Journal of Education and Science (ISSN 1812-125X), Vol: 29, No: 2, 2020 (241-249)

# Using of Acetylacetone-formaldehyde Reagent in Spectrophotometric Determination of Aniline in Various Water Samples

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(Received October 17, 2019; Accepted January 06, 2020; Available online June 01, 2020)

DOI: 10.33899/edusj.2020.126192.1022, 

## Abstract

A simple and accurate spectrophotometric method for the estimation of aniline in various water samples was done. The method was based on the condensation reaction of acetyl acetone-formaldehyde (AC-FA) reagent with aniline. to produce a yellow colored product, with maximum absorption at 417 nm, which has good stability at room temperature and it is very soluble in water (the medium of reaction). Beer's law is applied in the concentration range of 2.5 to 50 µg. $ml^{-1}$ of aniline with a molar absorptivity $3.864\times10^3$ $l.mol^{-1}.cm^{-1}$ and Sandell's sensitivity index 0.0241 $\mu g.cm^{-2}$ , a relative error of – 0.51 to +4.15 % and a relative standard deviation of ±0.78 to ±1.28% depending on the concentration level. The study also included the effect of organic compounds on the recovery of aniline in water samples. Aniline is the simple type of primary aromatic amines as it enters into many industrial fields and is considered as an important material. Aniline regarded as major pollutant of water, thus, its estimation was studied in different samples of water such as river, tap and Zamzam well waters.

**Key words:** aniline, acetylacetone-formaldehyde reagent, determination, waters.

# استخدام الكاشف اسيتيل اسيتون – فورمالديهايد في التقدير الطيفي للانلين في نماذج مختلفة من المياه

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**الخلاصة**

اجريت طريقة طيفية بسيطة وسهلة لتقدير الانلين في نماذج مختلفة من المياه .الطريقة تعتمد على تفاعل تكثيف للكاشف اسيتيل اسيتون– فورمالديهايد مع الانلين ويتكون ناتج اصفر، يمتلك اقصى امتصاص عند 417 نانوميتر، يتصف الناتج بالاستقرارية الجيدة ويكون ذائبا بالماء. كانت الامتصاصية المولارية3.864× $10^3$ لتر. مول$^{-1}$.سم$^{-1}$ ومعامل دلالة ساندل 0.0241 مايكروغرام .سم $^{-2}$. كذلك تم حساب الخطأ النسبي ووجد بان قيمته تراوحت بين−0.51 و+4.15 والتي تعبر عن الدقة العالية وكذلك حسب الانحراف القياسي النسبي والذي يعبر عن توافقية الطريقة ومن خلال النتائج التي تم الحصول عليها والتي تراوحت بين 0.78± و% 1.28± . وامكن تقدير الانلين بمدى التركيز من 2.5 الى50 مايكروغرام.مل $^{-1}$ ..وتضمن العمل الحالي ايضا دراسة تأثير بعض من المركبات العضوية في استعادة الانلين وذلك بإضافة تراكيز كبيره من المتداخل الى نماذج المياه فيد الدراسة. الانلين يعد ابسط نوع من الامينات الاروماتية الاولية اذ يدخل في مجالات صناعية عديده ويعتبر من المواد المهمة .الانلين يعتبر من الملوثات الرئيسية للمياه . الطريقة طبقت في تقدير الانلين في نماذج مختلفة من المياه وتضمنت مياه النهر والأسالة وبئر زمزم

**الكلمات الدالة:** الانلين وكاشف الاسيتيل اسيتون –فورمالديهايد والتقدير والمياه

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## Introduction

Aniline is an organic compound that has the formula $C_6H_5NH_2$. It consists of amino group which attached to one position of a phenyl group , it is the typical simple aromatic amine. The main uses of aniline are in the manufacture of precursors to polyurethane and other industrial chemicals. Like most volatile amines, aniline has the odor of rotten fish[1]. Aniline is used to produce an important chemical compounds that are used in manufacturing of rubber, it is also used in the preparation of phenylene diamine and diphenylamine, which are the most additives to rubber. Aniline is an important chemical substance used in manufacture the herbicides and fungicides that are used in extermination weeds and organisms having a destructive action to plants. Aniline and its derivative are essential in the formation of various dyes after diazotisation and coupling with other compounds such as phenol , derivative of phenol or activated carbon[2-5].In the late 19th century, acetanilide and phenacetin(is a pain-relieving and fever-reducing drug) which are the more important derivatives of aniline emerged in manufacturing of pharmaceutical preparations as analgesic drugs, with their cardiac-suppressive side effects often countered or emitted by using caffeine[6]. Aniline and other amines may exist in the environment as an outcome of manufacturing discharge from various factories that use anilines as intermediates or as a product of the degradation of some herbicides. Several aromatic amines compounds are identified to be toxic and are suspected to be one of the causes of cancer[7] especially for the workers who are in contact with these compounds. Therefore these workers and also who work with pigment should be cautious.

Many techniques or methods have been used in determination of aniline in various samples. These methods include solid phase analytical derivatization –GC [8],liquid phase microextraction-GC[9], liquid- liquid - liquid -microextraction-HPLC[10-11],solid phase extraction-HPLC[12],UHPLC[13],and capillary electrophoresis[14,15]. Most spectrophotometric methods include either diazotization of amino group and coupling with a specific reagent such as :2,6 –dihydroxybenzoic acid[5] or 2-methyl-8-hydroxyquinoline[16] , they may also include oxidative coupling reaction with other reagents such as p-N,N-dimethylphenylenediamine in presence of sodium meta periodate as oxidizing agent [17],quaiacol in presence of *N*-chlorosuccinimide [18] and promethazine in presence of hypochlorite ion [19] .Charge transfer reaction is also used in the determination of aniline using 7,7′,8,8′ tetracyanoquinodimethane[20,21].

The literary survey shows that significant uses of the acetyl acetone – formaldehyde reagent were observed in the estimation of many primary amines containing drugs such as: pramipexole di-hydrochloride[22], some cephalosporins[23], mono sopropylamine[24], Baclofen[25], midodrine hydrochloride[26] and some sulpha drugs[27].

Aniline and derivatives are considered as major pollutant of water, thus, the proposed method has been applied in estimation of aniline in different samples of water such as river tap and Zamzam well waters.

## Experimental

### Apparatus

The absorbance measurements have been done by JASCOV - 630 UV / Vis spectrophotometer (Japan), with 1cm matched glass cells. pH measurements have been done by using HANNA 211 pH-meter.

### Materials and solutions

All materials used in this work are of analytical grade except for aniline and acetyl acetone which need purification via distillation .

**Aniline solution,250 µg.ml$^{-1}$**. After the purification of aniline by distillation, 10000 µg.ml$^{-1}$ aniline solution has been prepared by diluting 0.99 ml of aniline to 100 ml in a volumetric flask using distilled water(in presence of 5 ml ethanol), then 2.5 ml of above solution diluted to the mark of a 100 ml volumetric flask to prepare 250 µg.ml$^{-1}$.

**Acetylacetone-formaldehyde reagent.** The preparation was comprised of mixing 3.9 ml of freshly distilled acetyl acetone with 7.5 ml of formaldehyde (36%). After that 8 ml of 0.2 M sodium acetate and 17 ml of 0.2 M acetic acid were added. The resulting mixture was kept in a boiling water-bath for 5 minutes. The solution was left in room temperature for cooling and then the pH had been adjusted at 4.3 by adding diluted sodium hydroxide. Finally the volume was diluted to 100 ml in a volumetric flask by adding distilled water .The AC-FA reagent was prepared daily[27].

### Samples of Waters

Different kinds of water are used in this study. They are Zamzam well water (a well in Kingdom of Saudi Arabia), river water from Tiger (a river in Mosul-Iraq) and tap water from the laboratory of chemistry in Mosul University (in Mosul –Iraq).

### General procedure and calibration graph

The effect of the aniline concentration has been studied by transferring a liquid of aniline solution (250 µg.ml$^{-1}$) into a 20 ml volumetric flasks to covered the concentration from 2.5 to 50 µg.ml$^{-1}$,and then 4 ml of AC-FA reagent had been added, the mixture was left for 25 minute in water-bath at 40°C. After that the volumes were completed to the mark with distilled water, the absorbance was read at 417 nm against the reagent blank. Beer's law has been applied from 2.5 to 50 µg aniline / ml (Fig. 1).The molar absorptivity has been found to be $3.864\times10^3$ l.mol$^{-1}$.cm$^{-1}$.

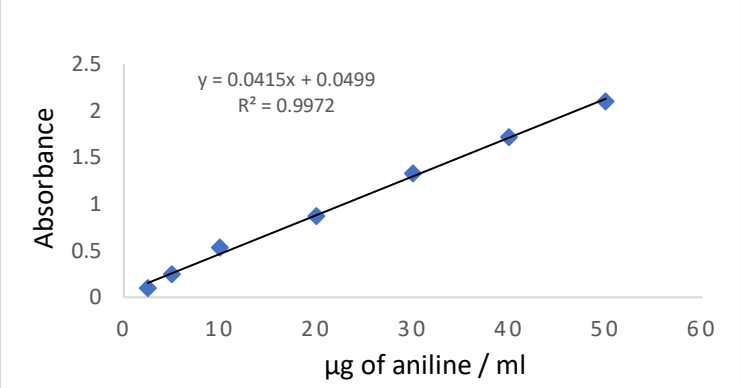



**Fig. 1. Calibration Graph of Aniline Determination.**

Some of the important analytical parameters of the present method have been illustrated in Table 1.

**Table 1. Analytical Parameters of The Method .**

| | |
|---|---|
| $\lambda_{max}$ , nm | 417 |
| Reagent used | Acetyl acetone - formaldehyde |
| Beer's law, µg. $ml^{-1}$ | 2.5-50 |
| Molar absorptivity factor, l. $mol.^{-1}$ $cm^{-1}$ | $3.864\times10^{3}$ |
| Temperature ,˚C | 40 |
| Regression equation | y = 0.0415x + 0.0499 |
| Slop | 0.0415 |
| Intercept | 0.0499 |
| X | Concentration in µg. $ml^{-1}$ |
| Relative error ,RE% | -0.51 to +4.15% |
| Relative standard deviation, RSD% | ±0.78 to ± 1.28 |
| Color of product | Yellow |
| Stability, minutes | 60 |

## Result and Discussion

All the parameters that affected the intensity of the yellow products have been tested and the optimum state of each parameter has been selected, these parameters included: the optimum pH of acetyl acetone – formaldehyde reagent .Three pH (2, 4.3 and 6)of the final solutions of AC-FA reagent have been tested in the estimation of 400 µg of aniline in 20 ml total volume. The results indicated that pH=4.3 was optimum pH which has been selected.

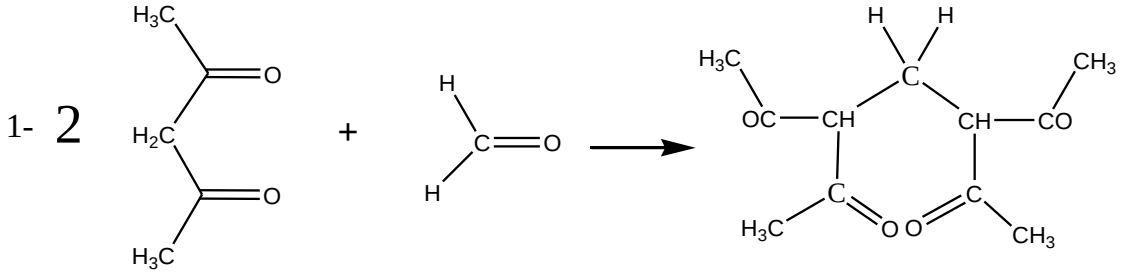
The quantity of AC-FA reagent has been also studied in this work. The results of the experiments indicated that the little amount of AC-FA reagent(2 or 3 ml) gave turbid solutions .An increase in the absorbance of the colored product was observed with increasing in the amount of the reagent. The results indicated that the volume of 4 ml is the optimum volume and was fixed in the subsequent experiments. The effect of the surfactant has been studied by adding 3 ml of various

type including positive ,negative and neutral types named CPS ,SDS and triton FX-100 respectively. There is no improvement in absorbance by adding these types. Therefore they have been canceled in the next experiments. An analytically important factor is the stability of the product (meaning the absorbance remains constant over time). The results in table 2 indicated that the yellow products produced from reaction of 10 and 20 µg.ml$^{-1}$ of aniline with AC-FA reagent in a final volume of 20 ml have good stability for at least 1 hour

**Table 2:The stability of the product.**

| µg.ml$^{-1}$ | A/ Time , minute | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | After dilution | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 10 | 0.511 | 0.514 | 0.513 | 0.515 | 0.508 | 0.504 | 0.501 | 0.499 |
| 20 | 0.868 | 0.867 | 0.865 | 0.887 | 0.884 | 0.874 | 0.872 | 0.871 |

The diagram below shows the important reaction steps: The first step is the conformation of the AC-FA reagent and the second step is the link between the reagent component of AC-FA with aniline. The closure of the ring is produced to form a heterogeneous ring, nitrogen of aniline one of the ring's atoms[27] .




Acetylacetone Formaldehyde Acetyl acetone-Formaldehyde

## Estimation of Absorption Maximum

AC-FA reagent was reacted with aniline to produce a yellow product. The absorption spectra in Fig. 2 shows that maximum absorption wavelength for AC-FA- aniline yellow product that was recognized to be 417 nm.

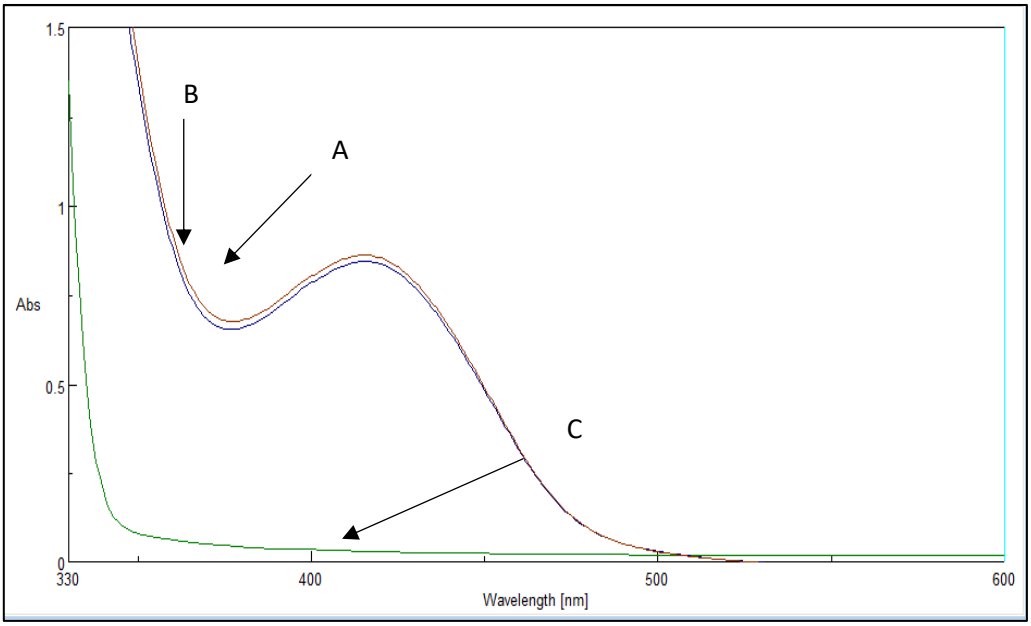



**Fig.2.Absorption spectrum of: A-The AC-FA- aniline against blank ,B- AC-FA- aniline against distilled water. C- Blank against distilled water**

## Interferences

The effect of various compounds on the estimation of 40 µg.ml$^{-1}$ aniline by using AC-FA reagent has been studied. The results were shown in table 3.

**Table 3: The Effect of Interferences.**

| Compound | Recovery of 400 µg aniline / µg amino compound in 20 ml | |
|---|---|---|
| | 500 | 1000 |
| Atenolol | 103.13 | 99.18 |
| 3-amino pyridine | 111.36 | 121.06 |
| Isoniazid | 104.63 | 105.01 |
| Histidine | 113.70 | 124.61 |
| Nitrobenzol | 104.63 | 105.58 |
| Resorcinol | 100.68 | 100.54 |
| 4-Picoline | 102.86 | 105.17 |
| Tri- methylamine | 103.72 | 104.83 |
| Di-secondarybutylamine | 102.11 | 103.85 |
| Sodium nitrite | 51.36 | 25.34 |

The results illustrated in table 3 indicated that only 3-amino pyridine and histidine interfered in the determination of aniline by using AC-FA reagent according they are considered as primary amines. The results also show that the addition of sodium nitrite reduced the recovery of aniline which is due to the diazotisation of the amine group.

## The Application of The Method

The suggested procedure has been applied in the determination of aniline in various samples of water by adding two amount of aniline 400 and 800 µg in 20 ml (20 and 40 $\mu g.ml^{-1}$) to 5 ml of waters sample (tap, well and river waters).The results illustrated in table 4 included satisfactory recovery. This demonstrates the possibility of spectrophotometric estimation of aniline using AC-FA reagent without interference of the studied water components.

**Table 4: The Estimation of Aniline in Waters Samples.**

| Water sample | 400 µg in 20 ml | | 800 µg in 20 ml | |
|---|---|---|---|---|
| | Recovery*% | RSD % | Recovery*% | RSD % |
| Tap | 99.68 | ±0.75 | 100.51 | ±0.16 |
| River | 100.34 | ±0.78 | 96.64 | ±0.88 |
| Well | 97.63 | ±1.28 | 95.85 | ±0.51 |

***Average of five determinations.**

## The Comparison of The Methods

Table 5 shows the comparison between some of analytical parameters obtained from the suggested method with those of other available spectrophotometric methods.

**Table 5: The Comparison of The Methods**

| Analytical parameter | Present method | Method in Ref.(21) | Method in Ref.(5) |
|---|---|---|---|
| Reagent | Acetylacetone-formaldehyde | 7,7′,8,8′-Tetracyano-quinodimethane | 2,6-Dihydroxy-benzoic acid |
| $\lambda_{max}$ , nm | 417 | 323 | 432 |
| pH | 4.3 | 6.02 | 10.36 |
| Linearity | 2.5-50 | 0.5- 2.5 | 0.2 -3.2 |
| Temperature | 40°C | R.T | R.T |
| Molar absorpitivity $L.mol.^{-1} cm.^{-1}$ | $3.864\times10^3$ | $1.72\times10^4$ | $4.2\times10^4$ |
| RE% | - 4.16 | +1.7 | +1.13 to +4.4 |
| RSD% | < ±1.29 | < ±3.69 | < ±0.77 |
| Application | Water samples | ……. | Water samples |

The results illustrated in Table 5 show that the present method has good sensitivity, but the diasotisation and charge transfer methods are more sensitive.

## Conclusion

A direct and simple spectrophotometric method for the estimation of aniline in various water samples was done .The method doesn't need any step of separation of aniline from its water samples . The method can be considered a sensitive method depending on the good molar absorpitivity value.

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