# Kinetic Technique as an Analytical Tool in Determining Salicylic Acid in Commercial Aspirin Brands in Nigerian Market.

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## ABSTRACT

The salicylic acid content of three common brands of aspirin tablets in Nigerian markets was determined by a kinetic method. The kinetic approach of determination was compared with the more conventional titrimetric method, and the result showed that there was no significant difference between the two methods. By applying Pearson's correlations, the coefficient between the two methods was found to be 1.0. This implied that there was a perfect relationship between the two techniques. Furthermore, it is an indication that the kinetic method is as good as the conventional method and can therefore be adapted as an analytical tool; only that it has the advantage of being simple, cost effective and requires no laboratory settings.

(Keywords: aspirin, bromination, kinetic, titrimetric, laboratory)

## INTRODUCTION

Phenols and its derivatives are often estimated by bromination of their dilute aqueous solutions (Vogel, 1989; Burgess and Latham, 1966). The commonest method of determining phenols is to add an excess of standard solution of bromate and bromide to an acidified solution of the phenol or its derivative. After the complete bromination of the phenolic substance, an excess of standard iodide solution is added to generate iodine which can then be back-titrated with standard thiosulphate solution. There are other methods of determining phenolic compounds, some which are mentioned below.

Electrochemical methods (Peng, *et al.*, 2008; Latha, *et al.*, 2010; Kozak and Fernando,1962), high performance liquid chromatography methods (Bruni, 2007; Furusawa, 2001), electrophoresis (Peng, *et al.*, 2008; Versasari, *et al.*, 2004), gas chromatographic methods,(Silva, 2005), colorimetric methods (Roura, *et al.*, 2006; George *et al.*, 2005), ultraviolet spectrometry (Kitamura, *et al.*, 1984) as well as mass-spectrometric methods (Garrido-Frenich, *et al.*, 2005), and several host of others (Lee, *et al.*, 2001; Mattila, *et al.*, 2001; Gill, *et al.*, 2000; Cano, *et al.*, 1998 ) have also been used, especially to determine phenols in micro amounts.

This study shows that phenolic compounds can be estimated bromometrically in dilute aqueous solution without the necessity of the laborious titrations or the use of any expensive laboratory apparatus usually used in conventional methods. This method can be put to effective use in an economy like Nigeria where NAFDAC is trying its best to monitor the quality of chemicals and drugs imported into the country and, where standard laboratories are lacking, especially in rural areas, where substandard products are usually sold unmonitored. The simple colorimetric technique can be used in such areas for testing the quality of drugs such as aspirins, ascorbic acids, and other chemicals like disinfectants and mouth-washes that contain phenolic groups.

The theoretical basis of the method used in this study is that, when an acidified mixture of bromate and bromide ions are mixed with phenol or its derivative, a stationary –state concentration of bromine is generated in accordance with the reactions below in Equations 1 and 2; and this is

maintained until all the phenols are monobrominated (Burgess and Latham, 1966):

$KBrO_3 + HBr \rightarrow Br_2 +$ other by-products **(1)**

$Br_2 + C_6H_5OH \rightarrow C_6H_4BrOH + HBr$ **(2)**

## EXPERIMENTAL METHOD

### Sample Collections

Three brands of aspirin tablets from different manufacturers, coded EZ, MC, and JH Aspirins, were purchased from Farmeks Medicine Store in Samaru, Zaria and were used without further purification.

## REAGENTS

### Preparation of $H_2SO_4$ - Methyl Orange Solution

2.0 $cm^3$ of 98% $H_2SO_4$ was dissolved in 250 volumetric flask $cm^3$ containing about 150.0 $cm^3$ of distilled water and 2.5 mg of methyl orange. After stirring, more distilled water was added and the volume made up to the mark. The solution was then standardized using a standard solution of sodium carbonate.

### Preparation of 0.2 $Moldm^{-3}$ KBr Stock Solution

Potassium bromide, analytical grade, was dried in an oven at 80°C and cooled in a desiccator until constant weight was obtained. 6.0 g of the bromide was weighed and dissolved in 250.0 $cm^3$ of distilled water.

### Preparation of 0.2 $moldm^{-3}$ $KBrO_3$ stock solution

Potassium bromate was dried in an oven at 80°C and cooled inside a desiccator until a constant weight was obtained. 20.0 g of the $KBrO_3$ was weighed and then dissolved in 250.0 $cm^3$ of distilled water.

### Preparation of Standard Solution of Salicylic Acid (0.044 $Moldm^{-3}$)

A saturated solution of analytical grade of salicylic acid (May & Baker) was made and then filtered. The filtrate was standardized against a standard solution of sodium carbonate.

### Preparation of Standard Solution of Sodium Carbonate

Anhydrous sodium carbonate (analytical grade) was dried for 30 minutes at 80°C in an oven. 13. 0 g of the sodium carbonate was weighed and dissolved in 250.0 $cm^3$ of distilled water.

### Preparation of assay solutions

The average weight of five tablets determined, and the tablets were ground to a fine powder by a mortar and a pestle. A portion of the powder equivalent to 500mg of aspirin, the amount stated on the label by the manufacturers, was weighed accurately and transferred into a 100 $cm^3$ volumetric flask. Distilled water was added to the mark and the mixture was shaken vigorously until a homogeneous solution was obtained. The solutions obtained were used as stock solution of the various brands of aspirins.

## PROCEDURE

12.5 $cm^3$ of sulphuric acid–methyl orange solution was placed in 12 different 25.0$cm^3$ calibrated flasks. To each of these flasks various concentrations (ranging from$1.0 \times 10^{-4} - 1.2 \times 10^{-3}$ $moldm^{-3}$) of the salicylic acid were transferred. Equimolar solutions of bromide–bromate were prepared from their stock solutions and kept. 10.0 $cm^3$ of the bromide–bromate prepared above was taken into clean test tube, and the content of this test tube was transferred to each of the flasks containing the sulphuric acid–methyl orange solution and salicylic acid mixtures, one at a time.

Each time before the transfer, a stop clock was started and uniformity of composition was ensured by transferring the resulting solution quickly from the flask to the test tube and back again twice. The time when the last tinge of red color of the methyl orange disappeared was recorded.

The experiment was repeated twice for each concentration of the salicylic acid, and the average of the time recorded in seconds.

Readings for blanks were also taken in duplicate, and the differences between the experimental values and the blanks recorded as shown in table 1. A calibration curve was then obtained by using GraphPad Prism 5.02 software to plot concentration versus time as shown in Figure 1. The actual concentration of salicylic acid content of the various aspirin tablets were obtained by extrapolation from the calibration curves of the standard salicylic acid.

The second part of the experiment involved a conventional titration of solutions of the various brands of aspirin tablets, and comparing the results from the kinetic method and that obtained by the conventional titrimetric method, as shown in Table 2.

## RESULTS

Results are shown in Table 1, Figure 1, and Table 2 below.

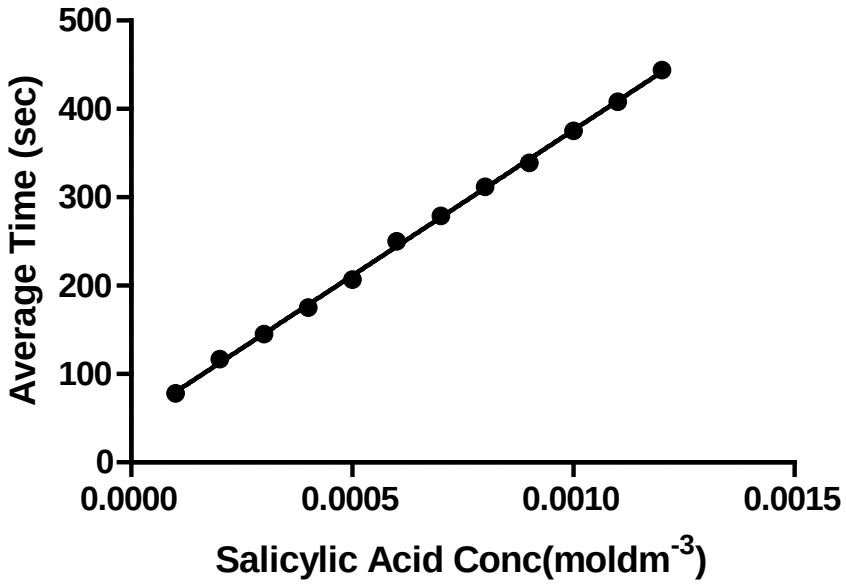


**Figure 1:** Calibration Curve of Average Time versus Concentration.

**Table 1:** Time Required for the Bromine to Consume the Salicylic Acid (SA).

| **[SA ] X $10^{-4}$ (moldm$^{-3}$)** | 1.0 | 2.0 | 3.0 | 4.0 | 5.0* | 6.0 | 7.0 | 8.0 | 9.0 | 10.0 | 11.0 | 12.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Ave. time (sec)** | 78 | 117 | 145 | 175 | 207 | 250 | 279 | 312 | 339 | 375 | 408 | 444 |

* = *Extrapolation time (sec) for* 5.0 X $10^{-4}$ MOLDM$^{-3}$ 0F THE VARIOUS ASPIRIN BRANDS
MC ASPIRIN = 198; EZ ASPIRIN = 201; JH ASPIRIN = 205

**Table 2:** Comparison of the Results Obtained using the Kinetic and Conventional Titrimetric Methods.

| Samples | Theoretical concentrations ($moldm^{-3}$) | Experimental concentrations ($moldm^{-3}$) | |
|---|---|---|---|
| | | Kinetic | Titrimetric |
| MC Aspirin | $5.0 \times 10^{-4}$<br>$8.0 \times 10^{-4}$ | $4.5 \times 10^{-4}$<br>$7.3 \times 10^{-4}$ | $4.4 \times 10^{-4}$<br>$7.2 \times 10^{-4}$ |
| EZ Aspirin | $5.0 \times 10^{-4}$<br>$8.0 \times 10^{-4}$ | $4.6 \times 10^{-4}$<br>$7.5 \times 10^{-4}$ | $4.6 \times 10^{-4}$<br>$7.4 \times 10^{-4}$ |
| JH Aspirin | $5.0 \times 10^{-4}$<br>$8.0 \times 10^{-4}$ | $4.8 \times 10^{-4}$<br>$7.8 \times 10^{-4}$ | $4.7 \times 10^{-4}$<br>$7.7 \times 10^{-4}$ |

## DISCUSSION

Figure 1 showed the calibration curve of the kinetic titration of the salicylic acid from which the average times for $5.0 \times 10^{-3}$ $moldm^{-3}$ of each of the various brands of aspirin were consumed. The standard deviation was found to be 1.5 seconds, meaning that the method is capable of giving an accuracy of ±2%.

Table 1 showed average time required for the bromine to consume the salicylic acid. As all the salicylic acids were consumed, the liberated $Br_2$ bleached the methyl orange to colourless, thus giving an indication of the time taken for the completion of bromination reaction. Whereas it took 207 sec. for $5.0 \times 10^{-4}$ of the pure salicylic acid to be bleached, it took 198 sec. for MC; 201 for EZ and 205 for JH brand of aspirins respectively for the same calculated concentration. It showed that the concentration of aspirin per tablet of the JH and EZ brands of aspirins were closer to the quoted claims of the manufacturers on their labels than that of the MC brand of aspirin.

Table 2 showed the comparison of the theoretically calculated and experimentally determined concentrations of the samples, MC, EZ and JH brands of aspirins determined using the kinetic and the conventional titrimetric methods respectively, at two different concentrations arbitrarily selected.

The results obtained using the 2 methods also showed that there is a good agreement between the two methods. Using statistical analysis, the correlation coefficient between the two methods was calculated using Pearson's correlations, and the result was found to be 1.0. This coefficient implied that there is perfect relationship between the two methods. Furthermore, it is an indication that the kinetic method is as good as the conventional titrimetric method, and can therefore be adapted as an analytical tool; only that it has the advantage of being simple, cost effective and requires no laboratory settings.

Table 2 also showed that, of the three brands of aspirin brands, sample JH aspirin has the highest amount of aspirin, followed by EZ aspirin, with MC brand having the least aspirin content.

## CONCLUSION

The result obtained using the kinetic method when compared with that of the conventional method, namely, titrimetry showed great concordance between the two methods. Correlation coefficient, r, obtained using Pearson's correlations was found to be 1.0, suggesting that a perfect positive relationship exists between the two methods. This therefore, showed that the kinetic method is a good analytical method as the conventional titrimetric method; and even more, as no sophisticated equipment are required, it is less expensive and can be used even outside a laboratory settings.

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## SUGGESTED CITATION

Shallangwa, G.A., A. Hamidu, Y.A. Dallatu, M. Haliru, F.G. Okibe, and N.C. Nwokem. 2012. “Kinetic Technique as an Analytical Tool in Determining Salicylic Acid in Commercial Aspirin Brands in Nigerian Market”. *Pacific Journal of Science and Technology*. 13(2):238-242.

Pacific Journal of Science and Technology