

Statistical Treatments and Comparison between Normal Calibration and Ultimate Precision Methods in Spectrophotometric Determination of Aspirin in APC Tablets

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الخلاصة

تم في هذا البحث إجراء مقارنة إحصائية بين تقنيتين، الأولى طريقة المعايرة القياسية و الثانية طريقة الدقة الفائقة لتعيين الأسبرين بالطريقة الطيفية. حيث تعتمد الطريقة الثانية على تكبير منطقة محددة من منحنى المعايرة و قياس العينة في هذه المنطقة للحصول على دقة أعلى. حيث وجد إن الخطأ النسبي قل من 6% إلى 2% باستعمال طريقة الدقة الفائقة عند قياس عينة محضرة و معروفة التركيز. كذلك كان مقدار الانحراف القياسي النسبي 0.86% و 0.54% لطريقة المعايرة القياسية و الدقة المتناهية، على التوالي. كذلك تم حساب حد الثقة بنسبة 95 % للطريقتين. كذلك تم اشتقاق معادلة لحساب تركيز العينة بطريقة الدقة الفائقة من خلال القيم المستحصلة من المنحنى القياسي و منحنى الدقة الفائقة حيث إن هذه المعادلة يمكن استعمالها بصورة عامة لتطبيقات طيفية أخرى.

ABSTRACT

In this work a statistical comparison were carried out between two techniques, normal calibration (NC) and ultimate precision (UP) technique, for the spectrophotometric determination of Aspirin (acetyl salicylic acid) in APC tablets, where the second method provide a means of expanding the scale of readout limited instrument and decreasing error significantly. It was found that the relative error was decreased from 6% to 2% on using the UP technique with RSD of 0.86% and 0.54% for NC and UP technique, respectively, Where these data were calculated for synthetic sample with known concentration. The 95 % confidence limit was also calculated for NC and UP methods.

An equation was also derived for direct calculation of concentration of unknown from UP technique. Where this equation could be applied for most spectrophotometric determination of sample by UP procedure.

INTRODUCTION:

In the normal practice of spectrophotometry, errors become quit large at both extremes of the absorbance scale. As means of alleviating this situation, the technique of precision spectrophotometry is frequently employed^(1,2).

The accuracy of many photometers and spetrophotometers is limited by the sensitivities of there readout devices⁽³⁾. Differential method provides a means of expanding the scale of readout-limited instrument and thus decreasing this type of error significantly⁽⁴⁾. These methods employ standard solutions of the analyte to adjust the zero and the 100% transmittance (T) setting with a standard solution somewhat more concentrated than the unknown, and the 100% T is set using a standard solution somewhat less concentrated than the unknown.

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The method of ultimate precision could be presented in Fig (1).

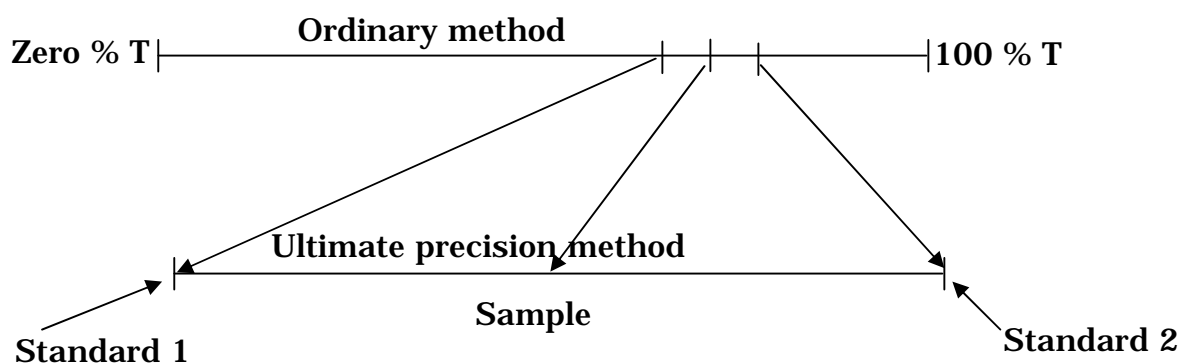


FIG 1 . EXAMPLE OF ULTIMATE PRECISION SPECTROPHOTOMETRY

APC tablets are a mixture of Aspirin, Phenacetin, and Caffeine in an inert binder⁽⁵⁾. The sample is partitioned between chloroform and 4% aqueous sodium bicarbonate with the Aspirin going only to the aqueous layer. The Aspirin solution is acidified, extracted back into chloroform, and determined spectrophotometrically⁽⁵⁾.

EXPERIMENTAL:

Instruments:

Shimadzu UV-Visible recording spectrophotometer, Type UV-160A

Reagents:

APC tablets or Anacin, were obtained from SDI and ASIA (Jordanian Drug Company). The chemicals used in this work were of analytical reagent grade. Doubly distilled deionized water were used for the preparation of standard and sample solutions.

Extraction of Aspirin from APC tablets⁽⁵⁾:

3 APC tablets were crushed to a fine powder in a 250ml beaker contained 100ml of chloroform, the chloroform solution were extracted in 250ml separatory funnel with three 30ml portion of chilled 4% sodium bicarbonate solution then with 20ml portion of water. The combined aqueous extract portions were washed with three 20ml portions of chloroform. The bicarbonate solution was acidified with few drops of 1 M H₂SO₄. The acidified solution was extracted with six 40ml portions of chloroform. The chloroform extracts were filtered through chloroform wetted filter paper into 500ml volumetric flask which were diluted to the mark with chloroform, then 10ml portion were pipet into 100ml volumetric flask and diluted to the mark with chloroform.

Aspirin stock solution (50µg/ml):

12.5mg of acetyl salicylic acid (Aspirin) ASA were dissolved in 150ml of chloroform in 250ml volumetric flask and diluted to the mark with chloroform.

Standard Calibration Curve:

5, 10, 15, 20, 30, and 40ml of the 50µg/ml solution were pipeted in 50ml volumetric flasks and diluted to the mark with chloroform. The absorbance of each standard solution was recorded using chloroform as blank. The synthetic samples were prepared by the subsequent dilution of the stock solution.

Ultimate precision method:

After determining the concentration of unknown sample from the calibration curve, the next lower concentration of standard was used to set the 100% T and the next higher concentration of standard was used to set the zero% T.

RESULTS AND DISCUSSION:

Aspirin absorb in the ultraviolet with principle absorption maxima at 277nm as shown in Figure (2). The absorbance of Aspirin is directly related to its concentration and that can be used for its spectrophotometric determination.

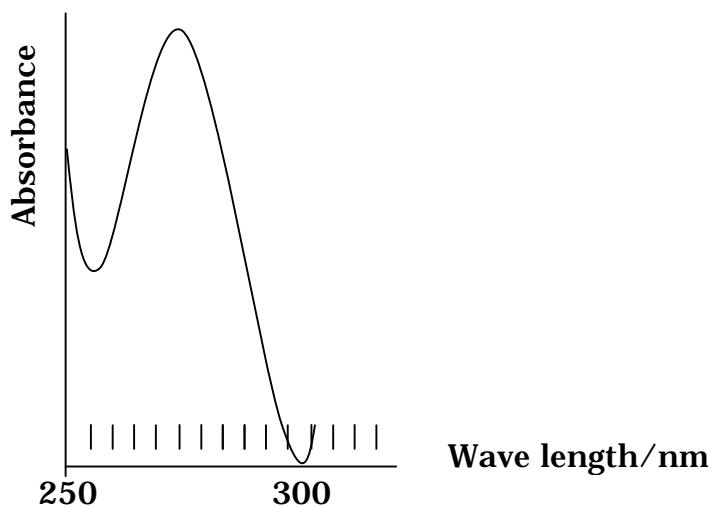


Figure 2 . Absorption spectra of the aqueous solution of 10⁻⁴ M acetylsalicylic acid

The calibration curve:

Linear calibration graph were obtained over the concentration range 5 to 30 μ g/ml for Aspirin (figure (3)). The correlation coefficient of the line was 0.9995 with a limit of detection of 4 μ g/ml.

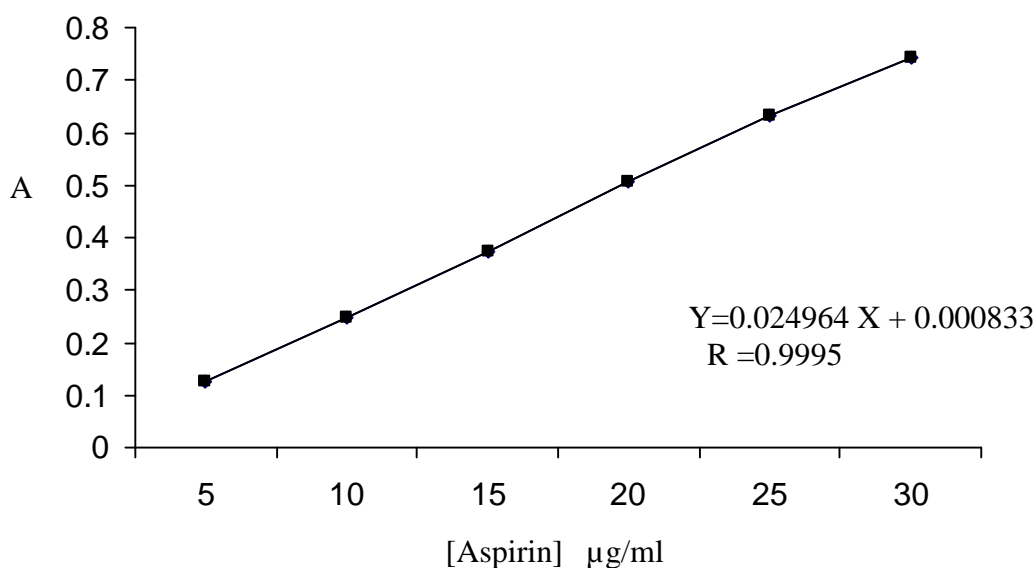


FIG 3 . CALIBRATION GRAPH OF ASPIRIN

The concentration of Aspirin in APC tablets and in four synthetic samples were determined on the linear calibration graph, and they were 14.12, 13.05, 24.05, and 31.94 $\mu\text{g/ml}$, respectively. Two standards were selected that bracket each sample concentration (for example, 10 and 15 $\mu\text{g/ml}$ for the determination of Aspirin in APC tablets); these two standards will be used for the ultimate precision curve. The following figure shows the ultimate precision curve for the precise determination of Aspirin in APC tablets and synthetic sample of concentration of 13 $\mu\text{g/ml}$:

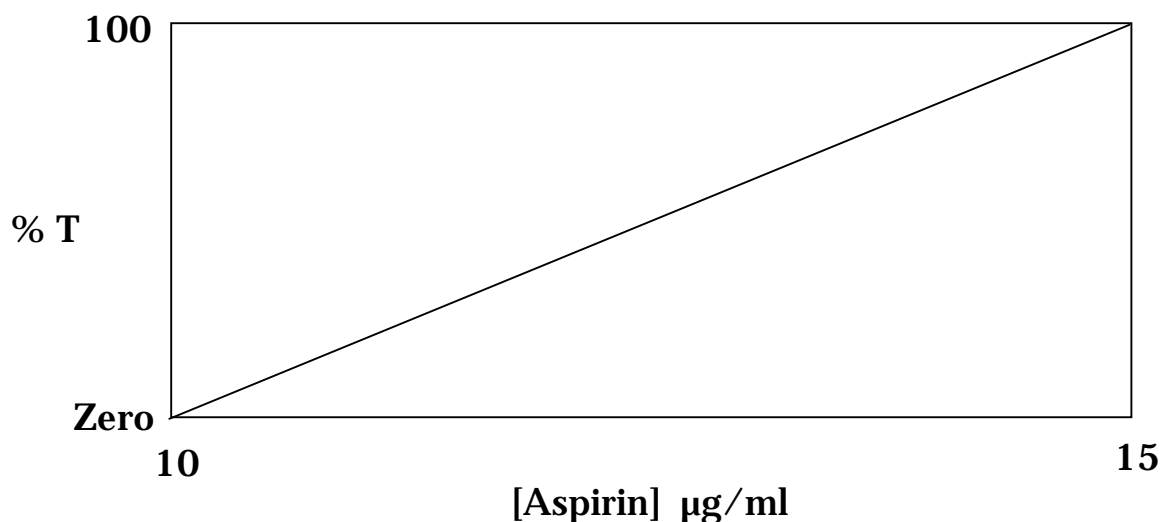


FIG 4 . CALIBRATION GRAPH OF ULTIMATE PRECISION METHOD FOR THE DETERMINATION OF ASPIRIN

The following tables show the results obtained in the determination of three synthetic samples and the unknown sample by the calibration and ultimate precision methods.

Table 1 . The determination of Aspirin in known and unknown samples by calibration and ultimate precision methods.

Aspirin Sample	Conc. $\mu\text{g/ml}$	Spectrophotometric method							
		Calibration				Ultimate precision			
		Conc*. $\mu\text{g/ml}$	% RE	% RSD	95% Confidence limit	Conc*. $\mu\text{g/ml}$	% RE	% RSD	95% Confidence limit
Synthetic	13.00	12.597	3.1	0.86	12.59 \pm 0.134	12.93	0.57	0.49	12.93 \pm 0.078
	24.00	23.33	2.78	0.54	23.33 \pm 0.156	23.86	0.6	0.38	23.86 \pm 0.113
	32.00	30.848	3.6	0.76	30.85 \pm 0.291	31.86	0.45	0.4	31.86 \pm 0.158
APC tablet	—	14.12	—	0.58	14.12 \pm 0.102	14.1	—	0.31	14.1 \pm 0.054

*Each value is the mean of five measurements where RE is the Relative Standard Deviation and RE is the Relative Error

The above data give good indication that the method of UP give less %RE with respect to the synthetic known samples 0.57%, 0.6%, and 0.45% compared to that of NC, 3.1, 2.78, and 3.6%. Also a better value for the %RSD was obtained with UP method which could be supported by the value of 95 % confidence limit.

For the calculation of sample concentration by the UP method an equation has been derived that could be applied to calculate the concentration by this method. If the absorbance of unknown sample is A_X , and the absorbance of standard solution that was less than the concentration of sample is A_{S1} , and the absorbance of standard solution that was more than the concentration of sample is A_{S2} , and the % transmittance of unknown on the UP curve is T_X , then the precise absorbance of sample will be A_{XP} .

$$A_{XP} = A_{S1} + (A_{S2} - A_{S1}) \times T_X$$

when this equation was applied for the Aspirin sample the parameters were as follow:

$A_{S1} = 0.250$ for $10\mu\text{g/ml}$

$A_{S2} = 0.375$ for $10\mu\text{g/ml}$

$\%T_X = 82.24\%$ for the unknown sample on the UP graph

$A_{XP} = 0.352$

When this value was applied in the line equation it gave a conc. of $14.09\mu\text{g/ml}$ for the unknown sample. And the same value for the synthetic known sample.

CONCLUSIONS:

It is clear from the above data that the method of ultimate precision gives very good indication about the precise concentration of substance in samples, which could be seen from the values of %RSD, %RE, and the 95% confidence limit. Also the method of ultimate precision is easy to apply for any spectrophotometric method.

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