_{(0\text{-}180)}$	16	0.08-50	40.99±8.86+22.42±0.44[x]	0.9973 99.46	2.145<<50.783	
N_L	12	1.00-50	62.31±1.24-0.96±0.054[x]	0.9845 96.92	2.228<<50.098	
N_R	12	1.00-50	13.18±0.13-0.15±0.01[x]	0.9937 98.75	2.228<<28.107	
$N_{(L+R)}$	12	1.00-50	55.67±2.47-1.13±0.11[x]	0.9583 91.84	2.228<<10.608	

y^: Estimated response (mV) for (n=3), [x]: [Bi(III)] (mmol.L^{-1}), r: correlation coefficient, r^2%: linearity percentage, t_{tab}: $t_{0.05/2}$, n-2 at 95% confidence level.

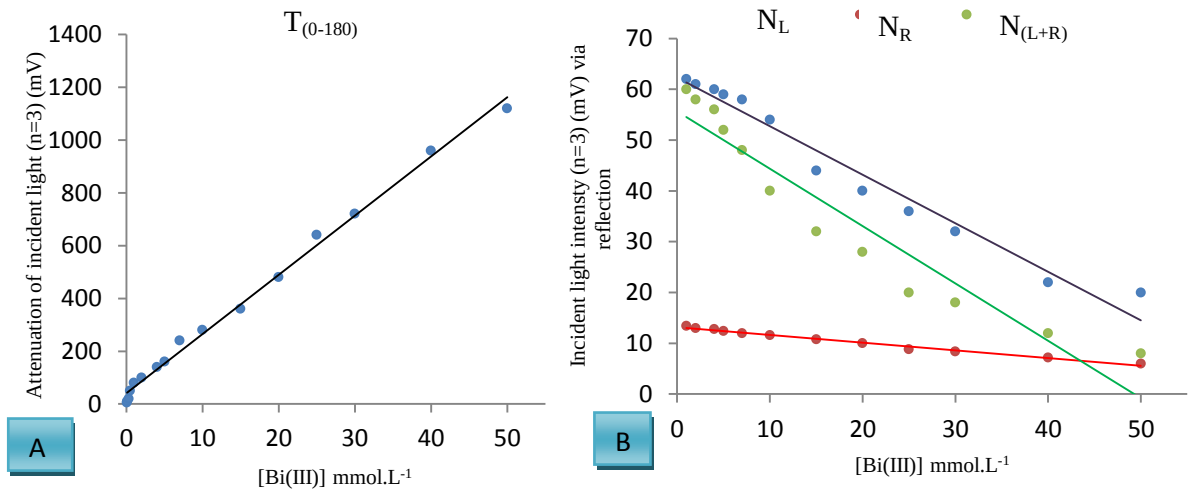


Fig.9: Linear calibration graph for the instrument response versus Bi (III) concentration by direct method using simple linear equation of y= a+ b x;(A) attenuation of incident light, (B) scattering of light at two opposite directions and the algebraic sum of them.

Three different approaches were used. Gradual dilution of lowest concentration in the calibration graph or detection based on the numerical value of slope and from the linear regression plot. Table no.8 summarizes the limit of detection of Bi(III) carried out through three methods .

Table 8: Detection limit of Bi(III) at optimum parameters depend on $T_{(0-180)}$. (40µl injection sample volume)

Theoretical based on the value of slope $X=3S_B/slope$	Theoretical based on the linear equation $\acute{Y}=Y_B+3S_B$	Practically based on gradual dilution for the minimum concentration
0.059 mmol.L^{-1}	3.58 mmol.L^{-1}	0.06 mmol.L^{-1}

X: value of L.O.D based on slope, S_B: Standard deviation of blank, Y_B: Average response for blank.

The relative standard deviation expressed as percentage which is equally to the repeatability of the measurements. A repeated measurements for six successive injections were measured at fixed concentrations of Bi(III) while mainly two concentrations were used and the obtained results is tabulated in table no.9.The percentage of relative standard deviation less than 3% indicate a reliable measurement can be achieved using this method. Figure no.10 is shown response profile of repeatability at 25 and 45 mmol.L^{-1} respectively.

Table 9: The repeatability of Bi(III) at optimum parameters by CFIA- method.

[Bi(III)] mmol.L^{-1}	Type of measurement	Average response $\bar{y}_i$(mV) (n=6)	σ_{n-1}	R.S.D%	Confidence interval of the average response (95% confidence) $\bar{y}_i \pm t_{0.05/2}\ \sigma_{n-1}/\sqrt{n}$
45	$T_{(0-180)}$	1032	3.860	0.762	1032±4.051
	N_L	24	0.413	1.721	24±0.433
	N_R	8	0.082	1.020	8±0.086
	$N_{(L+R)}$	20	0.258	1.290	20±0.271
25	$T_{(0-180)}$	638	3.350	0.525	638±3.516
	N_L	32	0.252	0.788	32±0.265
	N_R	12	0.333	2.775	12±0.350
	$N_{(L+R)}$	25	0.490	1.960	25±0.514

$t_{0.05/2,\ n-1}$ = 2.571 , n=6.

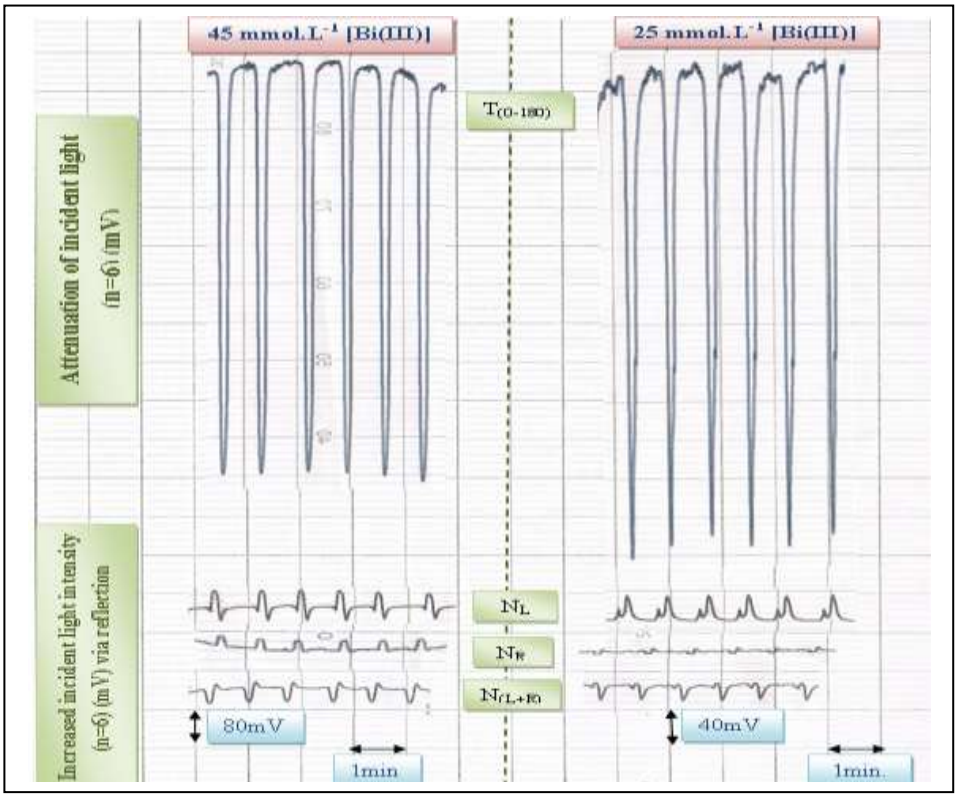


Fig. 10: Repeatability study showing six successive measurements for the attenuation of incident light, scattering of light at two opposite directions and the algebraic sum of them via reflection by CFIA method.

Analysis of Pharmaceutical Formulation

The CFIA via turbidity (T_{0-180}) and scattered light at two opposite position ($2N\pm_{90}{}^{o}$) method using Ayah $4S_W$-3D-T_{180} - $2N_{90}$ - Solar - CFI Analyzer achieved in this work was used for the analysis of Bismuth ion in sample of pharmaceutical preparation (SDI, powder) and was compared by spectrophotometric method . The standard addition method for the CFIA method was applied by preparing a series of solution from pharmaceutical drug by transferring 6.25ml (20 $mmol.L^{-1}$ Bi(III)) to each of the six volumetric flask (25ml), followed by the addition of 0, 3.0 , 6.0, 9.0,12.0 and 15.0ml of 41.67$mmol.L^{-1}$ standard solution of Bi(III) in order to have the concentration range from 0 -25 $mmol.L^{-1}$. Results were mathematically treated for standard addition method. The results were tabulated in tables' no. 10 and 11. Figure no. 11A,B shows the linear part of the scatter plot diagram by standard addition method.

Table 10: Summary of linear regression equation for estimate of Bi(III) ion by Sn(II)-OH^- - Bi(III) system(standard addition method). (range 0-25 $mmol.L^{-1}$ Bi(III)).

Type of measured	y^(mV)=a± S_at+ b± S_bt[x] at confidence level 95%, n-2	r r^2%	t_{tab} at 95% confidence level, n-2	$t_{cal}=\frac{\lvert r\rvert\sqrt{n-2}}{\sqrt{1-r^2}}$
$T_{(0-180)}$	121.43±22.64+26.29±1.50[x]	0.9936 98.72	2.778<<19.122	
N_L	67.90±1.92-1.73±0.13[x]	0.9892 97.86	2.778<<27.048	
N_R	14.16±0.55-0.37±0.04[x]	0.9812 96.29	2.778<<20.376	
$N_{(L+R)}$	61.71±1.51-1.89±0.10[x]	0.9945 98.91	2.778<<38.102	

y^: Estimated response (mV) for (n=3),[x] : [Bi(III)] ($mmol.L^{-1}$), r: correlation coefficient, r^2%: linearity percentage, t_{tab}: $t_{0.05/2}$, n-2 at 95% confidence level.

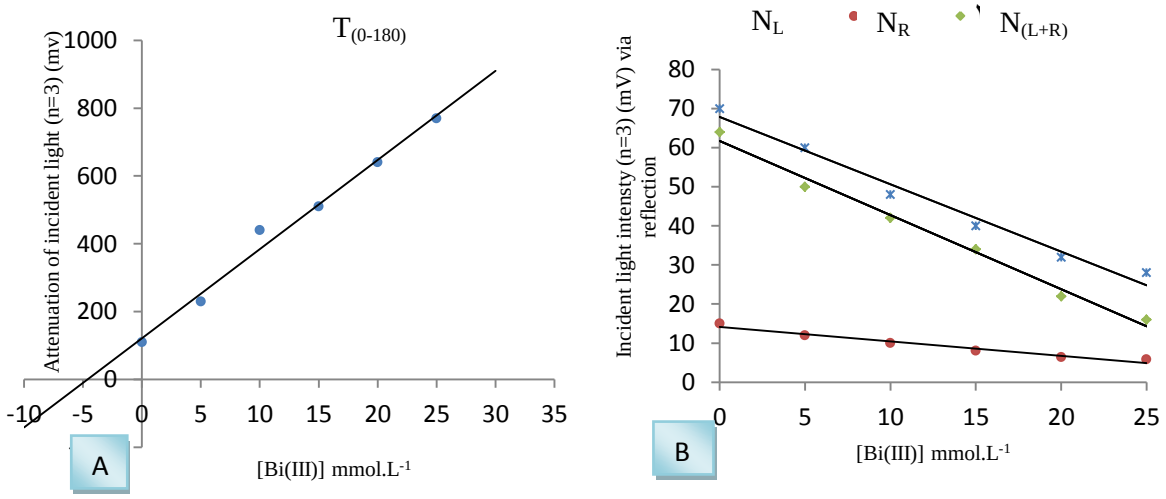


Fig. 11: Linear calibration graph for the instrument response versus Bi (III) concentration by standard addition method using simple linear equation of y= a+ b x; (A) attenuation of incident light, (B) scattering of light at two opposite directions and the algebraic sum of them.

Table 11: Bismuth determination in pharmaceutical sample using FI – T&N method (depend on $T_{(0-180)}$) by standard addition method.

Information of pharmaceutical drug	Theoretical calculation			Practical calculation			Recovery%
	$[(BiO)_2CO_3]$ prepared in 100ml	Wt (g) of $[(BiO)_2CO_3]$ prepared 20 mmol.L^{-1} in 100ml	Volume taking to prepare 5mmol.L^{-1} $(BiO)_2CO_3$	$[(BiO)_2CO_3]$ mmol.L^{-1} in 25ml	$[(BiO)_2CO_3]$ mmol.L^{-1} in 100ml	Wt (g) in100ml	
$(BiO)_2CO_3$ (SDI) powder 509.92g/mol	20 mmol.L^{-1}	1.0200 g	6.25 ml	4.95 mmol.L^{-1}	19.79 mmol.L^{-1}	1.0093 g	98.95%

While spectrophotometric method [14] via the measurement of λ_{max} at 465nm as shown in figure no.12, linear calibration curve was obtained for the concentration range of 0.00478 - 0.033 mmol.L^{-1} ,correlation coefficient was 0.9881 and limit of detection was 0.003 mmol.L^{-1}. The preparation of standard addition calibration plot to spectrophotometric method was prepared by different aliquots of 0 , 0.4, 0.8, 1.2, 1.6 and 2.0 ml from 0.1195mmol.L^{-1} standard solution of Bi(III) in order to have a concentration range of 0 - 0.0239 mmol.L^{-1} these solutions were transferred into a series of 10 ml calibrated flasks , to each flask 0.4 ml of drug (0.1195 mmol.L^{-1} Bi(III)) were added, 1ml of 1:5 v/v sulfuric acid and 5ml of 20% potassium iodide solutions, mixed well Then, The volume was diluted to the mark with water and mixed. The absorbance of each solution was measured at 465nm against water blank after 5 min. Figure no.13 shows the linear part of the scatter plot diagram by direct and standard addition method. All the results were illustrated in tables' no.12 and 13.

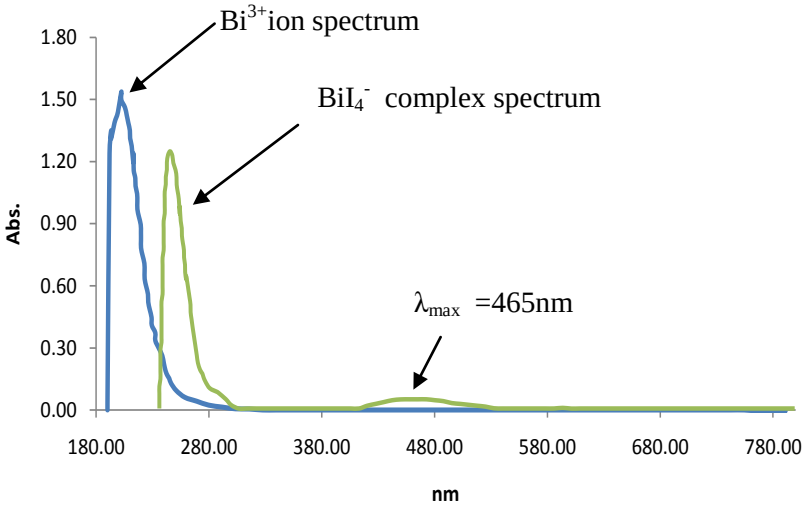


Fig. 12: UV-VIS spectrum for Bi(III) ion and BiI_4^- complex.

Table (12): Summary of linear regression equation for estimate of Bi(III) ion by spectrophotometric method

Type of measured	No. of measurement	Range of [Bi(III)] mmol.L^{-1}	y^= a± S_at+ b± S_bt[x] at confidence level 95%, n-2	r r^2%	t_{tab} at 95% confidence level,n-2	$t_{cal} = \frac{\lvert r\rvert\sqrt{n-2}}{\sqrt{1-r^2}}$.
Direct method	7	0.00478 - 0.033	- 0.017±0.056+40.254±2.807[x]	0.9881 97.63	2.571<<14.352	
Standard addition method	6	0.0 - 0.0239	0.1769±0.050+42.978±3.48[x]	0.9971 99.42	2.778<<12.338	

y^: Estimated response (absorbance) for (n=3), [x]:[Bi(III)] (mmol.L^{-1}), r: correlation coefficient, r^2%: linearity percentage, t_{tab}: $t_{0.05/2}$, n-2 at 95% confidence level.

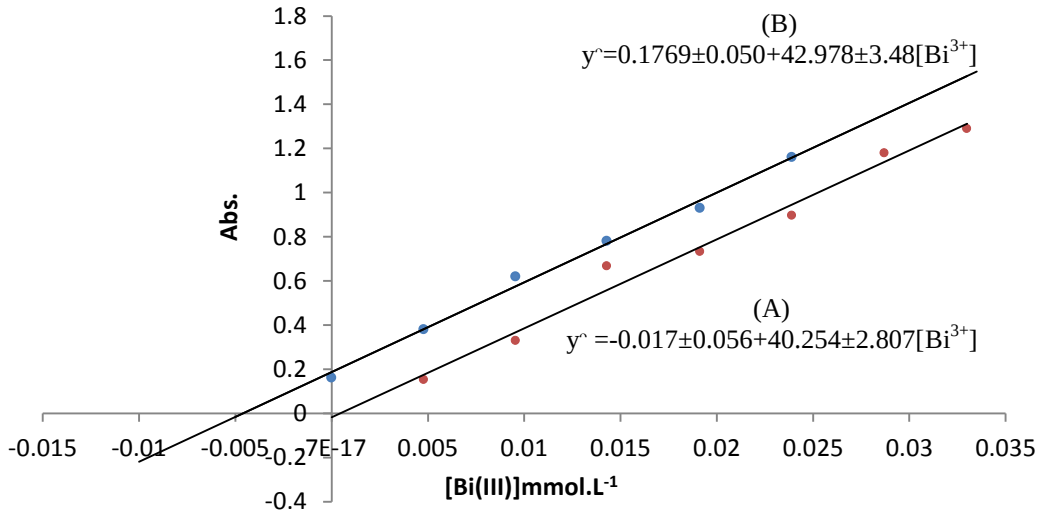


Fig. 13: Linear calibration graph for the absorbance versus Bismuth(III) concentration using simple linear equation of y = a+ bx, (A) Direct method, (B) Standard addition method.

Table (13): Bismuth determination in pharmaceutical tablets using spectrophotometric method.

Information of pharmaceutical drug	Type of measurement	Theoretical calculation		Practical calculation		Recovery%
		$[(BiO)_2CO_3]$ sample in 10 ml	Wt (mg) for 4.78µmol.L^{-1} of $(BiO)_2CO_3$ sample in 10 ml	$[(BiO)_2CO_3]$ in 10ml	Wt (mg) of practical concentration in 10ml	
$(BiO)_2CO_3$ (SDI) powder 509.92 g/mol	Direct method	4.78 µmol.L^{-1}	0.2437 mg	4.458 µmol.L^{-1}	0.2273 mg	93.27%
	Standard Addition method			4.600 µmol.L^{-1}	0.2341 mg	96.23%

Paired t-test was used in order to compare the new FI– T&N method with the spectrophotometric (classical) method. The obtained results as shown in table (14) indicate clearly that there was no significant differences between newly FIA – T&N method and the spectrophotometric method at 95% confidence interval as the calculated t-value is less than critical tabulated t-value.

Table (14): Paired t-test for the new proposed method (CFI-depend on $T_{(0-180)}$) and the spectrophotometric method for the determination of Bi(III) in pharmaceutical drugs by standard addition method.

Type of measurement	Type of system & range of concentration used in mmol.L^{-1}	Theoretical [Bi(III)] (µ)	Practical [Bi(III)] $\bar{x}$	σ_{n-1}	n	Paired t-test /t/=($\bar{x}$- µ) $\sqrt{n}$ /σ_{n-1}	t_{tab} ($t_{0.025,2}$) at 95% confidence interval, n-1
Proposed method (FI – T&N)	Bi(III)-SnO_2^{2-} 0-25	20 mmol.L^{-1}	19.79 mmol.L^{-1}	1.12	3	0.325<<4.303	
Spec. method	Bi(III)-I^- 0-0.0239	4.78 µmol.L^{-1}	4.60 µmol.L^{-1}	1.98		0.160<<4.303	

FI-T&N: CFIA via turbidity (T_{0-180}) and scattered light at two opposite position ($2N\pm_{90}{}^{o}$) method, Spec.: spectrophotometry method.

Conclusion

The proposed FIA method is a simple, rapid and sensitive for the determination of Bi(III) ion by using SnO_2^{2-}ion to form a black precipitate (Bi). The precipitate is measured via the attenuation of incident light and it's scattering in two opposite directions also the algebraic sum of them by using Ayah $4S_W$-3D-$T_{180}{}^{o}$ -$2N_{90}{}^{o}$ -Solar - CFI Analyser. An alternative analytical method is found through this research work which was based on simple parameter conditions.

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