American Journal of Applied Chemistry
2016; 4(1): 91-96
http://www.sciencepublishinggroup.com/j/ajac
doi: 10.11648/j.ajac.20160403.14
ISSN: 2330-8753 (Print); ISSN: 2330-8745 (Online)

Research/Technical Note

Betacarotenes Dosage by Hydrofluoric Acid Solution and Validation of This New Process by SPC

Andry Tahina Rabeharitsara, Phandry Nomena Ndjiva Rabearimihaja

Department Genie Chimique of E.S.P.A, Polytechnic University of Antananarivo, Antananarivo, Madagascar

Email address:

rabeharitsara_andrytahina@yahoo.fr (A. T. Rabeharitsara), phandryrandjiva@gmail.com (P. N. N. Rabearimihaja)

To cite this article:

Andry Tahina Rabeharitsara, Phandry Nomena Ndjiva Rabearimihaja. Betacarotenes Dosage by Hydrofluoric Acid Solution and Validation of This New Process by SPC. *American Journal of Applied Chemistry*. Vol. 4, No. 3, 2016, pp. 91-96. doi: 10.11648/j.ajac.20160403.14

Received: April 11, 2016; **Accepted**: April 20, 2016; **Published**: May 13, 2016

Abstract: The betacarotenes rate in a V volume extracted on unrefined palm oil by acetic acid solvent was given by dosage with hydrofluoric acid. This dosage of betacarotenes by hydrofluoric acid was investigated like a process. We used Statistical Process Control SPC to exploit the dosage results in V volume and we noticed that these data follow a normal distribution. That is to say, the dosage is statistically in control and ready to give results which respect the quality six sigma. Moreover, the exploitation of the data enable us to deduce that during the dosage only nine double combined connections of each betacarotene molecule participate in the addition reactions with nine H^+/F^- molecules to form a fluorinated betacarotene molecule.

Keywords: Betacarotene, Dosage, Hydrofluoric acid, Statistical Process Control SPC, Quality Sigma, Process, Process Aptitude C_p, Ratio Aptitude C_{pk}

1. Introduction

Betacarotenes molecules have been widely used in food and pharmaceutical industries. They were seen in many natural products such as: palm grains, carrots, tomatoes, spinach, etc.… [1]. The aim of this study is to show a new chemical process for determining the betacarotenes rate in any organic products which contain its molecule. So, a dosage model with pure betacarotenes extracted on unrefined palm oil by acetic acid solvent [2] was investigated using hydrofluoric acid as titrating solution. The submission of the hydrofluoric moles data at the equivalence point on Statistical Process Control SPC [3] allow us to notice that first, these data follow a normal distribution consequently they are statistically in control. Then, data gathering shows that betacarotenes molecule dosage by hydrofluoric acid process is statistically apt to give results with quality six sigma, the process aptitude C_p is equal to 2.4 and the ratio aptitude C_{pk} is sensibly 2.4 too. This equality indicates that the middle value of the normal distribution data of hydrofluoric acid moles at the equivalence point which is 2.632×10^{-6} moles is the nearest of the nominal value which is betacarotene rate in the V volume. Finally, we dosed betacarotene rate in three organic compounds such as carrot, unrefined palm oil and kaki. The results was shown in table 7 and confirm that kaki contains betacarotenes molecules. Then, the betacarotenes rate in carrot and unrefined palm oil samples confirm not only the bibliography data but also the selectivity of this process to dose betacarotenes rate which is the most widespread form of carotenoids in organic products.

2. Dosage of Betacarotenes by Hydrofluoric Acid Process

2.1. Solutions Preparation

2.1.1. Preparation of the Hydrofluoric Acid Titrating Solution

We putted a drop of fluoric acid (40% of purity) in 1liter of distillated water. A drop of fluoric acid corresponds to 1/10 [ml] so the HF concentration [HF] was

$$C_{HF}= [HF] = \frac{n}{V} = \frac{m}{M.V} = \frac{\rho V_x}{M.V} = 2{,}610^{-3} \text{ [mole/l]}$$

Such as: $V_x=0.4\times \frac{1}{10x} = 0.4 \times \frac{1}{10}$ and x: one (1) drop number of fluoric acid 40%

M_{HF}=20 [g/mole] molecular weight of fluoric acid

V= 1[l] distillated water volume

ρ_{HF} =1.298 [g/cm^3] density of hydrofluoric acid

The pH of this fluoric acid solution is 2.58. This pH is less than pKa=3.2 [4] so there were H^+/F^- ions but the majority of the fluoric acid is non dissociated HF form [5].

2.1.2. Preparation of the Betacarotenes Solution to Be Titrated

We used the betacarotenes extracted on unrefined palm oil by acetic acid solvent [2]. To prepare the betacarotenes solution to be titrated, we took a beaker 250 [ml] and putted inside X [ml] of betacarotenes (by syringe) with 30 [ml] distillated water. Then, we added 5 drops of bromophenol blue. It's an indicator that the zone of turn is between 6.0 and 7.6 [6]. The color of the solution turn to blue.

2.2. Materials Used for Dosage and Procedure

2.2.1. Materials and Reagents

The materials used during the dosage of betacarotenes by hydrofluoric acid was:

- Oil-can 25 [ml]
- Syringe 5 [ml]
- Magnetic stirrer
- Beaker 250 [ml]
- Hydrofluoric Acid (40% of purity)
- Bromophenol blue (turn zone: 6.0-7.6)

2.2.2. Procedure

The fluoric acid solution (cf. §2.1.1) was introduced in 25 [ml] oil-can, the air bubble was driven out and zero was adjusted. Then, the solution to be titrated and 5 drops of bromophenol blue within the beaker was stirred on the magnetic stirrer. The dosage reaction is not other than addition reactions between the double combined connections of betacarotenes [2] and ions H^+/F^- (cf. §2.1.1). Start gradually the dosage. Once introduced into the basic solution of betacarotenes, the HF molecules was dissociated in H^+/F^- ions [4, 5]. The formation of fluorinated betacarotenes [Figure 1] started, then the dosage was stopped when the color of the solution turn to transparent yellow. That is to say, V [ml] of the titrating solution was been used for the dosage. We knew that betacarotenes molecules contain eleven (11) double combined connections. We compared the betacarotenes moles number to be titrated and the H^+/F^- (cf. §2.1.2) moles number used during the dosage; the one way to explain the equality of these numbers is that the totality of the double combined connections didn't take part in the addition reactions. The equality of these moles was checked for this dosage if and only if firstly, ortho and para methyl group inductions effects [7], secondly the electronegativity of the nearest fluor molecule of each benzene molecules, and finally obstructions steric occurred by methyl groups and the nearest fluor molecule [Figure 1] are considered during the addition reactions between H+/F- and the eleven (11) double combined connections [7-8]. Consequently, the two olefins which belong to cyclohexenes [Figure 1] don't participate in the addition reactions. In other words, only nine (9) double combined connections of each β-carotene molecule participate in the addition reactions with nine H^+/F^- molecules to form a fluorinated betacarotene molecule [Figure 1]. So,

$$n_{\text{betacarotène}} = \frac{n_{HF}}{9} = \frac{C_A V}{9}$$

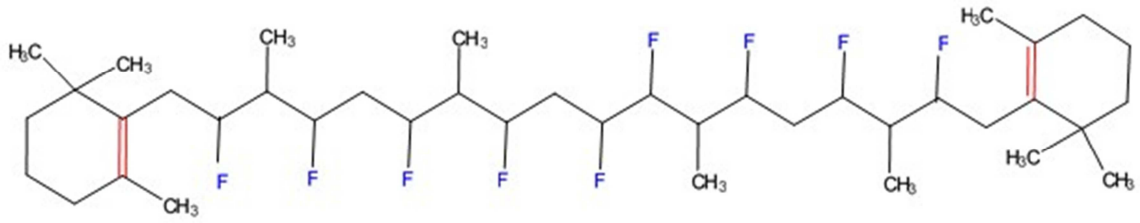

Figure 1. *Fluorinated betacarotene molecule.*

This explanation was also confirmed by the color of the solution to be titrated during the dosage which doesn't turn to bright yellow. This color stay transparent yellow because of the basicity of doublets electrons which belong to the olefins of cyclohexenes [Figure 1].

3. Results of Betacarotenes Dosage by Hydrofluoric Acid Process

Betacarotenes was extracted according to the process number 1 by acetic acid [2] and five sampling were carried out. We obtain the five extractions [column extraction in Table 1 volume V_i]. For each extraction we took volumes V and V_i such as i is a naturel number integer going from 2 to 4 which corresponds to a volume i times the volume V. For each volume V and V_i we had dosed the quantity of betacarotene following the procedure described previously (§2.2.2). We obtain observations in the table 1 corresponding to the volumes of hydrofluoric acid titrating solution observed at the equivalence point for volumes V and V_i.

Table 1. *Volumes of hydrofluoric acid titrating solution observed at the equivalence point for volumes V and V_i.*

SAMPLING [Extractioni]	Volumes of hydrofluoric acid titrating solution observed at the equivalence point for volumes V and V_i			
	V	V_2=2×V	V_3=3×V	V_4=4×V
Extraction 1	9	19	28	35
Extraction 2	8.5	18.5	26.5	38
Extraction 3	9.5	18	27	37
Extraction 4	8.8	19	27.15	36
Extraction 5	9.5	17.5	28.5	36.5

Bringing back to V all volumes of hydrofluoric acid titrating solution observed at the equivalence point by dividing all volumes V, V_2, V_3, V_4 respectively by the multiplier coefficients 1, 2, 3, 4. We obtain the table 2 corresponding to the volumes of hydrofluoric acid titrating solution at the equivalence point bringing back to V for volumes V and Vi.*ng solution at the equivalence point bringing back to V for volumes V and Vi*.

Table 2. *Volumes of hydrofluoric acid titrating solution at the equivalence point bringing back to V for volumes V and Vi.*

SAMPLING [Extractioni]	Volumes of hydrofluoric acid titrating solution at the equivalence point bringing back to V for volumes V and Vi			
	V	V2	V3	V4
Extraction 1	9.0	9.5	9.33	8.75
Extraction 2	8.5	9.25	8.83	9.5
Extraction 3	9.5	9.0	9.0	9.25
Extraction 4	8.8	9.5	9.05	9.0
Extraction 5	9.5	8.75	9.5	9.13

Moles of betacarotene at the equivalence point corresponding to the volumes of hydrofluoric acid titrating bringing back to V for volumes V and Vi were $\text{n betacarotène} = \frac{\text{n HF}}{9} = \frac{C_A V}{9}$ such as: C_A= 2.6×10-3 [mole/l] and V are volumes of hydrofluoric acid titrating solution at the equivalence point bringing back to V for volumes V and Vi. The table 3 corresponding to the moles of betacarotene at the equivalence point corresponding to the volumes of hydrofluoric acid titrating bringing back to V for volumes V and Vi is obtained.

Table 3. *Moles of betacarotene at the equivalence point corresponding to the volumes of hydrofluoric acid titrating bringing back to V for volumes V and Vi*

SAMPLING [Extractioni]	Moles of betacarotene at the equivalence point corresponding to the volumes of hydrofluoric acid titrating bringing back to V for volumes V and Vi			
	V	V2	V3	V4
Extraction 1	2.600	2.736	2.687	2.520
Extraction 2	2.448	2.664	2.543	2.736
Extraction 3	2.736	2.600	2.600	2.664
Extraction 4	2.534	2.736	2.606	2.600
Extraction 5	2.736	2.52	2.736	2.628

4. Statistical control and Aptitude of Betacarotenes Dosage by Hydrofluoric Acid Process

4.1. Statistical Process Control (SPC) Tools Used for Controlling the Dosage Process

Variation is present in any process, deciding when the variation is natural and when it needs correction is the key to quality control. Statistical Process Control is an analytical decision making tool which allows us to see when a process statistically in control is working correctly and when it is not. The foundation for Statistical Process Control was laid by Dr. Walter Shewart working in the Bell Telephone Laboratories in the 1920s conducting research on methods to improve quality and lower costs. He developed the concept of control with regard to variation, and came up with Statistical Process Control Charts which provide a simple way to determine if the process is in control or not [3]. For over 50 years clinical laboratories have embraced Shewhart's ideas and incorporated statistical process control into standard operating procedures for clinical laboratory quality control [9-10-11] and proficiency testing [12]. So, the statistical control of the processes is a tool for data analysis. It consists in applying statistical techniques to determine if the outgoing ones of a process are in conformity with their specifications. Statistical Process Control is an analytical decision making tool which allows you to see when a process is working correctly and when it is not. As regards Statistical Process Control, one exploits primarily diagrams and charts. There are two types of charts used on Statistical Process Control, once there are bell-curve like histogram or normal probability plot charts which confirm if the process is statistically in control or not and second there are control charts such as Range R –chart and x-bar graphics [3].

4.1.1. Bell-Curve: Normal Probability Plot and Histogram of Moles Hydrofluoric Acids Number Data at the Equivalence Point

For each sampling the moles number of hydrofluoric acids at the equivalence point are between the neighboring of the medium value (x-bar) minus standard deviation (δ) and the medium value plus standard deviation [Table 4]. That is to say, the dispersion of these moles are stable along the time. It confirm that betacarotenes dosage by hydrofluoric acid process is statistically in control.

Table 4. *Moles of betacarotene at the equivalence point corresponding to the volumes of hydrofluoric acid titrating bringing back to V for volumes V and Vi*

SAMPLING [Extractioni]	Moles of betacarotene at the equivalence point corresponding to the volumes of hydrofluoric acid titrating bringing back to V for volumes V and Vi							
	V	V2	V3	V4	$\bar{x}$	δ	$\bar{x} - \delta$	$\bar{x} + \delta$
Extraction 1	2.600	2.736	2.687	2.520	2.635	0.095	2.540	2.730
Extraction 2	2.448	2.664	2.543	2.736	2.597	0.128	2.469	2.725
Extraction 3	2.736	2.600	2.600	2.664	2.650	0.065	2.585	2.715
Extraction 4	2.534	2.736	2.606	2.600	2.619	0.085	2.534	2.704
Extraction 5	2.736	2.52	2.736	2.628	2.655	0.103	2.552	2.758

If we trace the figure of normal probability plot [figure 2] which is the z-value according to the sorted data, we obtain points which are roughly in a straight line. It indicates that the data of the moles number of hydrofluoric acids at the

equivalence point have a normal distribution [13], in other words they are statistically in control [3]. This affirmation is confirmed by the histogram of the data [figure 3] which is a bell-curve. We considered that the data 2.74 (quantity: 6 / total quantity: 20) are aberrant.

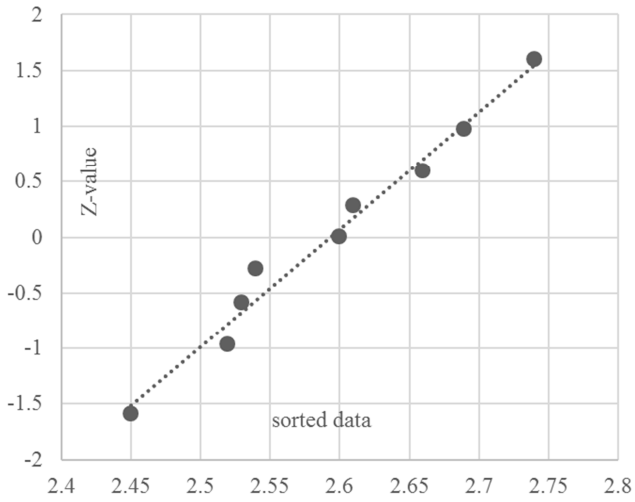

Figure 2. *Normal probability plot for moles of betacarotenes data at the equivalence point*

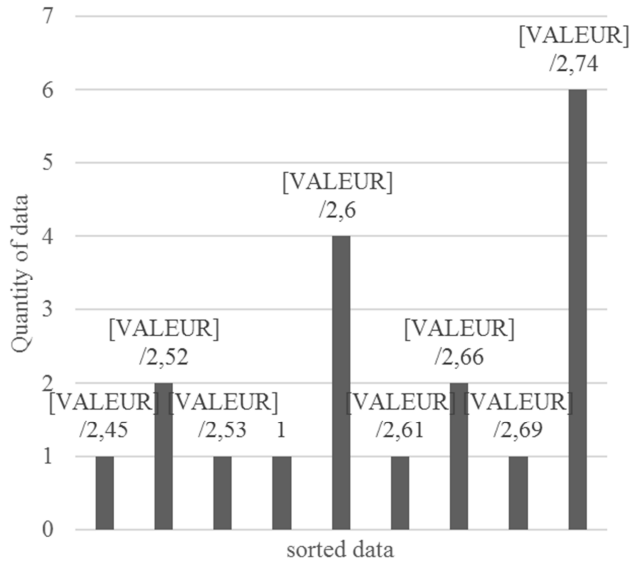

Figure 3. *Histogram for moles of betacarotenes data at the equivalence point.*

4.1.2. Control Charts of Moles Hydrofluoric Acids Number Data at the Equivalence Point

Control charts show the variation in a measurement during the time period that the betacarotenes dosage by hydrofluoric acid process was observed. Not only they confirm that the process is statistically in control but also they show its capabilities to give data inside the control limits of Range R-chart [figure 4] and X-bar chart [figure 5] [3] [14]. The R-value which is the difference between the maximum data and the minimum data and the X-bar value of each sampling are shown in the table 5 [Table 5].

Table 5. *R-values and X-bar values for moles of betacarotene data at the equivalence point corresponding to the volumes of hydrofluoric acid titrating bringing back to V for volumes V and Vi.*

SAMPLING [Extractioni]	**Moles of betacarotene at the equivalence point corresponding to the volumes of hydrofluoric acid titrating bringing back to V for volumes V and Vi**					
	V	**V2**	**V3**	**V4**	**R**	$\bar{x}$
Extraction 1	2.600	2.736	2.687	2.520	0.216	2.635
Extraction 2	2.448	2.664	2.543	2.736	0.288	2.597
Extraction 3	2.736	2.600	2.600	2.664	0.136	2.650
Extraction 4	2.534	2.736	2.606	2.600	0.202	2.619
Extraction 5	2.736	2.52	2.736	2.628	0.216	2.655

From this table we deduce the Lower Control Limit (LCL) and the Upper Control Limit (UPL) for R and X-bar values [14]. For every sampling both the R and X-bar points are in the limits zone [Figure 4 – Figure 5]. It means that betacarotenes dosage by hydrofluoric acid process occurs all of the time with stability and consistent (99.7%) [figure 4 – figure 5]. These normal fluctuations at the second and third sampling are attributed to statistical variability.

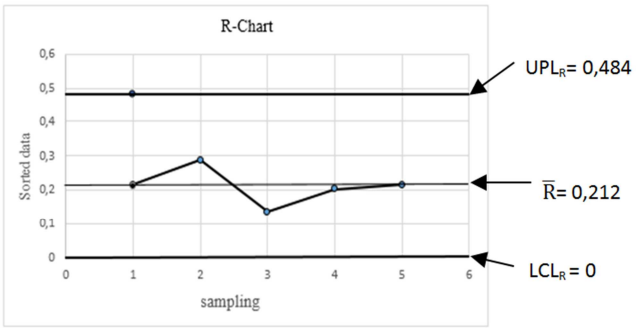

Figure 4. *Range R-Chart for the moles of betacarotene data at the equivalence point.*

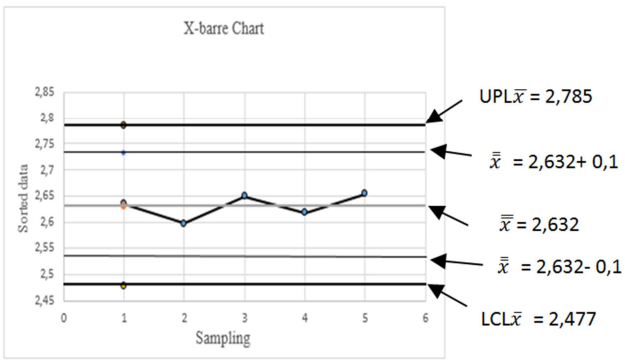

Figure 5. *X-bar Chart for the moles of betacarotene data at the equivalence point.*

4.2. Aptitude of Betacarotenes Dosage by Hydrofluoric Acid Process

The techniques of statistical control make it possible to maintain a distribution of the processes constant in terms of average and variance. The limits LCL-UPL of control of the diagrams announce any change [figure 4 – figure 5]. The aptitude of betacarotenes dosage by hydrofluoric acid process measures the degree of conformity of this one compared to the

specifications for a given service. The specifications are often expressed in target, supplied with a tolerance. In this case, we have taken first the LCL and UPL values to express the specifications and at the second we think that if we consider the tolerance of the oil-can 25 [ml] which is ± 0.1 [ml] the specifications may be the X-bar-bar value ± 0.1 [ml] [figure 5].

There are two indicators to measure the aptitude of a process. Initially, there is the aptitude ratio of the process Cp, then there is the index of aptitude of the process Cpk [14]. A process is suited to the production when, in its distribution, the extreme values remain inside the tolerances specified for the product or the service and the difference between the high tolerance and the tolerance low, called width of tolerance, must be higher than a standard deviation of 6.

4.2.1. Aptitude Ratio Cp of Betacarotenes Dosage by Hydrofluoric Acid Process

$$\mathrm{Cp} = \frac{High\ tolerance\ - Low\ tolerance}{6\sigma}$$

Such as σ the standard deviation of the normal distribution of betacarotenes dosage by hydrofluoric acid process is equal to 0.023.

We show in the following table [Table 6] the Cp results of betacarotenes dosage by hydrofluoric acid process according to the two cases of specifications. It indicate that this dosage process produce results with a quality six sigma. That is to say statistically the betacarotenes dosage by hydrofluoric acid process will produce only 0.002% defects results per million.

Table 6. *Cp and quality values of betacarotene dosage by hydrofluoric acid process according to the specifications.*

SPECIFICATIONS	HIGH TOLERANCE	LOW TOLERANCE	Cp	QUALITY
FIRST SPECIFICATION (LCL – UPL of X-barre)	2.785	2.477	2.232	SIX SIGMA
SECOND SPECIFICATION (oil-can tolerance with standard deviation)	2.778	2.474	2.203	SIX SIGMA

4.2.2. Aptitude index Cpk of Betacarotenes Dosage by Hydrofluoric Acid Process

$$\mathrm{C_{pk}}=\text{Minimum of }[\frac{\bar{\bar{x}}-\text{Low tolerance}}{3\sigma}, \frac{High\ tolerance - \bar{\bar{x}}}{3\sigma}]$$

We show in the following table [Table 7] the Cpk results of betacarotenes dosage by hydrofluoric acid process according the two cases of specifications. The Cpk value is more than 1.0 in all specifications. It confirm that betacarotenes dosage by hydrofluoric acid process is statistically apt to produce results with six sigma quality.

We notice also that the Cp and Cpk value are sensibly equal both in the first specification and the second specification, it indicates that the middle value of the normal distribution data of hydrofluoric acid moles at the equivalence point which is 2.632×10^{-6} moles is the nearest of the nominal value: betacarotene rate in the V volume [14].

Table 7. *Cpk values of betacarotenes dosage by hydrofluoric acid process according to the specifications.*

SPECIFICATIONS	HIGH TOLERANCE	LOW TOLERANCE	$\frac{\bar{\bar{x}} - \text{Low tolerance}}{3\sigma}$	$\frac{High\ tolerance\ - \bar{\bar{x}}}{3\sigma}$	Cpk
FIRST SPECIFICATION (LCL – UPL of X-barre)	2.785	2.477	2.246	2.217	2.217
SECOND SPECIFICATION (oil-can tolerance with standard deviation)	2.778	2.474	2.290	2.116	2.116

5. Dosage of Betacarotenes Rate in Carrot, Unrefined Palm Oil and Kaki by Hydrofluoric Acid

Betacarotene rate in carrot, unrefined palm oil and kaki was given by hydrofluoric acid dosage process. We show you in the following table 8 the quantity of betacarotene [µg] per 100 [g] of organic products such as carrot, unrefined palm oil and kaki.

Table 8. *Betacarotenes rate in organic products such as carrot, unrefined palm oil and kaki obtain by hydrofluoric acid dosage process.*

ORGANIC PRODUCTS	BETACAROTENE RATE BY HYDROFLUORIC ACID DOSAGE PROCESS (µg/100g)	BIBLIOGRAPHIC BETACAROTENE RATE (µg/100g)
CAROTT	10.861	11.210
UNREFINED PALM OIL	2.481.544,4	RICH ON BETACAROTENES
KAKI	217.135,14	–

Recent study shows that betacarotenes are able to improve health and its daily use with a certain dose can prevent a lot of illness [15].

6. Conclusion

This hydrofluoric acid titrating solution is apt to dose the rate of betacarotenes, which is the most widespread form of carotenoids, in all organic products. This dosage process is statistically in control and ready to give results which respect the quality six sigma.

Acknowledgements

Special Thanks to everyone who have supported and helped us to carry out this paper. As well, we express our sincere thanks to Director of E.S.P.A Polytechnics of the Antananarivo University and Chemical Engineering Laboratory staff. Special thanks to the company Savonnerie Tropical for giving us unrefined palm oil used during the experiences.

References

[1] "USDA National Nutrient Database for Standard Reference, Release 21". Retrieved 2009-07-24.

[2] Andry Tahina Rabeharitsara, Phandry Nomena Ndjiva Rabearimihaja. New Processes to Extract Pure Betacarotenes Molecules Using Acetic Acid Solvent. *American Journal of Applied Chemistry.* Vol. 4, *Issue 2*, April 2016, pp. 64-70.

[3] © 2007 Statit Software, Inc., 1128 NE 2nd St, Ste 108, Corvallis, Oregon 97330 Introduction to statistical process control techniques.

[4] Paul. ARNAUD, Cours de chimie organique, 15th éd., Eds. Dunod 199O.

[5] M. LAFFITTE, F. ROUQUEROL La réaction chimique Tome 2. Aspects thermodynamiques (suites) et cinétiques, 1991, Eds. Masson, Annexe 24 pp. 234-235.

[6] M. LAFFITTE, F. ROUQUEROL La réaction chimique Tome 2. Aspects thermodynamiques (suites) et cinétiques, 1991, Eds. Masson pp. 49-50.

[7] Paul. ARNAUD, Cours de chimie organique, 15th éd., Eds. Dunod 199O pp. 162.

[8] Paul. ARNAUD, Cours de chimie organique, 15th éd., Eds. Dunod 199O pp. 257.

[9] Levey S, Jennings E R. The use of control charts in the clinical laboratories. Am J Clin Pathol 1950201059–1066.1066 [PubMed].

[10] Henry R J, Segalove M. The running of standards in clinical chemistry and the use of the control chart. J Clin Pathol 19525305–311.311 [PMC free article] [PubMed].

[11] Westgard J O, Barry P L, Hunt M R. et al A multi‐rule Shewhart chart for quality control in clinical chemistry. Clin Chem 198127493–501.501 [PubMed].

[12] Carey N C, Cembrowski G S, Garber C C. et al Performance characteristics of several rules for self‐interpretation of proficiency testing data. Arch Pathol Lab Med 2005129997–1003.1003 [PubMed].

[13] Dr. Bill McNeese, Normal Probability Plots, June 2009, BPI Consulting, LLC.

[14] Larry Ritzmann, Lee Krajewski, Jacky Renart, Christopher, Management des opérations Principes et applications, 2013, 2ème Edition, Eds Nouveaux Horizon.

[15] The Mayo Clinic Diet “Eat well. Enjoy life. Lose weight.” Eds Rosetta books.