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A new mode for an on-line determination of Pyrocatechol, Resorcinol, and Pyrogallol in pure commercial samples using CFIA with homemade Ayah $3S_{BGR}$x3- 3D solar cell microphtometer analyzer.

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Abstract:

A new, simple, accurate, fast and sensitive spectrophotometric method has been developed for the analysis of Pyrocatechol, Resorcinol, and pyrogallolin pure commercial samples by continuous flow injection analysis. The method was based on the oxidation of the organic compounds with Ce(IV)sulfate in acidic medium to formed a brown colored species which determined using homemade Ayah $3S_{BGR}$ x3-3D solar cell flow injection microphotometer. Optimum conditions were obtained using a high intensity green light emitted diode as an irradiation source forPyrocatechol, Resorcinol, whileblue light emitted diode as an irradiation source for pyrogallol. The linear dynamic range for the instrument response versus Pyrocatechol, Resorcinol, and pyrogallol concentrationswere5-40mmol.L^{-1} while the L.O.D was of 36.63, 17.17, and 41.61ng / sample respectively. The correlation coefficient (r) was 0.9952, 0.9970, and 0.9960 while percentage linearity (r^2%) was 99.05%, 99.41% and 99.22%forPyrocatechol, Resorcinol, and pyrogallol respectively. RSD% for the repeatability (n=8,7, and 8) was 1.4%, 0.63%, 1.78% for the determination of Pyrocatechol, Resorcinol,andpyrogallol, respectively at concentration of 30 mmol.L^{-1}. The method was applied successfully for the determination of three organic compounds in purecommercial samples. A comparison was made between the newly developed method and the classical method (UV-Vis spectrophotometry) at wave length 492, 481, and 438 nm forPyrocatechol, Resorcinol and pyrogallolrespectively of analysis using the standard additions method via the use of paired t-test. It was noticed that there is no significant difference between two different methods for analysis three different organic compounds; in addition to no significant difference in the contribution of the Pyrocatechol, Resorcinol and pyrogallol to the oxidant reaction path, at 95% confidence level.

Key words: Pyrocatechol, Resorcinol, Pyrogallol, Flow injection analysis, Spectrophotometry.

نمط جديد للتقدير الأني للبايروكتكول، ريزورسينول و البايروكالول في نماذج تجارية النقية بأستخدام التحليل بالحقن الجرياني المستمر عن طريق استخدام محلل طيفي مايكروي مصنع محليا Ayah $3S_{BGR}$ x3-3D solar cell.

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الخلاصة:

طورت طريقة طيفية جديدة، بسيطة، سريعة، مظبوطة، وحساسة لتحليل البايروكتكول، الريزورسينول، والبايروكالول في نماذج تجارية نقية بأستخدام التحليل بالحقن الجرياني المستمر. استندت الطريقة على اكسدة المركبات العضوية بكبريتات السيريوم (IV) في الوسط الحامضي لتكوين اصناف ملونة بنية والتي قدرت

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بأستخدام مطياف مايكروبيالحقن الجرياني المستمر مع Ayah $3S_{BGR}$ x3−3D solar cell المصنع محليا. تم دراسة الظروف الفضلى التي تم التوصل اليها بأستخدام ثنائي الوصلة باعث للضوء الاخضر وبشدة عالية كمصدر لتشعيعالبايروكتكول والريزورسينول، بينماثنائي الوصلة باعث للضوء الازرق وبشدة عالية كمصدر لتشعيع البايروكالول . المدى الخطي الفعال لعلاقة تغير الاستجابة الألية مع التركيز ٥− ٤٠ مللي مول.لتر$^{-1}$ بينما حدود الكشف 36.63, 17.17,٤١.٦١ ناغم / انموذج. وان معامل الارتباط (r) ٠.٩٩٥٢, ٠.٩٩٧٠، و ٠.٩٩٦٠ بينما نسبة الخطية r^2 % = ٩٩.٠٥، ٩٩.٤١، و ٩٩.٢٢. الانحراف القياسي النسبي المؤي (RSD%) للتكرارية(n= 8,7,8)١.٤، ٠.٦٣، ١.٧٨ % لمحلول البايروكتكول، الريزوسينول، والبايروكالول بتركيز ٣٠ مللي مول .لتر$^{-1}$للبايروكتكول، الريزوسينول والبايروكالول طبقت الطريقة بنجاح لتقدير المركبات العضوية الثلاثة في نماذج تجارية نقية. اجريت مقارنة بين الطريقة المطورة والطريقة التقليدية (مطياقية UV−Vis) عند طول موجي ٤٣٨، ٤٨١،و ٤٩٢ نانو متر للتحليل باستخدام منحني الاضافات القياس من خلال استخدام اختبار t− المزدوج. لوحظ انه لايوجد فرق جوهري بين الطريقتين لتحليل المركبات العضوية الثلاثة بالاضافة الى عدم الاختلاف في مساهمة كل من البايروكتكول ، الريزورسينول و البايروكالول على مسار تفاعل الاكسدة عند مستوى قناعة ٩٥%.

Introduction:

Aromatic hydroxyl phenols are common chemicals used in industries as well as in clinical and biochemical applications [1].Polyphenols are common constituents of the human diet, present in most foods and beverages of plant origin. Polyphenol are considered to contribute to the prevention of various degenerative diseases, including cardiovascular diseases [2]. Polyphenol compounds are highly abundant in nature, since they are the essential raw materials and byproducts of vast chemical industries. Some of these compounds are extremely toxic and resistant to biotic and abiotic degradation [3,4]. Polyphenols and phenolic compounds are found mostly in plants and effluents of industries, such as coal conversion, paper and pulp manufacturing, wood preservation, metal casting, polyphenol compounds are considered to be hazardous pollutants [5]. Furthermore, the breakdown products of polyphenol may be more harmful when phenol is incompletely degraded by physical and chemical methods or by natural oxidation. Therefore, the complete removal of these substances from industrial and domestic water bodies is of great importance for conservation of native biodiversity [6].
Catechol (Cat, figure-1A) , 1,2-dihydroxybenzene, 1,2-benzediol, pyrocatechol, this chemical was first obtained by dry distillation of catechin by Reinsch in 1839. It is widely distributed in nature and found in plants (onion, eucalyptus, crudebeetsugar), coal and tobacco smoke. It is a colourless crystalline solid (monoclinic crystals) and discolours when in contact with air and light. It readily dissolves in water and hydrophobic organic solvents (ethanol and acetone) [7]. Cat is used in a variety of applications. It is used as a reagent for photography, dyeing fur, rubber and plastic production, pesticides and in pharmaceutical industries[8,9]. Catechols can undergo a variety of chemical reactions, such as complex formation and redox chemistry of catechols. In presence of heavy metals such as iron or copper, stable complexes can be formed [10 -12]. Substituted catechols, especially chlorinated and methylated catechols, are by-products in pulp and oil mills [13,14].
Resorcinol (Res, figure-1B) is the 1,3-isomer of benzenediol [15]. Res is a dihydric phenol and exhibits the typical reactivity of a phenol [16]. Res is a white to off-white needle-like crystals, flakes or powder. When exposed to light and air resorcinol crystals acquire a pale red [17,18]. Res is a monoaromatic compound with two hydroxyl group in meta position to each other. It occurs naturally in fossil fuels, in heartwood of Artocarpus and Morus (Moraceae) species [19]. And in exudates of Nupharlutea [20].Res readily soluble in water, alcohol, and ether, but insoluble inchloroform and carbon disulfide [21]. The resorcinol moiety has been found in a wide variety of natural products. In particular, the plant phenolics, of which resorcinol ring-containing constituents are a part, are ubiquitous in nature and are well documented[22]. Res used externally, it is an antiseptic and disinfectant, and is used 5 to 10% in ointments in the treatment of chronic skin diseases such as psoriasis, hidradenitissuppurativa, andeczema [23].Resorcinol is a monomeric by-product of the reduction, oxidation, and microbial degradation of humic substances [24,25].

Pyrogallol (Pyr, figure- 1C) is an organic compound: 1,2,3-benzenetriol, 1,2,3-trihydroxybenzene .It is a white solid crystals; grayish on exposure to air and light, although because of its sensitivity toward oxygen, samples are typically brownish. It is one of three isomeric benzenetriols [26,27]. Pyr (1,2,3-trihydroxy benzene), a polyphenol has been exploited in a variety of industrial sector, for example, as a developer in photography, to make colloidal solutions of metals, as a mordant for wool, for staining leather, in process engraving, in the manufacture of various dyes, and in the dyeing of fur, hair. In analytical chemistry it is used as a reagent for antimony and bismuth. [28,29]. Pyr was the first synthetic organic dye used on human hair, Pyr is used as a modifier in oxidation dyes . Pyr is present in 42 hair dyes and colors . And the Pyr concentration in the dyes and colors typically ranges from 0.25 to 0.38% by weight [30,31] . Pyr is the end product in ruminal bacteria like Selenomonas ,and Streptococcus. [32,33].

Methods have been reported for determination of Cat, Res, and Pyr, , GC- FID [34,35]. HPLC [36- 38] .voltammetry [39-43]. Spectrophotometry [44-46].

The proposed method based on the oxidation of Cat, or Res, or Pyr byCe (IV) sulfate in acidic medium. The oxidation product yields as a brown color which measured by Ayah $3S_{BGR}$x3-3D solar cell CFIA microphotometer (homemade) [47] at 492,481, 438 nm for Cat, Res, and Pyr respectively. The procedure is simple, rapid and is proposed for the control analysis as an alternative analytical procedure.

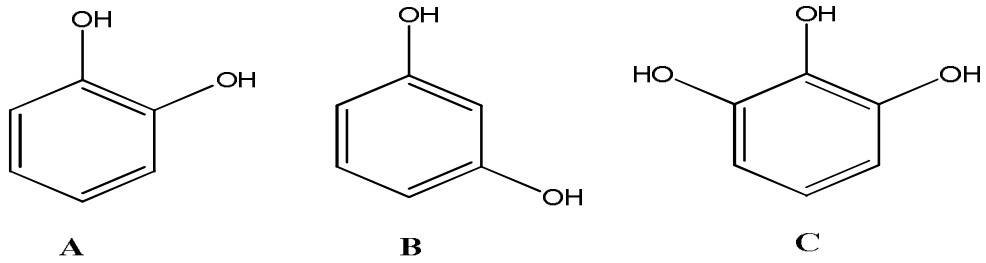


Figure 1- Chemical structure of ; A: Cat, B: Res, C: Pyr.

Experimental:

Chemicals:

All chemicals were used of analytical-reagent grade while distilled water was used to prepare the solutions. A standard solution 0.5 M of Cat (C_6H_4 $(OH)_2$M.Wt. 110.1 g.mol^{-1}, BDH) was prepared by dissolving 13.7625 g in 250 ml of distilled water. A standard solution 0.5 M of Res (C_6H_4 $(OH)_2$M.Wt. 110.1 g.mol^{-1}, BDH) was prepared by dissolving 13.7625 g in 250 ml of distilled water. A standard solution 0.5 M of Pyr (C_6H_4 $(OH)_3$M.Wt. 126.11 g.mol^{-1}, BDH) was prepared by dissolving 15.76372 g in 250 ml of distilled water. A stock solution 0.1M of Ce(IV) sulfate ($Ce(SO_4)_2$M.Wt 332.298 g.mol^{-1} , Hopkin& Williams LTD) was prepared by dissolving 16.614 g in 500 ml of sulphuric acid 1M, (H_2SO_4, M.Wt 98 g.mol^{-1}, 18 M, sp.g 1.84g.ml^{-1}, percentage 96%, BDH) (standardized against 1M Na_2CO_3 solution) was prepared by diluting 27.7ml of the sulphuric acid in distilled water to final volume 500ml by using volumetric flask 500 mL..Hydrochloric acid solution1M (35%, 1.19 g.ml^{-1}, BDH) were prepared by pipetting 21 mL of concentrated hydrochloric acid and completed of the volume with distilled water in 250 mL volumetric flask. Nitric acid solution 1M (70%, 1.42 g.ml^{-1}, BDH) was prepared by pipetting 16 mL of concentrated nitric acid and completed the volume with distilled water into 250 mL-volumetric flask. All acids were standardized with Na_2CO_3 solution. A stock solution 1M of sodium carbonate (Na_2CO_3, 106 g.mol^{-1} , BDH) was prepared by dissolving 26.50 g in 250 mL.

Sample preparation: pyrocatechol – Readeldehean, resorcinol- Randwin, and pyrogallol- Readeldehean, were weighted: 5.505 g , 5.505, and 6.3055 g respectively, which dissolved in 100 ml of distilled water to obtained concentration equivalent to 500 mmol.l^{-1} for each sample.

Apparatus and manifold:

The flow system used for the determination of Cat, Res, and Pyr shown schematically in figure- 2, peristaltic pump four channels variable speed (Ismatec, Switzerland). Valve 6 – port medium pressure injection valve (I D E X corporation, USA) with sample loop (1 mm i.d., Teflon ,variable

length). The instrument response was measured by Ayah $3S_{BGR}$ x 3 – 3 D solar cell continuous flow injection analysis microphotometer (homemade) [47] by using three super bright blue470 nm , green 525nm and red 635 nm light emitted diode (LED) as a source , three solar cell as a detector. The output signals were recorded by potentiometric recorder (Siemens, Germany, 1- 500 Volt, ١-500 mV). Peak height was measured for each signal. UV-Vis Spectrophotometer digital double beam type (UV- Vis spectrophotometer: UV-1800, shimadzu, and spectronic 20D +, Japan) were also used to scan the spectrum of colored species using 1cm glass cell.

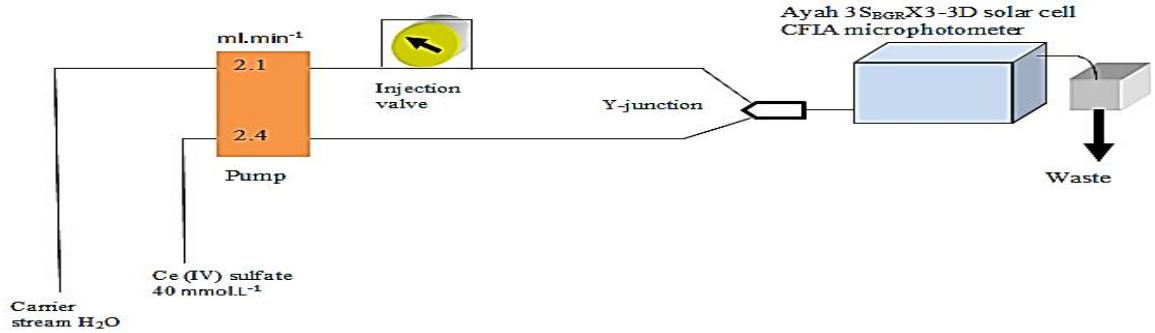
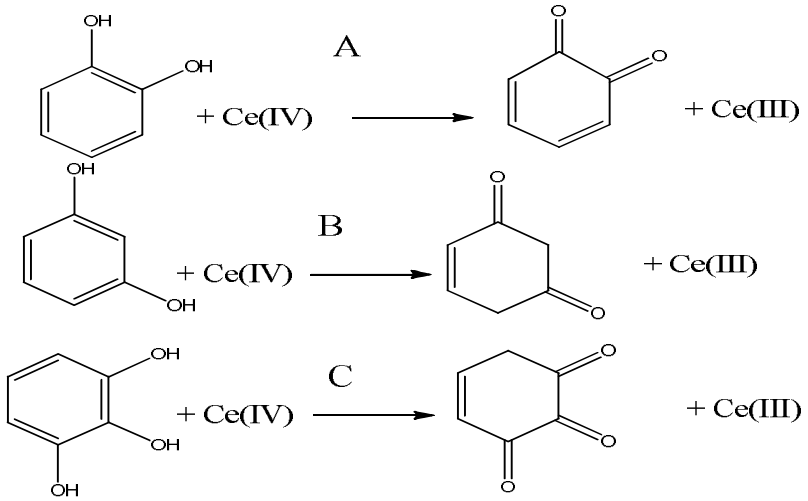


Figure 2-schematic diagram of Continuous Flow Injection Analysis system with Ayah $3S_{BGR}$ x

3 - 3D solar cell CFIA microphotometer, for determination of Cat, Res, and Pyr.

Methodology:

The whole reaction manifold system of Cat, Res, and Pyr determination by direct oxidation via Ce(IV) sulfate in acidic medium to form colored species was shown in Figure- 2 . The manifold system is composed from two lines: The first line supplied distilled water as a carrier stream at 2.1 $ml.min^{-1}$ which leads to the injection valve for carrying samples with 165, 156, and 165 µ L for Cat, Res, and Pyr respectively sample volume (loop length: 21.0, 19.82, and 21.0 cm, with 1mm I.D.) , the second line supplied Ce(IV) sulfate 40 $mmol.L^{-1}$ in acidic medium (500 $mmol.L^{-1}$ of H_2SO_4) at 2.4 $ml.min^{-1}$. Both of lines meet at junction (Y- junction) with an outlet for reactants product from brown colored species which passes through Ayah $3S_{BGR}$ x3- 3D solar cell CFIA microphotometer. The variation of response was monitored using green light emitted diode LED (525 nm) for determination of Cat, and Res, while blue light emitted diode LED (470 nm) for determination of Pyr, throughout the reaction to obtain transducer energy response in mV versus time. Each solution was assayed triplicate. A proposed mechanism for oxidation of Cat, Res, and Pyr by Ce(IV)sulfate in acidic medium is presented in scheme(1) [48-52].



Schematic 1- proposed mechanism of reaction between: A- Cat, B- Res, C- Pyr and Ce(IV) sulfate in acidic medium.

Results and discussion:

Scanning of spectrum for org. comp. – Ce(IV) sulfate – H_3O^+ :

A scanning between 200-600 nm was carried out to obtained λ_{max} for colored product (brown) by oxidation of Cat, Res, and Pyr (5 mmol.L^{-1}) with Ce(IV)sulfate (12 mmol.L^{-1}) in acidic medium (H_2SO_4, 500 mmol.L^{-1}). It can be seen clearly that a maximum absorbance at 492, 481, and 438 nm for Cat, Res, and Pyr respectively against reagent blank (Ce(IV) sulfate), as shown in figure- 3A.

Second spectroscopic study for colored species (brown) was monitoring by a homemade Ayah $3S_{BGR}$x3-3D solar cell CFIA microphotometer at three different super bright light diode (LED) as a source including blue 470nm, green 525 nm, and red 635 nm, selected conditions were used, two lines system (figure- 2), 165 µL as a sample volume of Cat, Res, and Pyr with concentrations 20, 50, and 50 mmol.L^{-1} respectively which injected into the carrier stream (H_2O) at 2.1 ml.min^{-1} , while the Ce(IV) sulfate 50 mmol.L^{-1} at 2.4 ml.min^{-1} (second line) meet with Cat, Res, and Pyr at Y- junction point in later stage of reaction. A maximum response measured in mV (expressed as transducer energy response) was obtained using high intensity super bright green light emitted diode (LED) for Cat, and Res, while super bright blue light emitted diode (LED) for Pyr. Figure- 3B indicate the profile of the response and intensity. Therefore, the green light emitted diode (LED) was used as a source for determination Cat, and Res, while blue light emitted diode (LED) was used as a source for determination Pyr.

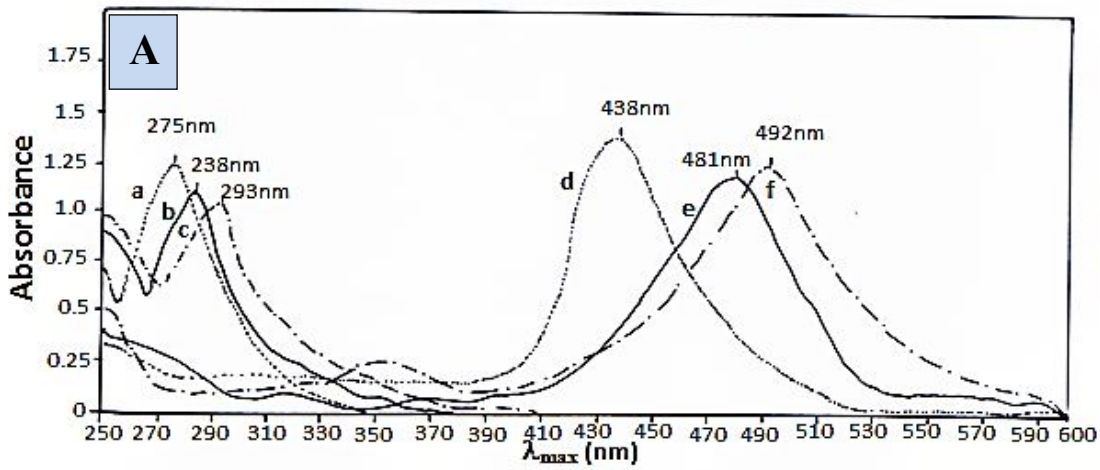


Figure 3-(A): Absorbance spectra for: a: Cat, b: Res, and c: Pyr, against the blank (H_2O), d: Pyr, e: Res, and f: Cat against the blank (Ce(IV)sulfate).

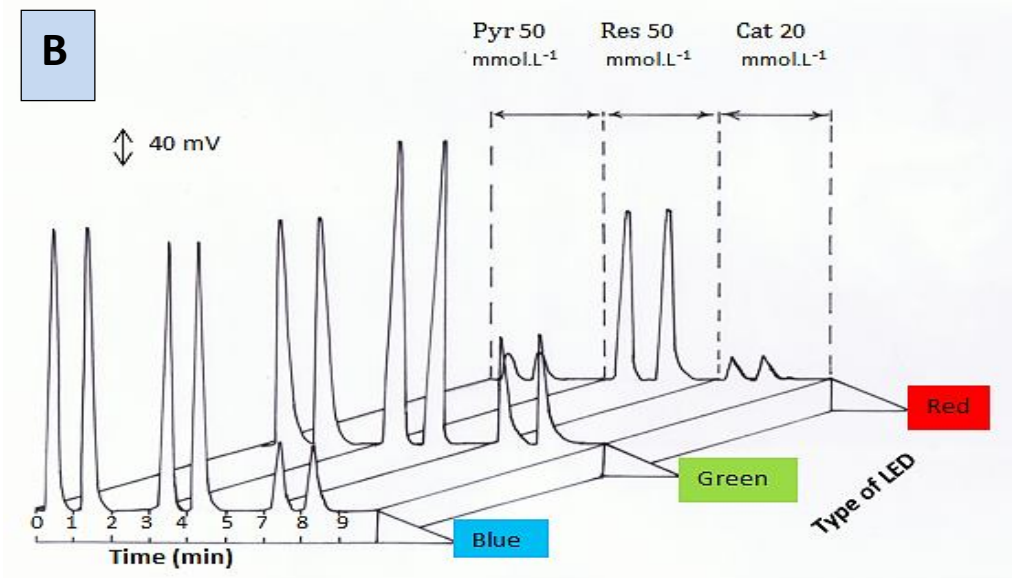


Figure 3-(B): Amaximum responses profile (mV) verses differences light emitted diode using Ayah $3S_{BGR}$ x 3 – 3D solar cell CFIA microphtometer for Cat(20mmol.l^{-1}), Res and, Pyr (50 mmol.L^{-1}) –

Ce(IV)sulfate (50 mmol.L^{-1}) – H_3O^+ system, with 165 µL as a sample volume, flow rate 2.1, and 2.4 ml.$min^{-1}$for the carrier stream and reagent (Ce(IV)sulfate) respectively.

Optimum conditions for oxidation of Cip with Ce (IV) Sulfate in acidic medium.

Chemical variables:

Effect of Ce(IV) sulfate concentration:

The effect of varying concentration of Ce(IV) sulfate was examined, using a series of solutions ranged 20 – 60 mmol.L^{-1} which diluted by 500 mmol.L^{-1} of H_2SO_4, at 20 mmol.L^{-1} of Cat, Res, and Pyr, 165 µL as a sample volume , while two lines manifold system was used at 2.1, and 2.4 ml.min^{-1} for the carrier stream (H_2O) and Ce(IV) sulfate respectively. The obtained results were tabulated in Table1, which Summarizes the average of three successive readings with relative standard deviation and confidence interval of the average response at 95% confidence ($\propto = 0.05$). Figure- 4 shows the plot of the results as it obtained from Ayah $3S_{BGR}$ x3 -3D solar cell CFIA microphotometer. It was noticed that an increase in the response of the colored species with increasing Ce (IV) Sulfate concentration up to 40 mmol.L^{-1} more than 40mmol.L^{-1} led to broadening in peak maxima and increase the peak base width (Δt_b). It is probable that it could be due to the restriction of the passage of incident light due to the accumulation of precipitate in front of the detector which in turn off act on the attenuation of incident light therefore , 40 mmol.L^{-1} was chosen as optimum concentration of Ce(IV) sulfate in next studies.

Table 1- Variation of Ce (IV) sulfate concentration on the transducer energy response of org. comp – Ce(IV)-H_3o^+ system .

Type of analyte	[Ce(IV) sulfate] mmol.L^{-1}	Average transducer energy response expressed as peak height n=3, $\bar{y}_i$ (mV)	RSD%	Confidence interval of the average response $\bar{y}_i \pm t_{0.05/2,\, n-1}\, \sigma_{n-1}/\sqrt{n}$
Cat	20	163	0.6	163 ± 2.49
	30	178	1.12	178 ± 4.97
	40	186	1.0	186 ± 2.86
	50	161.33	0.7	161.33 ± 2.86
	60	130	1.5	130 ± 4.97
Res	20	122	1.6	122 ± 4.97
	30	161	1.42	161 ± 5.71
	40	200	0	200 ± 0
	50	228	1.75	228 ± 9.94
	60	252	1.59	252 ± 9.94
Pyr	20	108.33	1.85	108.33 ± 4.97
	30	129.33	1.78	129.33 ± 5.71
	40	132	1.5	132 ± 4.97
	50	91.33	1.25	91.33 ± 2.85
	60	86	1.3	86 ± 2.85

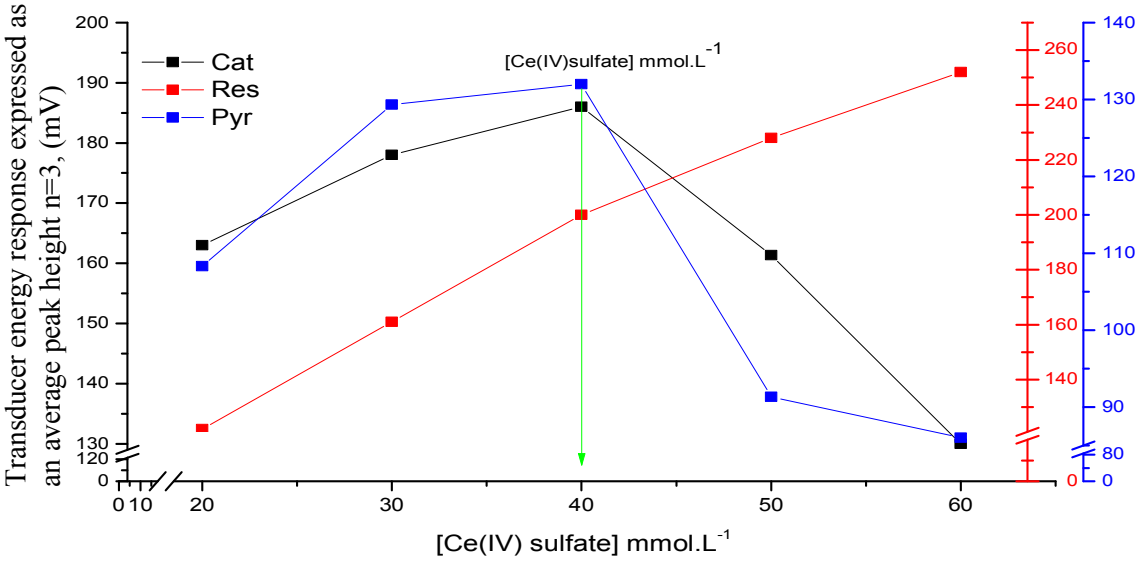


Figure4-Variation of [Ce(IV) sulfate] on transducer energy response (mV).

Effect of acidic medium as a carrier stream:

The reaction of Cat, Res, and Pyr with Ce(IV) sulfate can be conducted in acidic medium; therefore different acids were used (H_2SO_4, HCl, HNO_3, at 50 mmol.L^{-1}) in addition to H_2O as a carrier stream at 2.1 ml.min^{-1}, the optimum concentration of Ce(IV) sulfate 40 mmol.L^{-1} (in 500 mmol.L^{-1} of H_2SO_4) at 2.4 ml.min^{-1}, 20 mmol.L^{-1} of Cat, Res and Pyr with 165µL sample volume were used. Table 2 shows the obtained results, while figure-5 shows the plot and response profile, it can be seen that the effect of different acids was not very crucial on the decrease of the response heights (figure- 5B) which might be attributed to dissociation of some of the colored species, therefore, distilled water was chosen as optimum carrier stream, which gave suitable sensitivity and response profile.

Table 2- Variation acidic medium as a carrier stream on the transducer energyresponse of org. comp – Ce(IV)-H_3O^+ system.

Type of analyte	Type of acid	Average transducer energy response expressed as peak height n=3, $\bar{y}_i$ (mV)	RSD%	Confidence interval of the average response $\bar{y}_i \pm t_{0.05/2,\, n-1}\ \sigma_{n-1}/\sqrt{n}$
Cat	H_2O	161.33	0.71	161.33 ± 2.85
	H_2SO_4	155.33	1.28	155.33 ± 4.97
	HCl	160	0	160 ± 0
	HNO_3	160	0	160 ± 0
Res	H_2O	201.67	1.13	200.67 ± 5.71
	H_2SO_4	180	0	180 ± 0
	HCl	187.33	2.22	187.33 ± 10.34
	HNO_3	172	0	172 ± 0
Pyr	H_2O	122.67	1.88	122.67 ± 5.71
	H_2SO_4	101.33	2.27	101.33 ± 5.71
	HCl	121.33	2.0	121.33 ± 5.571
	HNO_3	118.33	2.75	118.33 ± 5.16

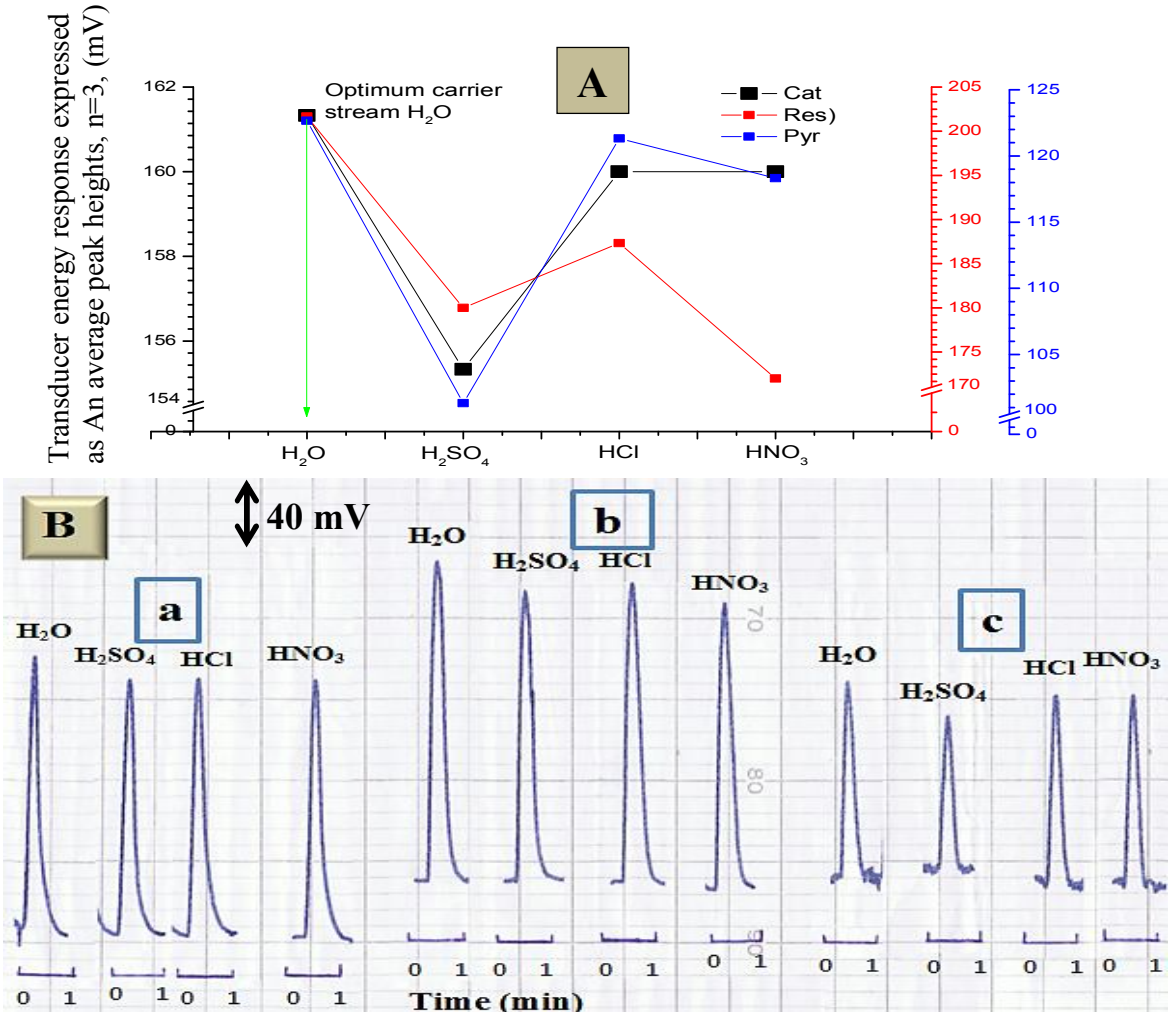


Figure 5- Variation type of acidic medium as a carrier stream on: A: Transducer energyresponse (mV), B: response profile using Ayah $3S_{BGR}X$ 3-3D solar cell CFIA, fordetermination of, a: Cat, b: Res, and c: Pyr.

Physical variables:

Flow rate:

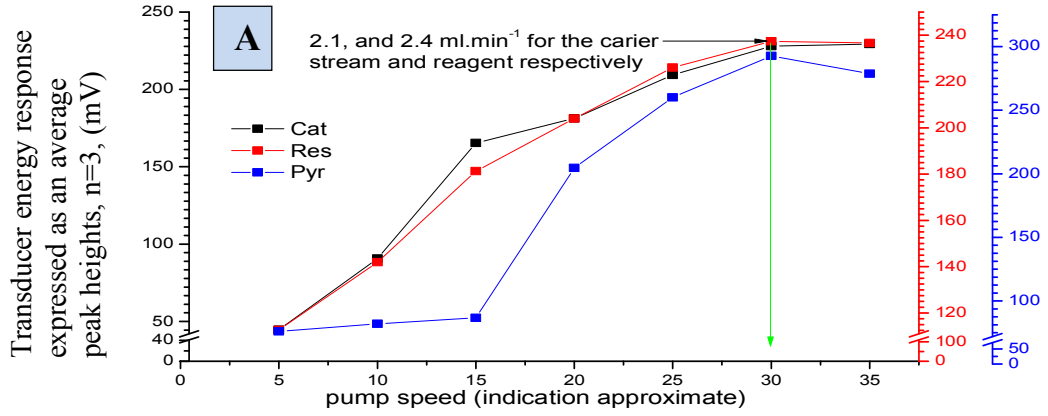
Flow rate was ranged 0.4-2.4, and 0.4-2.8 ml.min^{-1} for the carrier stream and the reagent (Ce(IV) sulfate) respectively. The flow rate of Cat, Res, and Pyr determination was investigated to conducted the optimize of preferred flow rate. The optimum concentration 40 mmol.L^{-1} of Ce(IV) sulfate, and using 30 mmol.L^{-1} of Cat, Res, and Pyr with 165 µL as a sample volume, while distilled water was used as a carrier stream. The obtained results were tabulated in Table 3, while figure- 6 shows the plot, and response profile. It was noticed that at low flow rate there were an increase in peak base width, with decrease peak height, and broadening at the peak maxima, which might be due to the dispersion and dilution leading to an irregular response profile (figure- 6B). But at high flow rate influence (up to pump speed 30) led to an increase in peak height, decrease the peak base width, and decrease time that required for arrive the colored species to the measuring flow cell. As compromise between sensitivity, peak shape, and consumption of the chemicals.A 2.1, and 2.4 ml.min^{-1} were chosen as optimum flow rate for the carrier stream and Ce(IV) sulfate respectively.

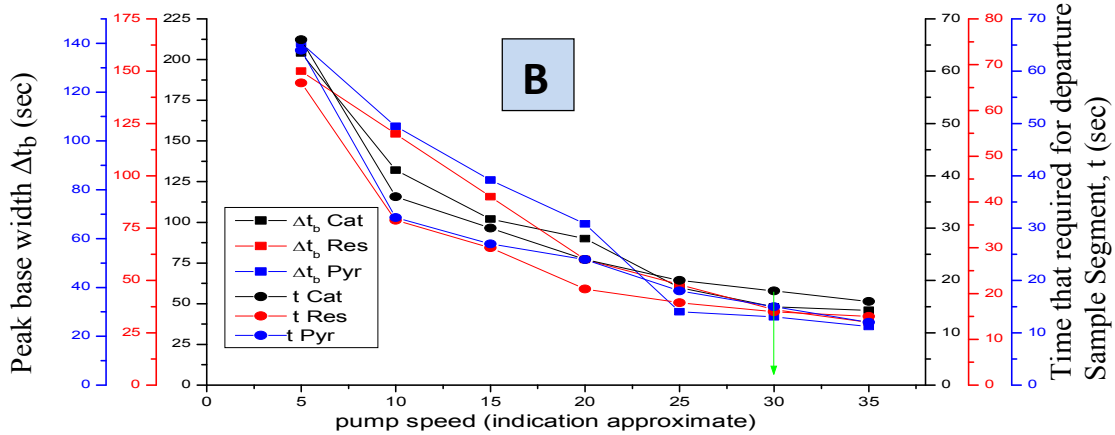
Table 3- Variation of flow rate (ml.min^{-1}) on the transducer energy response (mV).

Type of Analyte	Pump speed indication approximate	Flow rate (ml.min^{-1})		Average transducer energy response expressed as peak height n=3, $\bar{y}_i$ (mV)	RSD%	Confidence interval of the average response $\bar{y}_i \pm t_{0.05/2,\,n-1}\,\sigma_{n-1}/\sqrt{n}$	Δt_b sec	t sec
		Carrier stream	Ce(IV) sulfate line					
Cat	5	0.4	0.4	44.67	1.11	44.67 ± 1.41	204	66
	10	0.7	0.7	90.67	1.27	90.67 ± 2.85	132	36
	15	1.1	1.2	165.33	1.2	165.33 ± 4.97	102	30
	20	1.4	1.6	181.33	1.1	181.33 ± 4.97	90	24
	25	1.8	2.0	209.33	1.67	209.33 ± 8.72	60	20
	30	2.1	2.4	228	0	228 ± 0	48	18
	35	2.4	2.8	229.33	1.0	229.33 ± 5.71	46	16
Res	5	0.4	0.4	112.67	1.02	112.67 ± 2.85	150	66
	10	0.7	0.7	142	1.4	142 ± 4.97	120	36
	15	1.1	1.2	181.33	1.26	181.33 ± 5.71	90	30
	20	1.4	1.6	204	0.98	204 ± 4.97	60	21
	25	1.8	2.0	226	0.88	226 ± 4.997	48	18
	30	2.1	2.4	237.33	0.48	237.33 ± 2.85	36	16
	35	2.4	2.8	236.67	0.97	236.67 ± 5.71	30	15
Pyr	5	0.4	0.4	76	1.5	76 ± 2.85	140	64
	10	0.7	0.7	82	1.2	82 ± 2.48	106	32
	15	1.1	1.2	86.67	1.15	86.67 ± 2.48	84	27
	20	1.4	1.6	204.67	0.97	204.67 ± 4.97	66	24
	25	1.8	2.0	260	0	260 ± 0	30	18
	30	2.1	2.4	292.67	0.78	292.67 ± 5.71	28	15
	35	2.4	2.8	278.67	0.82	278.67 ± 5.71	24	12

Δt_b (sec): peak base width .

t (sec) : time for the departure of sample segment from injection valve reaching to the measuring flow cell.





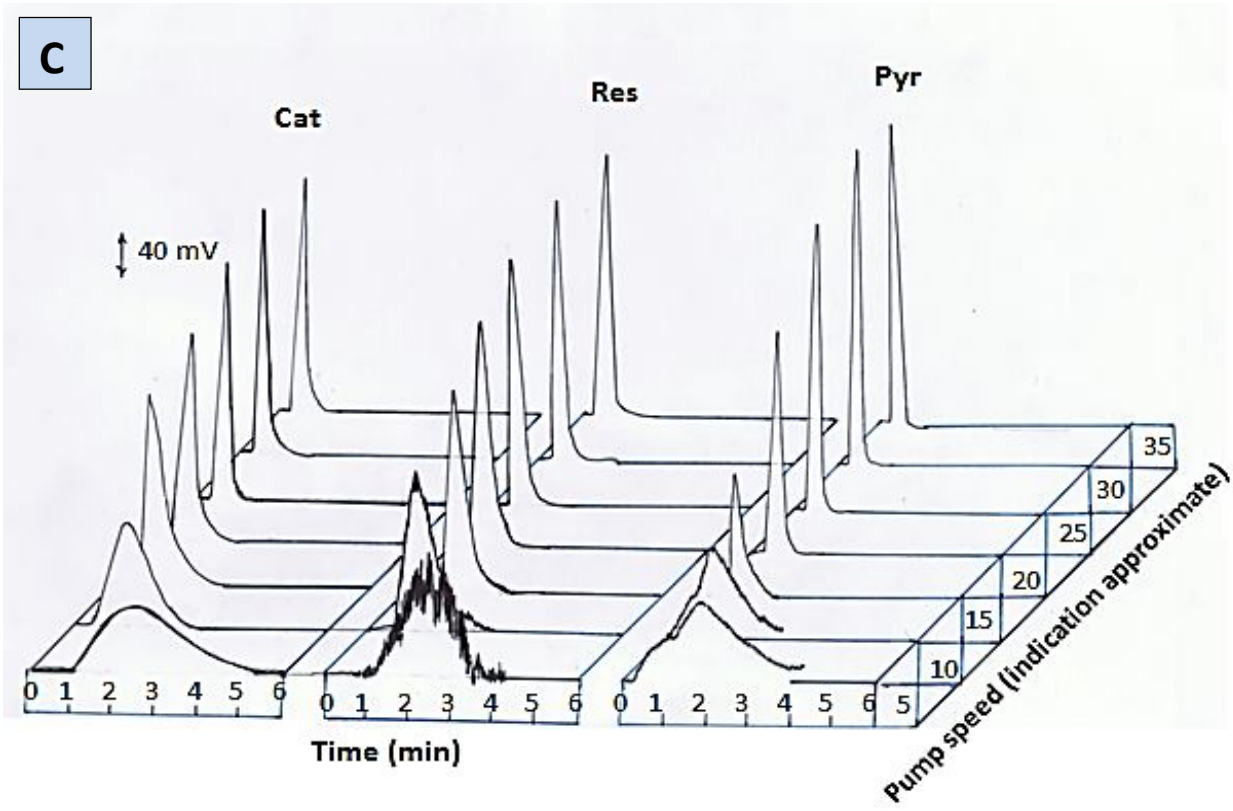


Figure 6- variation of flow rate on: A- transducer energy response for three org. comp.,B- peak base width(Δt_bsec), and time for the departure of sample segment from injection valvereaching to themeasuring flow Cell (t sec), C- response profileusing Ayah $3S_{BGR}$X 3-3D solarcellCFIA, fordetermination of Cat, Res, and Pyr.

Sample volume:

The study carried out using 2.1, and 2.4 ml.min^{-1} as optimum flow rate for the carrier stream and Ce(IV) sulfate (40 mmol.L^{-1} in acidic medium) respectively, with 20 mmol.L^{-1} of Cat, Res, and Pyr. Variable sample volumes were used which equivalent to 110, 156, 165, 211, and 297 µL which successively used with open valve mode. The results were tabulated in Table 4, which indicated that 165, 156, and 165 µL were the optimum sample volume for the Cat, Res, and Pyr respectively, which gave sharp and smooth response profile, in addition to economy and decrease the analysis time. It was noticed that an increase in sample volume led to an increase in the height of response without effecting on the response profile up to the sample volume 165, 156, and 165 µL for three organic compounds, more than led to a broadening at the peak maxima and an increase in the base width (Δt_b) which was most probably attributed to continuous long time duration of color segment in front of the detector; this is illustrated in figure- 7 which shows these effects.

Table 4- Variation of injected sample volume on transducer energy response**.**

Type of analyate	Loop length (cm)	Sample volume (µL)	Average transducer energy response expressed as peak height n=3, $\bar{y}_i$(mV)	RSD%	Confidence interval of the average response $\bar{y}_i \pm t_{0.05/2,\ n-1}\ \sigma_{n-1}/\sqrt{n}$	Δt_b Sec
Cat	14.00	110	77.33	0.6	77.33 ± 1.15	30
	19.82	156	104	0	104 ± 0	36
	21.00	165	154	1.29	154 ± 4.97	42
	26.80	211	226.67	1.01	226.67 ± 5.71	48
	35.60	297	234.67	0.49	234.67 ± 2.85	60
Res	14.00	110	182	1.09	182 ± 4.96	18
	19.82	156	206	0.97	206 ± 2.40	36
	21.00	165	212	0	212 ± 0	38
	26.80	211	208	0	208 ± 0	40
	35.60	297	202	0.99	202 ± 0.99	42
Pyr	14.00	110	85.33	1.34	85.33 ± 2.85	12
	19.82	156	112	1.1	112 ± 3.06	15
	21.00	165	146	1.36	146 ± 4.97	30
	26.80	211	162.67	1.41	162.67 ± 5.04	36
	35.60	297	164.67	1.85	164.67 ± 7.57	40

Δt_b (sec): peak base width.

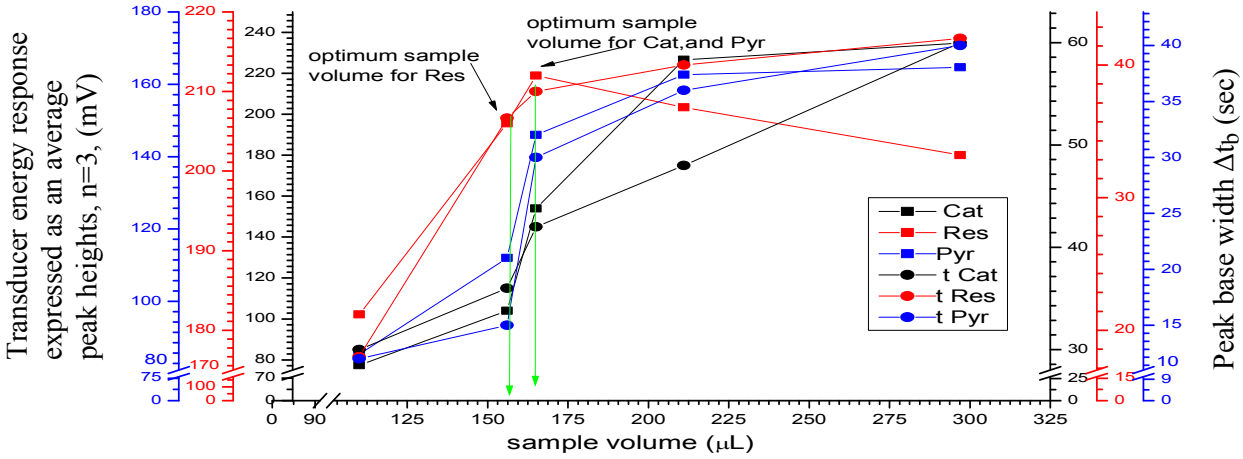


Figure 7- Variation of sample volume on transducer energy response, and peak base width (Δt_b) fordetermination of Cat, Res, and Pyr.

Purge time:

Using different purge time for the sample segment i.e, the allowed time was 5-40 sec in addition to open valve mode for the three organic compounds sample to passing through the injection valve (injection mode) followed by turning the injection valve to the load position. Optimum sample volume of Cat, Res, and Pyr (30 mmo.L^{-1}) 165, 156, and 165 µL respectively were used. Figure -8 shows the continuation of the increase in the height of response andΔt_b with increase of injection time up to open valve mode, therefore open valve mode as purge time was chosen as optimum time to the complete purge of sample segment from injection valve to the manifold of FIA system, which gave a better response profile (figure- 8B). The obtained results were tabulated in Table 5.

Table 5-Variation of purge time on the transducer energy response.

Type of analyate	Purge time (Sec)	Average transducer energy response expressed as peak height n=3, $\bar{y}_i$(mV)	RSD%	Confidence interval of the average response $\bar{y}_i \pm t_{0.05/2,\ n-1}\ \sigma_{n-1}/\sqrt{n}$	Δt_b (sec)
Cat	5	100	1.15	100 ± 2.85	44
	10	110	0.9	110 ± 2.48	46
	20	118	1.69	118 ± 4.97	50
	30	120	0	120 ± 0	54
	40	150	0	150 ± 0	54
	Open valve	208	0.55	208 ± 2.85	54
Res	5	140	1.4	140 ± 4.97	24
	10	168	0	168 ± 0	24
	20	209.33	0.55	209.33 ± 2.85	28
	30	216	0	216 ± 0	30
	40	220	0.9	220 ± 4.97	34
	Open valve	230	0.86	230 ± 4.97	36
Pyr	5	200	0.7	200 ± 3.48	22
	10	285.33	0.8	285.33 ± 5.71	24
	20	294	0.68	294 ± 4.97	27
	30	298	0	298 ± 0	30
	40	300	0.77	300 ± 5.71	30
	Open valve	310	0.64	310 ± 4.97	30

Δt_b (sec): peak base width.

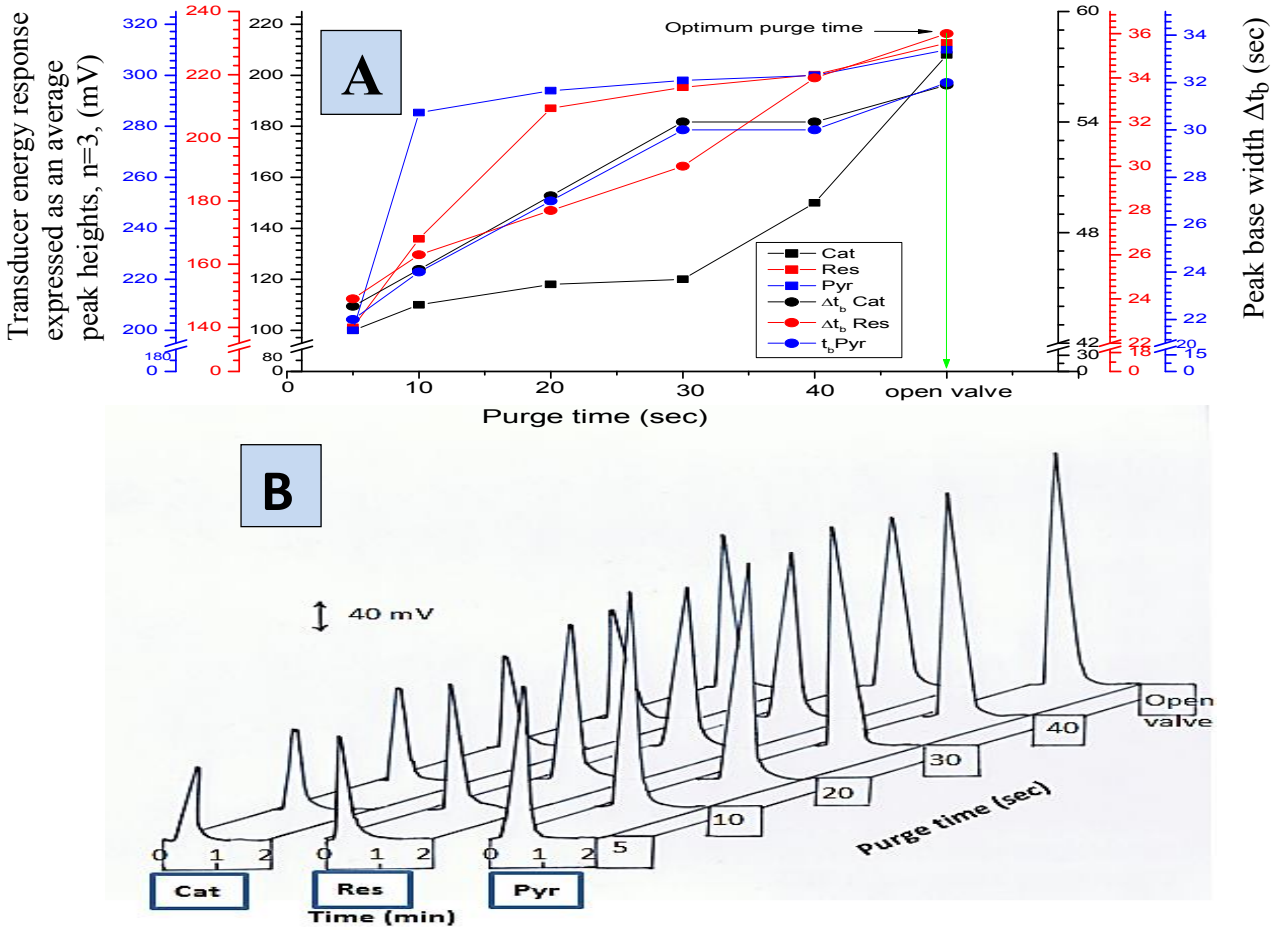


Figure 8- Variation of purge time on: A- transducer energy response, and peak base width (Δt_bsec). B-response profile using Ayah $3S_{BGR}X$ 3-3D solar cellCFIA.

Incident light intensity:

Variable intensity of light source was used 0.6 – 1.3 volt for the green light emitted diode, and 0.6-1.2 for the blue light emitted diode by variation of light intensity channel in Ayah $3S_{BGR}$ x 3- 3D solar cell CFIA microphotometer operation where read by AVO-meter. The optimum conditions were used; green light emitted diode (LED) 525 nm as an irradiation source for the Cat, and Res, while blue light emitted diode (LED) 470 nm as an irradiation source for the Pyr , 40 mmol.L^{-1} of Ce(IV) sulfate, flow rate was 2.1, and 2.4 ml.min^{-1} for the carrier stream and reagent line respectively, and sample volumes were165, 156, and 165 µL of Cat, Res, and Pyr respectively (20 mmol.L^{-1}). The obtained results tabulated in Table 6 which shows that an increase in the peak height with increase light intensity, therefore 1.2, and 0.9 volt was chosen as optimum voltage for the green light emitted diode(LED), and blue light emitted diode(LED) respectively, that can be supplied to give a better reproducible outcome as shown in figure- 9.

Table 6 - Variation of incident light intensity on transducer energy response.

Type of Analyate	Intensity of Source (volt)	Average transducer energy response expressed as peak height n=3, $\bar{y}_i$ (mV)	RSD%	Confidence interval of the average response $\bar{y}_i \pm t_{0.05/2,n-1}\sigma_{n-1}/\sqrt{n}$
Cat	0.6	121.33	0.9	121.33 ± 2.85
	0.7	140	0	140 ± 0
	0.8	156	0	156 ± 0
	0.9	170	0.9	170 ± 3.8
	1.0	184	0	184 ± 0
	1.1	194	0	194 ± 0
	1.2	200	0.4	200 ± 1.99
	1.3	191.33	0.6	191.33 ± 2.85
Res	0.6	86	1.1	86 ± 2.33
	0.7	130	0.9	130 ± 3.4
	0.8	156.67	1.1	156.67 ± 4.27
	0.9	180.67	0.8	180.67 ± 3.57
	1.0	206	0	206 ± 0
	1.1	217.33	0.6	217.33 ± 3.22
	1.2	224	0	224 ± 0
	1.3	226	0.88	226 ± 4.97
Pyr	0.6	116	0.5	116 ± 1.44
	0.7	156	0.66	156 ± 2.53
	0.8	181.33	0.95	181.33 ± 4.27
	0.9	186	0.88	186 ± 4.04
	1.0	180	1.2	180 ± 5.36
	1.1	172	0	172 ± 0
	1.2	142.67	0.55	142.67 ± 1.93

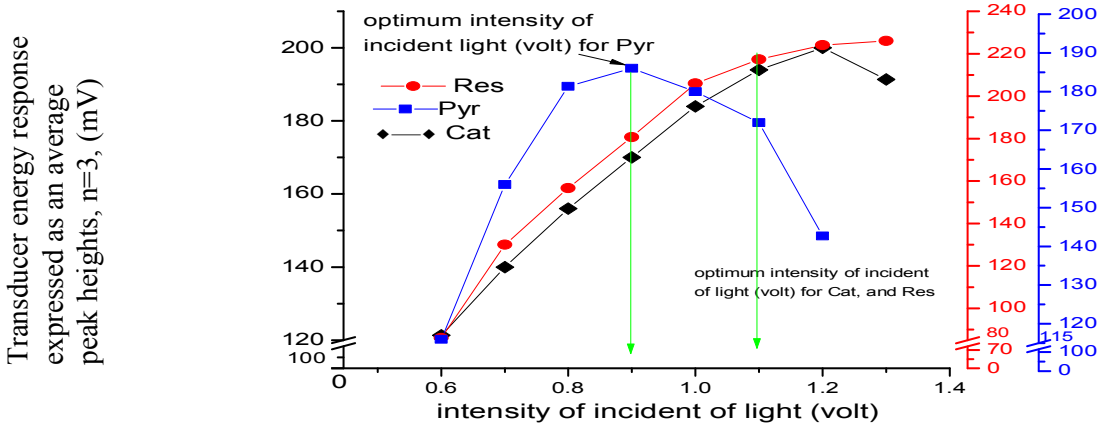


Figure 9- Variation of incident light intensity on transducer energy response .

Calibration graph:

At the established optimum conditions, a series of solution for three different organic compounds (1 - 100 mmol.L^{-1}) were prepared. Each measurement was repeated three times. Transducer energy response of the average peak height (mV) was plotted against the concentration of threeorganic compounds A straight –line graph (figure-10) from 5 – 40 mmol.L^{-1} of organic compounds were obtained. Above 40 mmol.L^{-1} the value for correlation coefficient will decrease and deviate from linearity most probably due to the increase of the colored species in front of detector and due to the effect of inner filter of the high intensity colored species present in solution, which might be due to attenuation in transmitted light. The summaries of results were tabulated in Table 7.

Table 7- summary of calibration graph results for the determination of using org. comp. -Ce(IV) - H_3O^+system.

Type of analyte	Measured [x] mmol.L^{-1}	Linear dynamic range mmol.L^{-1} n = 11	$\hat{Y}i$ (mV) = $a \pm ts_a + b \pm ts_b$ [x] mmol.L^{-1} at confidence level 95% , n – 2	r r^2 %	t_{tab}	$t_{cal} = r/\sqrt{\frac{n-2}{1-r^2}}$
Cat	1-100	5-40	-18.69±16.19+8.87±0.69[Cat]	0.9952 99.05%	2.306<< 28.97	
Res			70.11±8.39+ 5.86±0.34[Res]	0.9970 99.41%	2.306 << 36.91	
Pyr			- 33.33±17.22+10.43±0.73[Pyr]	0.9960 99.22%	2.306 << 32.03	

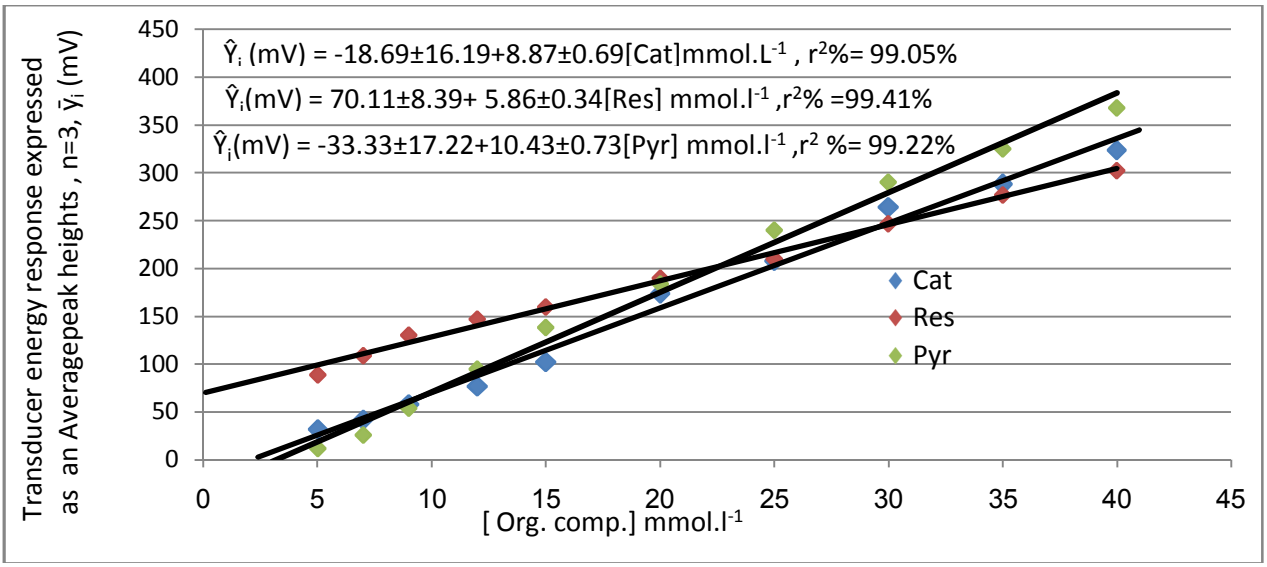


Figure 10- Calibration graph for the variation of Cat, Res, and Pyr concentration on transducer energy response expressed by linear equation using Ayah $3S_{BGR}$x3- 3D solar cell CFIAmicrphotometer**.**

Limit of detection (L. O. D):

Three different approaches were used for measuring L.O.D: gradual dilutionof lowest concentration in the calibration graph, or detection based on the numerical value of slope or from the linear regression plot. Table 8 tabulated all these calculation value of detection limit for organic compounds with sample volume: 165,156, and 165µL respectively.

Table 8-Summery of limit of detection based on different approaches.

Type of analyate	Gradual dilution for minimum concentration	Based on the value of slope $X = 3S_B$ / slope	Theoretical value from linear equation $\hat{Y}i\ (mV) = Y_B+3S_B$
Cat	36.63 ng	61.45 ng	69.21 µg
Res	17.17 ng	87.96 ng	51.35 µg
Pyr	41.61 ng	59.85 ng	71.69 µg

S_B: standard deviation of blank solution. , X= value of L.O.D based on slope.
Y_B: average response for the blank solution (equivalent to intercept in straight line equation).

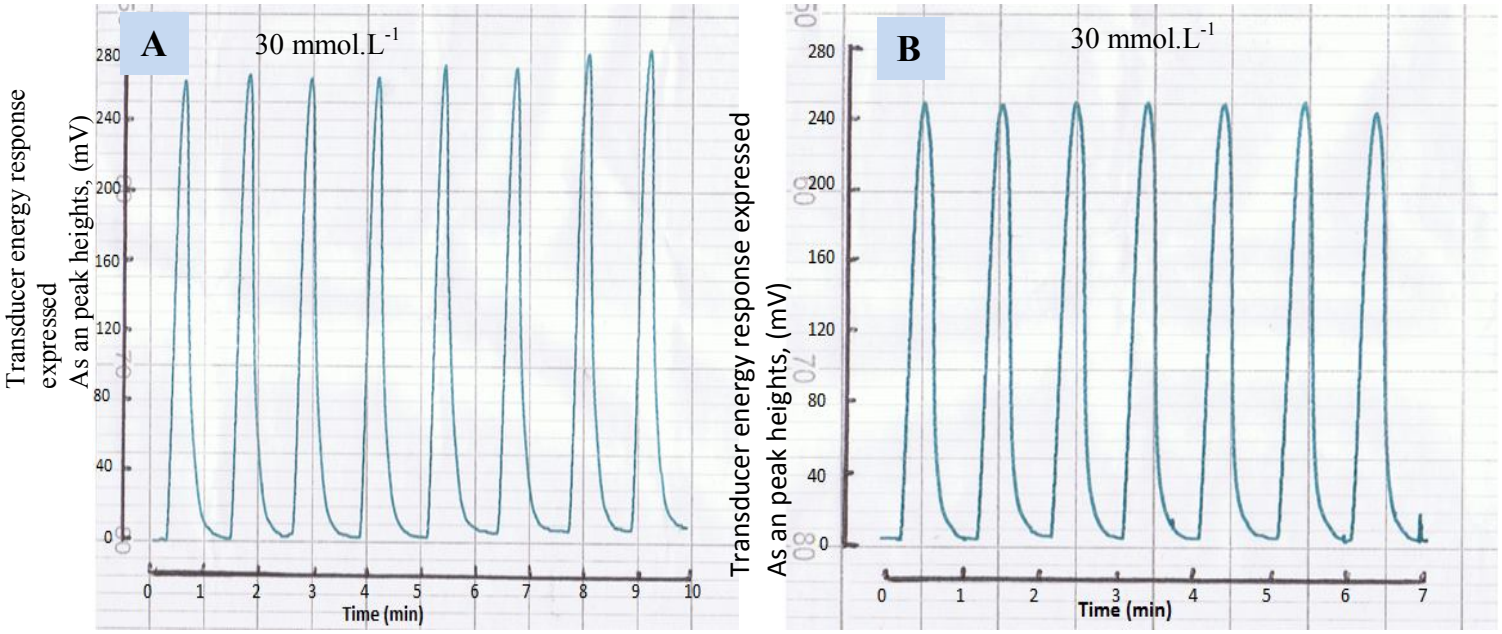
Repeatability:

The repeatability of measurement and the efficiency of homemade Ayah $3S_{BGR}$x 3 – 3Dsolar cell CFIA microphotometer were studied at fixed concentrations of Cat, Res, and Pyr were used, mainly one concentration was used30 mmol.L^{-1}, using the optimum parameters. The repeated measurements for eight and seven successive injections were measured and obtained results were tabulated in table 9which shows that the percentage relative standard deviation was less than 1.4, 0.63, and 1.78 forCat, Res, and Pyr respectively while figure-11 shows a kind of response-time profile for the used concentrations.

Tablet 9 - Repeatability of Cat, Res, and Pyr results obtained for the formation of colored species.

Type of analyate	[x] mmol.L^{-1}	no. of injection	Average transducer energy response expressed as peak heights $\bar{y}i$ (mV)	RSD %	Confidence interval of the average response 95 % confidence $\bar{y}i(mV)\pm t_{0.05/2,\ n-1}\ \sigma_{n-1}/\sqrt{n}$
Cat	30	8	268	1.4	268 ± 3.18
Res	30	7	247.14	0.63	247.14 ± 1.57
Pyr	30	8	290.25	1.78	290.25 ± 4.32

[x] = Cat, or Res, or Pyr.



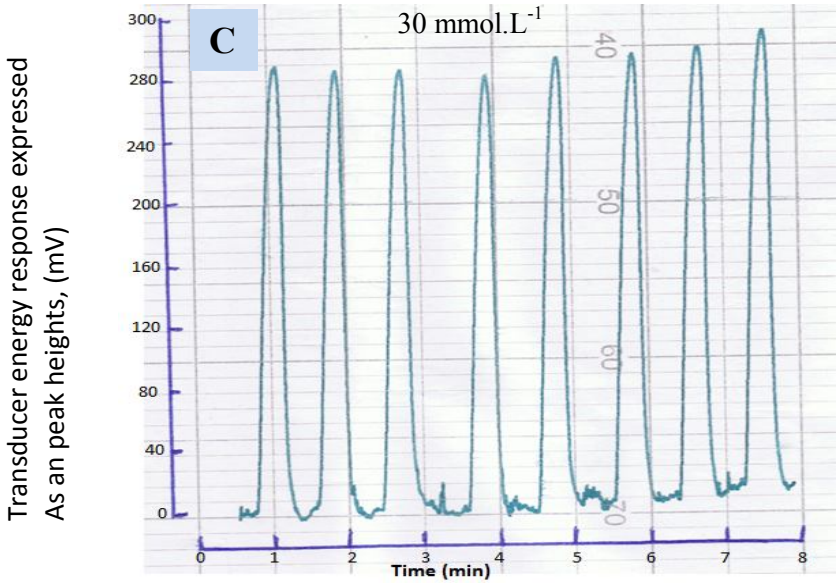


Figure 11- A Profile of successive repeatability measurements of: A-Cat, B- Res, C- Pyr (30 mmol.L^{-1}) using Ayah $3S_{BGR}$ x3S-3D solar cell CFIA microphotometer.

Evaluation of the use of Ayah $3S_{BGR}$ x 3S – 3D solar cell CFIA microphotometer in the determination of three organic compounds in pure commercial samples as an application:

The established method was used for the determination ofCat, Res, and Pyr, in pure formulation (pyrocatechol – Readeldehean- Germany, resorcinol- Randwin- india, and pyrogallol- Readeldehean-Germany), using Ayah $3S_{BGR}$ x 3S – 3D solar cell CFIA microphotometer and was compared with classical spectrophotometric method via the measurement of λ_{max}at 492, 481, and 438 nm for Cat, Res, and Pyr respectively . The standard addition method was applied by prepared a series of solutions from each sample (Cat, Res, and Pyr)via transferring 0.25 mL, (500 mmol.L^{-1}) of each sample, to five volumetric flask (25 mL) , followed by the addition of (0 , 0.25 , 0.35 , 0.45 , and 0.75) from standard solution of Cat, Res, and Pyr (500 mmol.L^{-1}) in order to have the concentration range from 0 – 15 mmol.L^{-1}, for the preparation of standard additions calibration plot. The measurements were conducted by both methods.

Results were mathematically treated for standard additions method. The results were tabulated in Table10 at confidence interval 95 %.

Paired t – test was used as shown in scheme 2. Which shows a comparison- treatment of data was subjected at two different paths.

First test: comparison between two methods of analysis (scheme 2-A), i.e. Ayah $3S_{BGR}$ x 3S – 3D solar cell CFIA microphotometer [47] with UV-Vis spectrophotometric as shown in table 11-A.

Assumption:

(Null Hypothesis) H_o: $\mu_{UV\text{-}Vis} = \mu_{Ayah\ 3S_{BGR}\ x3-3D}$

Against (Alternative Hypothesis) H_1: $\mu_{UV\text{-}Vis} \neq \mu_{Ayah\ 3S_{BGR}\ x3-3D}$

From the results, it was noticed that two methods of analysis proved to indicate that there is no significant difference between the means of two different methods for analyzing three different organic compounds (Pyrocatechol, Resorcinol, and Pyrogallol).

Since calculated t_{Value} of 0.12<< 4.303, therefore, H_o is accepted againstH_1.

now sinceH_o is valid. S_o a second test can be donce on the basis that since H_o is valid and we have started at the same concentration (500 mmol.L^{-1}), it mean that:

$Method_{UV\text{-}Vis} = Method_{Ayah\ 3S_{BGR}\ x3-3D}$ (no difference for any method used).

And conc. of Pyrocatechol= conc. of Resorcinol = conc. of Pyrogallol (Equal concentration).

Therefore, we are going to use another second test to distinguish between the three different organic compounds, and does the three different compounds give the same product output. i. e. structural variation or effects regarded a not significant and they contribution the same effects therefore,

(Null Hypothesis) $H_o = \mu_{Cat\ using\ both\ methods} = \mu_{Res\ using\ both\ methods} = \mu_{Pyr\ using\ both\ methods}$

(Alternative Hypothesis) $H_1 = \mu_{Cat\ using\ both\ methods} \neq \mu_{Res\ using\ both\ methods} \neq \mu_{Pyr\ using\ both\ methods}$

The values that were obtained for table 11-B, based on the scheme 2-B shows three pairs for comparison for pair 1: Cat. versus Res.

Assumpation:

$H_o = \mu_{Cat} = \mu_{Res}$ against $H_1 = \mu_{Cat} \neq \mu_{Res}$

$t_{calculate} = |-0.81| \rightarrow t_{Cal.} = 0.81 << t_{tab.}(12.706)$.

Therefore,H_o is accepted against H_1 there is no significant difference in the contribution of both compounds (Cat and Res) to the reaction path.

Pair 2: Cat. Versus Pyr.

$H_o = \mu_{Cat} = \mu_{Pyr}$ Against$H_1 = \mu_{Cat} \neq \mu_{Pyr}$

$t_{Calculated} = 0.61 << t_{tab}(12.706)$

$\therefore H_o$ is accepted against H_1.

i:e no significant difference in the contribution of both compounds (Cat and Pyr) to the reaction path.

Pair 3: Res versus Pyr.

$H_o = \mu_{Res} = \mu_{Pyr}$ Against$H_1 = \mu_{Res} \neq \mu_{Pyr}$

Since $t_{Calculated} = 0.1.28 << t_{tab}(12.706)$.

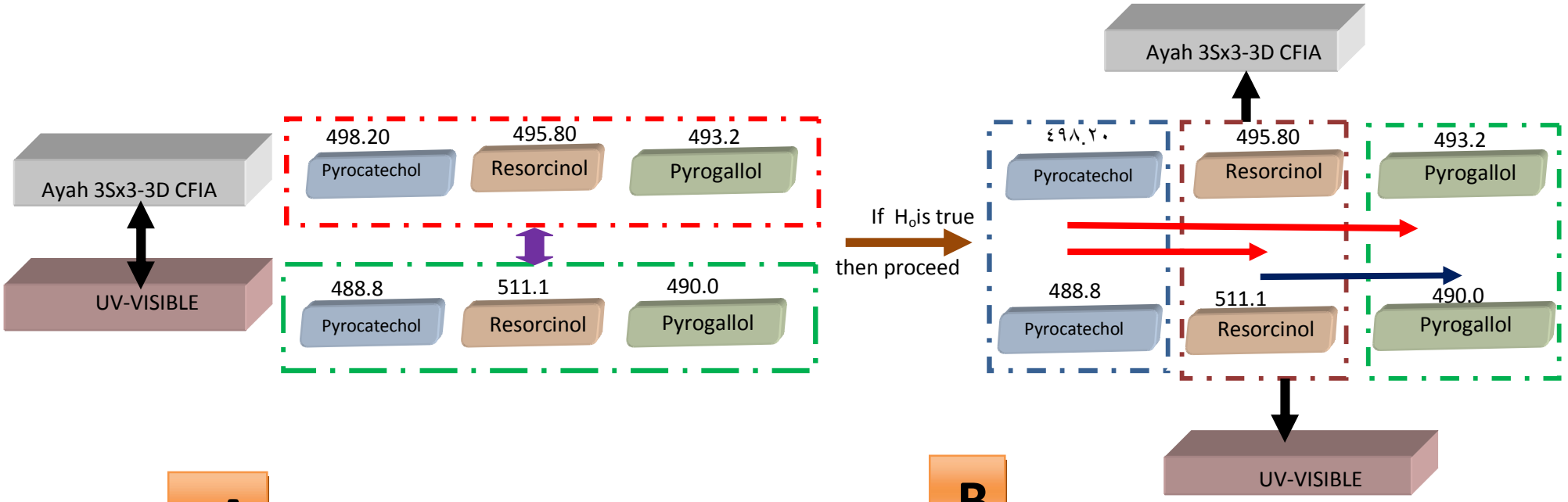
Therefore, H_o is accepted against H_1.

There is no significant difference using the two methods with the same concentration and structural effect does not add any significant difference. The above studied compounds give and behave similarly concerning used reaction and it cannot be differentiated or all what it concerns relating to the wags they are determined, therefore its have the same reaction pattern and cannot distinguish between them.

Table 10-Results for the determination of Cat, Res, and Pyr pure formulation using standard addition, with two methods Ayah $3S_{BGR}$ X3 -3D solar cell CFIA microphotometer and UV-Vis spectrophotometric method.

analyate	Sample commercial name, company country.	Theoretical weight in 100 mL (g)	Theoretical concentration mmol.L^{-1}, in 100 mL	Equation of standard addition curve at 95% for n-2 $\hat{Y}=a\pm s_a t+b\pm s_b t[x]$	r r^2%	Practical concentration mmol.L^{-1}, in 25 mL	Practical concentration mmol.L^{-1}, in 100 mL	Practical Weight(g) In 100 mL	Efficiency of determination (Rec %)
				AYAH $3S_{BGR}$ x3-3D Solar cell CFIA microphotometer					
				UV - Vis spectrophotometer					
Cat	Pyrocatechol, Readldehean, Germany.	5.505	500	27.95±6.01+5.61±0.67	0.9977 99.55%	4.982	498.2±6.89	5.485	99.64
				0.44±0.10+0.09±0.01	0.9954 99.09%	4.888	488.8±2.32	5.382	97.76
Res	Resoncinol, Randwin Indian	5.505	500	56.68±8.27+11.43±0.92	0.9989 99.79%	4.958	495.8±3.83	5.459	99.16
				0.46±0.09+0.09±0.01	0.9978 99.58%	5.111	511.1±7.31	5.627	102.22
Pyr	Pyrogallol, Readldehean, Germany.	6.3055	500	64.37±18.42+13.05±2.10	0.9960 99.22%	4.932	493.2±3.88	6.220	98.64
				0.49±0.09+0.10±0.10	0.9981 99.64%	4.900	490.0±3.32	6.179	97.99

$\hat{Y}i$ = estimated value for energy transducer response (mV) or absorbance. X: [Cat], [Res], and [Pyr] mmol.L^{-1}.



Paired t-test to compare methods of analysis

Paired t-test applied for different organic compounds only if H_o is true then Pyrocatechol, resorcinol, and pyrogallol can be compared for their legibility of having different paths for the precipitation and signal differentiation

Scheme 2: Paired t-test representation for the treatments of the data obtained in the analysis conducted by two different approaches. UV-Visible and Ayah3SX3-T-D-CFIA for three different organic compounds. (A) represent comparison of the two methods delivering data ; (B) represent IF $H_o$is accepted against the ALTERNATIVE H_1 then the test is conducted to evaluate whether the structural effect of these three different organic compounds contribute to the reaction to the same extent .

Table 11-A: paired t-test for two methods of analysis three organic compounds (Cat, Res, and Pyr, 500 $mmol.L^{-1}$)

Pair	Practical concentration $mmol.L^{-1}$			Mean $\bar{x}$ $mmol.L^{-1}$	Xd $mmol.L^{-1}$	$\bar{x}d$ $mmol.L^{-1}$	σ_{n-1}	N / df	$t_{cal} = \frac{\bar{x}d \sqrt{n}}{\sigma_{n-1}}$	t_{tab}
Ayah $3S_{BGR}$ x3 − 3D	498.2	495.8	493.2	495.73	9.4	-0.9	12.85	3	|-0.12| << 4.303	
UV-Vis	488.8	511.1	490.0	496.63	-15.3			2		
					3.2					

Xd: differences between two methods, $\bar{x}d$: difference mean, σ_{n-1}: difference standard deviation, N: no. of organic compounds.

$t_{critical} = t_{tab} = t_{\propto/2,\, n-1} = t_{0.05/2} = 4.303$, df: degree of freedom

Table 11-B: paired t-test between three different organic compounds.

No. of pair	Paired differences		$t_{cal} = \frac{\bar{x}d \sqrt{n}}{\sigma_{n-1}}$	t_{tab}
	$\bar{x}d$ $mmol.L^{-1}$	σ_{n-1}		
Pairs 1 Cat- Res	-9.95	17.46	|-0.18| << 12.706	
Pairs 2 Cat- Pyr	1.9	4.38	0.61 << 12.706	
Pairs 3 Res- Pyr	11.85	13.08	1.28 << 12.706	

$t_{critical} = t_{\propto/2,\, n-1} = t_{0.05/2}$, 1= 1.706, N= 2, df= 1.

Conclusion:

A spectrophotometric CFIA is proposed method for determination of Cat, Res, and Pyrwith application in the quality control analysis. The method based on the oxidation of Cat or Res or Pyr by Ce(IV) sulfate in acidic medium forming brown product . The experimental point of view, the manipulation is very simple and sequential measurement was permitted with sample frequency up to 30 samples per hour. The proposed method uses cheaper instrument and reagent. In this paper a more effective faster determination was achieved by Ayah $3S_{BGR}$ x 3-3D solar cell CFIA microphotometer , light emitted diode as source with a detection using solar cell . The standard additions method was used to avoid matrix effectsand over high sensitivity without the need for heating or extraction. Also this method can be applied to micro determination of Cat, Res, and Pyrin pure formulation.

Acknowledgement:

I would like to express my deepest gratitude to Prof. Dr. IssamM.A.Shakir Al-Hashimi for his appreciable advice, important comments, support and encouragement.

Reference:

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