Measurement System Analysis for Ultraviolet and Visible Absorption Spectroscopy

by

Mr. Polsak Chettanacharoenchai

A Final Report of the Three-Credit Course
CE 6998 Project

Submitted in Partial Fulfillment
of the Requirements for the Degree of
Master of Science
in Computer and Engineering Management
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Project Title	Measurement System Analysis for Ultraviolet and Visible Absorption Spectroscopy
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Academic Year	November 2004

The Graduate School of Assumption University has approved this final report of the three-credit course, CE 6998 PROJECT, submitted in partial fulfillment of the requirements for the degree of Master of Science in Computer and Engineering Management.

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ABSTRACT

This project aims to study the measurement system analysis of Ultraviolet and Visible Absorption Spectroscopy by using Six Sigma methodologies.

UV/Visible is an instrument that is used to measure the percentage of solvent concentration in many ranges. In this project, we need to reduce the measurement error from this instrument so we will set the target of gage R&R less than 7% gage contribution.

The basic concept of UV/Visible instrument is that reviews let us know and understand about this instrument. After that, Six Sigma methodologies also reviewed and applied UV/Visible measurement analysis system such as DMAIC concept, Cause and effect of Fishbone diagram, and the basic concept of gage R&R capabilities.

After we review all the entire literature reviews and concepts, measurement system analysis is needed to prepare before studying. Four appraisers were selected to study the gage R&R of UV/Visible at range 0.5%-1.15%. The data table was designed and analyzes the results by using Minitab statistical software.

With Six Sigma methodologies, we can use this methodology to reduce the mistake in measurement system of Ultraviolet and Visible Absorption Spectroscopy machine. The gage R&R of this instrument is 0.1 gage contribution which is less than 7% with 99% confidence in November, 2004.

In the future, we can do further studies of this project by studying the process capability/performance which uses UV/Visible instrument. What should you do to reduce the sigma process after you are confident of the measurement system?

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I. INTRODUCTION

1.1 General Background of the Project

Quality assurance is one important strategy in business since it can make customers satisfied in their products, and services. Many tools are used to improve the quality system such as ISO, QSR (Quality System Review), SIX SIGMA, etc. To manage the quality system, we need to do "Management by Fact". It can be logical for any information that can make the decision. The good information should explain the cause of studying that processes and it should be precise and accurate too. To emphasize the importance of the data for quality management or process improvement efforts, there is a popular motto which is applied: "You don't know what you can't measure!" We offer a modification to this motto: "How much you know depends on how well you measure." In this project, we have been concerned with characterizing the capability of a process, which is summarizing the inherent variability in the quality characteristic in question relative to the specifications. Clearly any error in measuring the true value of the quality characteristic can affect the ability to judge conformation of a particular item and more generally the capability of the overall process.

In general, any observed value x_{obs} can be assumed to be equal to the sum of two parts: the "true" value of the product characteristic x_{prod} and the measurement error ε. Thus, in equation form, we have

$$x_{obs} = x_{prod} + \varepsilon$$

A measurement system is assessed on the basis of two broad categories, generally known as accuracy and precision. The accuracy of a measurement system was defined as the extent to which the average of numerous repeated measurements on the same

item differed from the true value. Irrespective of the average value of the repeated measurements, precision is a measure of the extent of variation among the repeated measurements, that is, the ability of a measurement system to replicate identical measurements for the same item. To visualize the concepts of accuracy and precision, the equipment's name Ultraviolet Visible Absorption Spectroscopy model Cary 100 is selected to study the measurement system analysis in this project. This equipment is used to measure the absorption of the solvents. The concept of this equipment will be discussed in detail in the project later. Then, the results of the measurement will be discussed based on Minitab statistical program.

1.2 Objective of the Project

(1) To study the measurement system analysis of Ultraviolet and Visible Absorption Spectroscopy model Cary 100 environments

(2) Gage capability should be less than 7% gage contribution.

1.3 Scope of the Project

(1) The measurement system analysis is studied with Ultraviolet and Visible Absorption Spectroscopy model Cary 100 environments

(2) Analysis results are discussed based on Minitab statistical program.

II. LITERATURE REVIEW

2.1 Measuring System Introduction (Doebelin, 1990)

As background for our later detailed study of measuring instruments and their characteristics, it is useful first to discuss in a general way the uses to which such devices are put. Here we choose to classify these applications according to the following scheme:

(1) Monitoring of processes and operations

(2) Control of processes and operations

(3) Experimental engineering analysis

Each class of application is now described in greater detail.

Monitoring of Processes and Operations

Certain applications of measuring instruments may be characterized as having essentially a monitoring function. The thermometers, barometers, and anemometers used by the weather bureau serve in such a capacity. They simply indicate the condition of the environment, and their readings do not serve any control functions in the ordinary sense. Similarly, water, gas, and electric meters in the home keep track of the quantity of the commodity used so that the cost to the user may be computed. The film badges worn by workers in radioactive environments monitor the cumulative exposure of the wearer to radiations of various types.

Control of Processes and Operations

In another extremely important type of application for measuring instruments, the instrument serves as a component of an automatic control system. A functional block diagram illustrating the operation of such a system is shown in Figure 2.1. Clearly, to

control any variable by such a "feedback" scheme, it is first necessary to measure it; thus all such control systems must incorporate at least one measuring instrument.

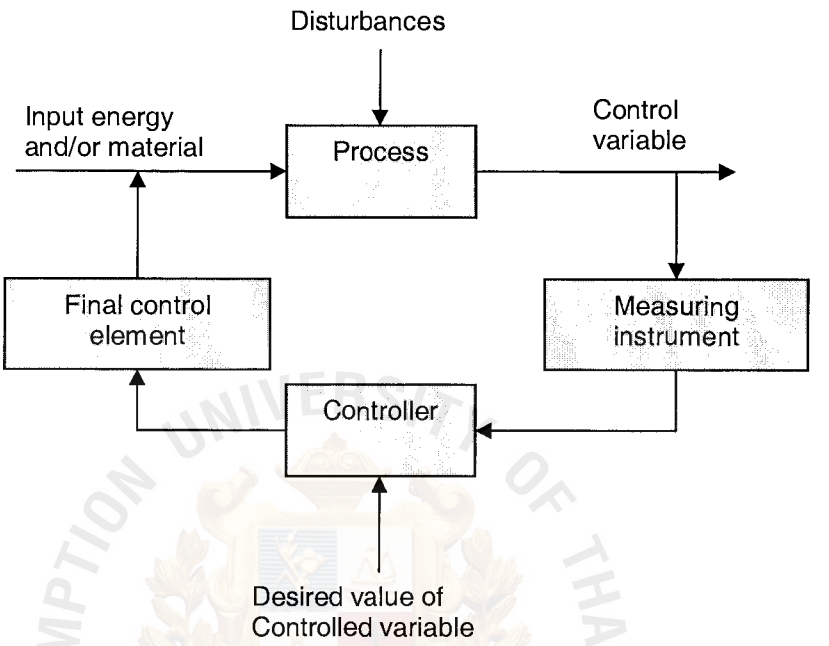

Figure 2.1. Functional Block Diagram.

Examples of this type of application are endless. A familiar one is the typical home-heating system employing some type of thermostatic control. A temperature-measuring instrument (often a bimetallic element) senses the room temperature, this providing the information necessary for proper functioning of the control system. Much more sophisticated examples are found among the aircraft and missile control systems. A single control system may require information from many measuring instruments such as pilot-static tubes, angle-of-attack sensors, thermocouples, accelerometers, altimeters, and gyroscopes. Many industrial machine and process controllers also utilize multisensor measurement systems.

In attempting to classify applications within your own experiences according to the three categories, you may find instances where the distinction among monitoring, control and analysis functions is not clear-cut. Thus the category decided on may depend on may depend somewhat on your point of view. The data obtained by the weather bureau, for instance, serve mainly in a monitoring function for the average person. For fruit growers, however, a report of cold weather may act in a control sense because it signals them to turn on smudge pots and apply other antifrost measures. Also, present weather data for large areas are correlated and analyzed to form the basis of short- and long-range weather predictions, so that you could say the instruments are supplying data for an engineering analysis. Once you recognize the possibility of a variety of interpretations, depending on the point of view, the apparent looseness of the classification should not cause any difficulty.

Experimental Engineering Analysis

In solving engineering problems, two general methods are available: theoretical and experimental. Many problems require the application of both methods. The relative amount of each depends on the nature of the problem. Problems on the frontiers of knowledge often require very extensive experimental studies since adequate theories are not available yet. Thus theory and experiment should be thought of as complementing each other, and the engineer who takes this attitude will, in general, be a more effective problem solver than one who neglects one or the other of these two approaches.

It may be helpful to summarize quickly the salient features of the theoretical and the experimental methods of attack. This is done in table 2.1 and 2.2.

In considering the application of measuring instruments to problem of experimental engineering analysis, it may be helpful to have at hand a classification of

the types of problem encountered. This classification may be accomplished according to several different plans, but one which the author has found meaningful is given in table 2.3.

Table 2.1. Features of Theoretical Methods.

1.	Often give results that are of general use rather than for restricted application.
2.	Invariably require the application of simplifying assumptions. Thus not the actual physical system but rather a simplified "mathematical model" of the system is studied. This means the theoretically predicted behavior is always different from the real behavior.
3.	In some cases, may lead to complicated mathematical problems. This has blocked theoretical treatment of many problems in the past. Today, increasing availability of high-speed computing machines allows theoretical treatment of many problems that could not be so treated in the past.
4.	Require only pencil, paper, computing machines, etc. Extensive laboratory facilities are not required. (Some computers are very complex and expensive, but they can be used for solving all kinds of problems. Much laboratory equipment, on the other hand, is special-purpose and suited only to a limited variety of tasks.)
5.	No time delay engendered in building models, assembling and checking instrumentation, and gathering data.

Table 2.2. Features of Experimental Methods.

1.	Often give results that apply only to the specific system being tested. However, techniques such as dimensional analysis may allow some generalization.
2.	No simplifying assumptions necessary if tests are run on an actual system. The true behavior of the system is revealed.
3.	*Accurate* measurements necessary to give a true picture. This may require expensive and complicated equipment. *The characteristics of all the measuring and recording equipment must be thoroughly understood.*
4.	Actual system or a scale model required. If a scale model is used, similarity of all significant features must be preserved.
5.	Considerable time required for design, construction, and debugging of apparatus.

Table 2.3. Types of Experimental-Analysis Problems.

1.	Testing the validity of theoretical predictions based on simplifying assumption; improvement of theory, based on measured behavior.
2.	Formulation of generalized empirical relationships in situations where no adequate theory exists.
3.	Determination of material, component, and system parameters, variables, and performance indices.
4.	Study of phenomena with hopes of developing a theory.
5.	Solution of mathematical equations by means of analogies.

2.2 Six Sigma Methodology (Brussee, 2004)

The Six Sigma methodology uses a specific problem-solving approach and Six Sigma tools to improve processes and products. This methodology is data-driven, with a goal of reducing unacceptable products or events.

The technical goal of the Six Sigma methodology is to reduce process variation such that the amount of unacceptable product is no more than 3 defects per million parts.

The real-world application of Six Sigma in most companies is to make a product that satisfies the customer and minimizes supplier losses to the point that it is not cost-effective to pursue tighter quality.

Average and Variation

First, no one knows how to make anything "perfect". If you order 50 1.000" diameter ball bearings and then measure the bearings once you get them, you will find that they are not exactly 1.000" in diameter. They may be extremely close to 1.000":, but if you measure them carefully, with a very good calibrated measuring device, you will find that the bearings are not exactly 1.000".

The bearings will vary from the 1.000" target in two ways. First, the *average* diameter of these 50 bearing will not be exactly 1.000". Whatever amount the average deviates from the target 1.000" is due to the bearing manufacturing process being off-center. Second, there will be a spread of measurements around the average bearing diameter. This spread of dimensions may be extremely small, but there will be a spread. This is due to the bearing process *variation.*

If the combination of the off-center bearing process and the bearing process variation is small compared with your needs, then you will be satisfied with the bearings. If, however, the combination of the off-center and variation is large compared with your needs, then you will not be happy. The Six Sigma methodology strives to make the

total effect of an off-center process and process variation small compared with the need (tolerance). This is illustrated below in Figure 2.2.

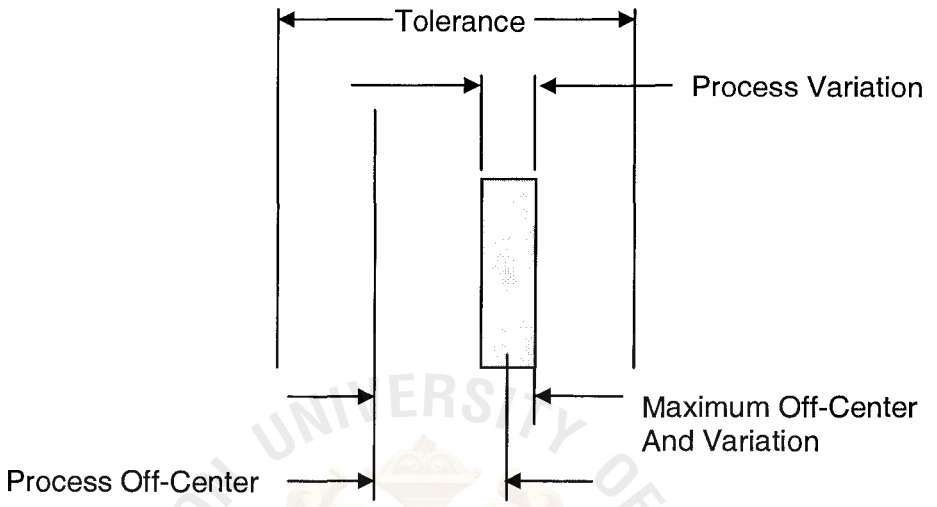

Figure 2.2. Off-Center and Variation.

Sigma

One of the ways to measure the variation of a product or a process is to use a mathematical term called *sigma*. We will learn more about sigma and how to calculate this value as we proceed, but for now it is enough to know that the lower the sigma value, the smaller the amount of process variation and the higher this sigma value, the greater the amount of the process's variation. Since the sigma calculation is normally done on a computer or calculator, it is more important that you gain a sense that sigma is a measure of the data spread (variation) than it is to be too involved with the detailed actual calculation of sigma.

Ideally, the sigma value is low in comparison with the allowable tolerance on a part of process. If so, the process variation will be small compared with the part or product tolerance a customer requires. When this is the case, the process is "right"

enough that, even if the process is somewhat off-center, the process produces product well within the customer's needs and specifications.

Most companies have processes with a relatively large variation compared with their customers' needs (a relatively high sigma value compared with the allowable tolerance). These companies run at an average ±3-sigma level (a 3-sigma process). This means that 6 sigma (±3 sigma) fit between the tolerance limits. The more sigma than fit between the tolerance limits, the better.

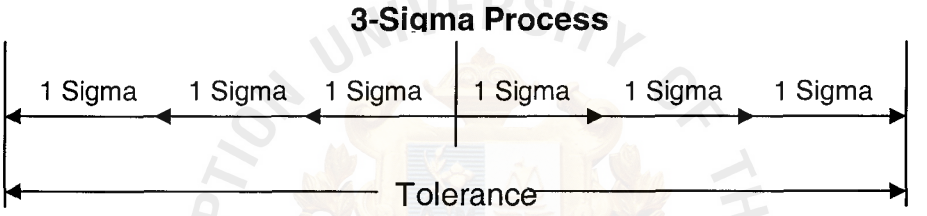

Figure 2.3. 3-Sigma Process.

Sigma level is calculated by dividing the process's allowable tolerance (upper specification minus lower specification) by twice the process's sigma value, since the sigma level of a process is normally stated as a ±value.

2.3 The Basic Six Sigma Roadmap (Brussee, 2004)

This is the roadmap that is followed for all projects and process improvements.

D-Definition

A problem is often initially identified very qualitatively.

(1) "The customer is complaining that the quality of the bearing races has deteriorated".

(2) "The new inventory tracking software program keeps crashing".

(3) "The losses on line#3 seem higher".

Before one can even think about possible solutions, the problem must be defined more specifically. Only then can meaningful measurements or data be collected. The above examples after some additional definition:

(4) "The inside diameter of the MQ18 bearing race became more varied starting week#14".

(5) "When the number of inventory items exceeds 1000, the inventory tracking software crashes several times per day".

(6) "The number of line#3 product being scrapped for loose wiring has doubled in the last week.

Table 2.4. DMAIC Problem-Solving Method.

DMIIC (Define, Measure, Analyze, Improve, Control) is the Six Sigma problem-solving approach used by Six Sigma people. This is the road map that is followed for all projects and process improvements, with the Six Sigma tools applied as needed.
D-Define – This is the overall problem definition. This definition should be as specific as possible.
M-Measure – Accurate and sufficient measurements/data are needed.
A-Analyze – The measurements/data must be analyzed to see if they are consistent with the problem definition and to identify a root cause. A problem solution is then identified. Sometimes, based on the analysis, it is necessary to go back and restate the problem definition and start the process over.
I-Improve – Once a solution is identified, it must be implemented. After the solution has been implemented, the results must be verified with independent data.
C-Control – A verification of control must be implemented. A robust solution (like a part change) will be easier to keep in control than a qualitative solution.

If there were quantitative values available, like the specific measurements related to the bearing diameter, they would be included in the problem definition. The more specific the initial problem definition, the better.

To get a good definition of the problem may be as simple as we are taking information from customer. Often, however, the improved definition will require much more effort. Some preliminary measurements may have to be taken to be sure that there even *is* a problem. It may be necessary to verify measurements and calculate sample sizes to ensure that we have valid and sufficient data. Sometimes the resultant measurements and analysis will show that the initial problem definition was erroneous and you then have to back up and formulate another definition.

M-Measure

Once the problem is defined, we must decide what additional measurements must be taken to quantify the problem. Several tools that will help identify the key process input variables to be considered and/or measured.

Samples must be sufficient in number, random, and representative of the process we wish to measure.

A-Analyze

Now we have to see what the data is telling us. We have to plot the data to understand the process character. We must decide if the problem as defined is "real" or just a random event without an assignable cause. These data will also be the base against which we will measure any implemented improvement. We may also have to measure appropriate key process input variables.

I-Improve

Once we understand the root cause of the problem and have quantitative data, we identify solution alternatives. Tests may be required to understand any interaction

between or among the input variable. Tolerances have to be examined. We analyze the error contributed by each component to see if one component is causing most of error. We then implement the solution and verify the predicted results.

C-Control

Quality control data samples and measurement verification can be scheduled. Control charts can be implemented to help the operator keep the process in control. Updated tolerances should reflect any change.

2.4 Cause-and-Effect or Fishbone Diagram (Brussee, 2004)

What we will learn in this section is that it's critical to identify and examine all of the possible causes for a problem. This section explains how a cause-and-effect diagram is used.

The fishbone diagram is used primarily in the Define, Analyze, and Improve steps of the DMAIC process. It helps identify which input variables should be studied further and gives focus to the analysis.

The purpose of a fishbone diagram is to identify all the input variables that could be causing the problem of interest. Once we have a complete input variables list we identify the critical few key process input variables (KPIVs) to measure and further investigate.

Table 2.5. Fishbone Diagram Applications.

Manufacturing – Do a fishbone diagram to list all the important input variables related to a problem. Highlight the KPIVs for further study. This focus minimizes sample collection and data analysis.
Sales and Marketing – For periods of unusually low sales, use a fishbone diagram to identify possible causes of the low sales. The KPIVs enable identification of probable causes and often lead to possible solutions.
Accounting and Software Development – Use a fishbone diagram to identify the possible causes of unusual accounting or computer issues. The people in these areas respond well to this type of analysis.
Receivables – Identify periods of higher than normal delinquent receivables. Then, use a fishbone diagram to try to understand the underlying causes.
Insurance – Look for periods of unusual claims frequency. Then, do a fishbone to understand underlying causes. This kind of issue usually has a large number of potential causes; the fishbone diagram enables screening to the critical few.

2.5 Fishbone Diagram Instructions (Brussee, 2004)

The specific problem of interest is normally the "head" of a fishbone diagram. There are six "bones" on the fish; on these "bones" we list input variables that affect the problem "head."

Each "bone" has a category of input variables that should be listed. Separating the input variables into six categories, each with its own characteristics, helps us make sure that no input variable is missed. The six categories are Measurements, Materials, Men, Methods, Machines, and Environment. (Some people remember these as the five M's

and one E.) The six categories are what make the fishbone diagram more effective than just simply listing the input variables.

Ideally, the input variables on a fishbone should come from a group of "experts" working together in one room. This enables a high degree of interaction among the experts. However, if this is not feasible, it is possible to do this process on the telephone, using a computer to regularly send updated versions of the fishbone diagram to all the people contributing. It is important for all contributors to be able to see the fishbone diagram as it evolves. This will cause everyone to constantly be triggered by the six categories. Below is an abbreviated example of a fishbone diagram (Figure 2.4) done on the problem "Shaft Diameter Error".

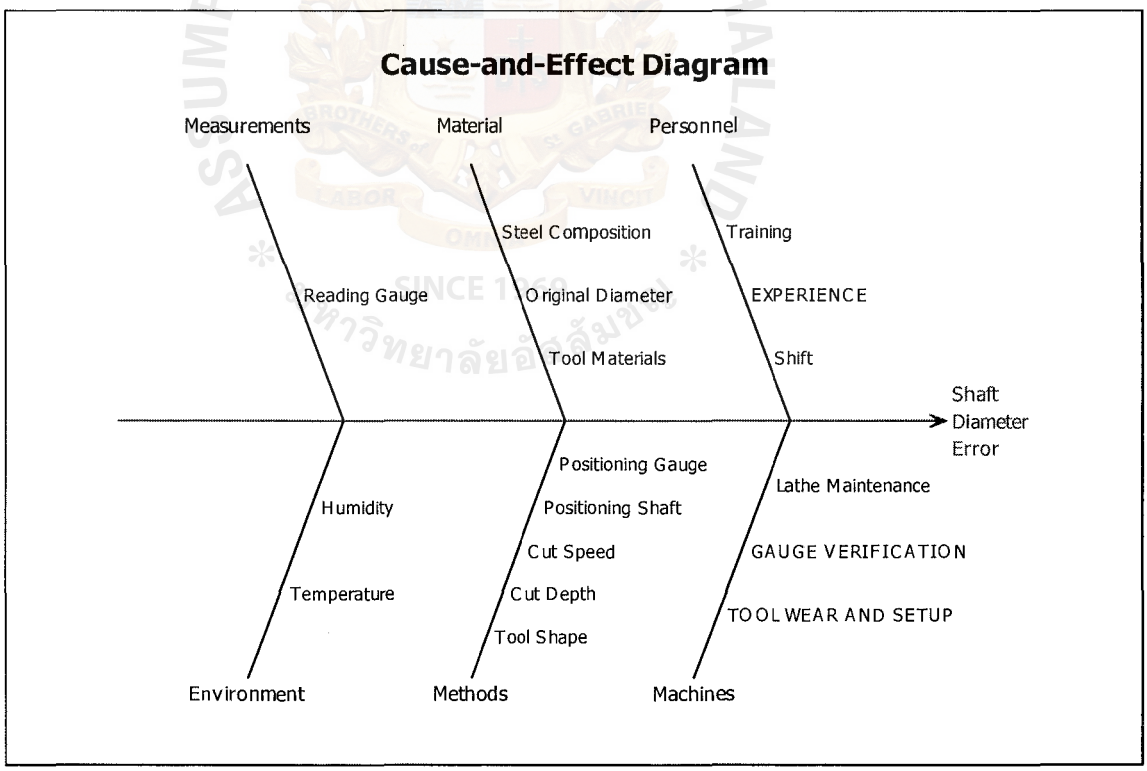

Figure 2.4. Fishbone Diagram Example.

After listing all the input variables, the same team of experts should pick the two or three KPIVs they feel are most likely to be the culprits. Those are highlighted in boldface and capital letters on the fishbone diagram.

The fishbone diagram is the recommended tool to identify what should be sampled in a process and to know what variables need to be kept in control during the sampling process. Without the kind of cause-and-effect analysis the fishbone diagram supports, the sampling will be less focused and more likely to be fraught with error. This is because the effort and control needed for good sampling and data collection is not trivial, so the amount of sampling must be minimized to allow everyone to get it right!

Sometimes just the process of doing the fishbone diagram leads to the solution, because you are getting the "experts" together to discuss the problem, which doesn't happen without a scheduled purpose.

2.6 Gage and Measurement System Capability Studies (Montgomery, 1997)

An importance of many statistical process-control implementation efforts is ensuring adequate gage and inspection system capability. In any problem involving measurements, some of the observed variability will be due to variability in the product itself, and some will be due to measurement error or gage variability. Expressed mathematically,

$$\sigma^2_{total} = \sigma^2_{product} + \sigma^2_{gage}$$

where σ^2_{total} is the total observed variance, $\sigma^2_{product}$ is the component of variance due to the product, and σ^2_{gage} is the component of variance due to measurement error. Control charts and other statistical methods can be used to separate these components of variance, as well as to given an assessment of gage capability.

2.7 Measuring Gage Capability

An instrument is to be used as part of a proposed SPC implementation. The quality improvement team involved in designing the SPC system would like to get an assessment of gage capability.

Figure 2.5 shows the $\bar{x}$ and R charts for these data. Notice that the $\bar{x}$ chart exhibits many out of control points. This is to be expected, as in this situation the $\bar{x}$ chart has an interpretation that is somewhat different from the usual interpretation. The $\bar{x}$ chart in this example shows the discriminating power of the instrument – literally, the ability of the gage to distinguish between units of product. The R chart directly shows the magnitude of measurement error, the gage capability. The R values represent the difference between measurements made on the same unit using the same instrument. In this example, the R chart is in control. This indicates that the operator is having no difficulty in making consistent measurements. Out of control points on the R chart would indicate that the operator is having difficulty using the instrument.

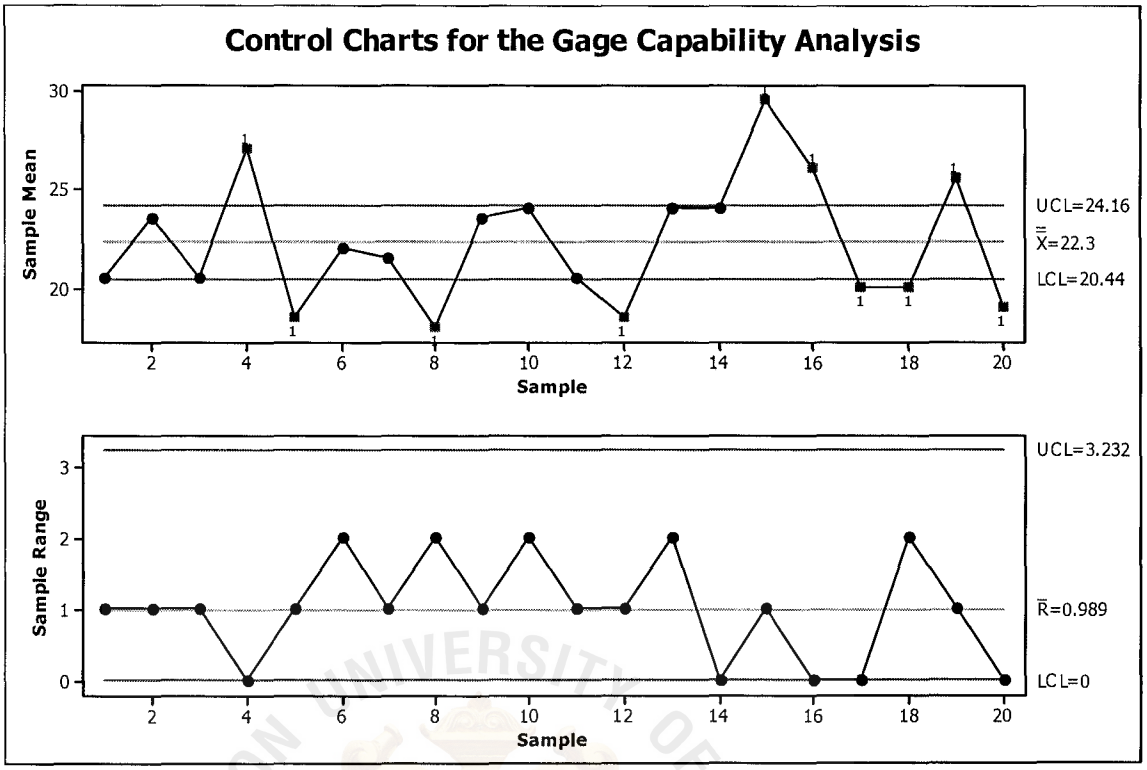

Figure 2.5. Control Charts For The Gage Capability Analysis.

2.8 Estimating Precision Components: Repeatability and Reproducibility (Alwan,2000)

Questions of accuracy deal with the mean level of the measurement errors, while precision deals with the variability of the measurement errors. The variability observed in measured values is due, in part, to the variability of the product and, in part, to the variability inherent in the measurement system.

Assuming the random variables for the product quality and the measurement error are independent (which is likely to be the case), we can write

$$\sigma^2_{total} = \sigma^2_{product} + \sigma^2_{gage} \qquad (1\text{-}1)$$

where σ^2_{total} is the overall total observed variance, $\sigma^2_{product}$ is the variance due to the product (process), and σ^2_{gage} is the variance due to the measurement system.

The primary goal is to design a study to separate and estimate the two variance components of the right-hand side of (1-1). This will enable us to assess the general capability of the measurement system, in terms of what proportion of the overall variation is due to the measurement errors relative to the inherent variation in the process. We then have an opportunity to assess the true capability of the process, in terms of the product itself, unclouded by the measurement errors.

Obtaining a realistic estimate of σ^2_{gage} requires an understanding of two potential sources for measurement errors:

(1) *Repeatability*: Even if a particular individual, using the same measuring device, measures the same item, variation in the measurement readings is expected. This variation is referred to as *repeatability*, or *within-operator variation*. Typically, poor repeatability is due to the measuring device itself; hence repeatability is sometimes called equipment variation.

(2) *Reproducibility*: When different operators use the same measuring device on the same item, variation again can be expected. This type of variation, called reproducibility, or between-operator variation, reflects the inability of operators to reproduce or match the results of other operators. Training problems and unclear measurement procedures are common explanations for reproducibility problems.

Given these two sources of variation, measurement error variance can be expressed as the combined effect of repeatability and reproducibility errors, namely,

$$\sigma^2_{gage} = \sigma^2_{repeatability} + \sigma^2_{reproducibility} \qquad (1\text{-}2)$$

The planning for a statistical study of measurement errors requires that we address three basic questions:

(a) How many operators (k) will be involved in making measurements?

(b) How many similar-type parts (m) will be measured?

(c) How many repeat measurements (n) will be made by each operator?

The number of operators, parts, and measurements can vary. For example,

(a) *Experiment* A: One operator, one or more parts, several measurements per part ($k = 1$, $m \geq 1$, $n > 1$). Such an experiment will provide a measure of consistency of readings on particular parts taken by one person. Since different operators are not considered, this experiment can be referred to as the *repeatability-only* experiment. If operator effects do indeed exist, a repeatability-only experiment will underestimate the measurement error variance.

(b) *Experiment* B: Several operators, one or more parts, one measurement per part ($k \geq 1$, $m \geq 1$, $n = 1$). Here the focus is on the consistency of readings among operators. With $n = 1$, the experiment, called a *reproducibility-only* experiment, does not permit the estimation of repeatability. If significant repeatability exists, a *reproducibility-only* experiment will underestimate the measurement error variance.

(c) *Experiment* C: Several operators, several parts, several measurements per part ($k > 1$, $m > 1$, $n > 1$). This experiment design is most popular since it permits for the estimation of both repeatability and reproducibility. Statistical studies attempting to estimate the separate effects of repeatability and reproducibility are called *gage R&R* studies. Even though a gage (or

gauge) is a specific type of measuring device, a gage R&R study generically applies to the study of any type of measurement system.

Once the experimental design has been chosen, there is then the question of deciding what statistical methodology should be used in the analysis of the experimental data. There are basically two approaches for the analysis of measurement data:

(1) *Analysis-of-variance (ANOVA) method*: ANOVA is a general framework of statistical techniques for estimating and testing the potential different sources of variability underlying some random variable under study. In a gage R&R study, it is typically assumed that the operators and parts involved in the study are samples taken from a larger population of operators and parts. With this assumption, the appropriate ANOVA model to be considered is called a *two-factor random effects* model, with operators and parts being the two factors. Montgomery and Runger (1993a, b) provide a detailed discussion of the use of the two-factor random effects model for gage R&R studies. Even though an ANOVA method might be considered the definitive approach, these authors also illustrate potential pitfalls with the ANOVA approach when certain estimation procedures are used. An excellent reference, concerning the issues related to the estimation of the components of variance in a two-factor random effects model, is by Searle, Casella, and McCulloch (1992).

(2) *Range Method*: For much the same historical reasons as for the implementation of many SPC methods, gage R&R studies are typically based on the easy-to-hand-compute range statistic. The most obvious shortcoming of a range-based approach is the less efficient use of the data relative to an ANOVA approach. Ranges only consider the largest and

smallest of a given set of data points, while ANOVA estimators (akin to the sample standard deviation) utilize all the observations in a data set. However, as will be demonstrated by the next example, the range approach is attractive because it lends itself naturally to the construction of a control chart which has an interesting interpretation.

Even with the less efficient use of the data by the range approach, both methods will give very similar results for most applications. There is, however, one situation that only the ANOVA approach can handle appropriately, and this is the study of a subcomponent of variability known as an *interaction effect*. In gage R&R studies, this would mean an operator-part interaction. Such interaction reflects some sort of nonindependence between operators and parts. For example, an operator might tend to measure small parts on the high end, whereas large parts tend to be measured on the low end. If significant interaction effects are present, the range method will overlook these effects, resulting in a significant underestimation of the true measurement-error variance. Any suspicion of interaction effects should be grounds for pursing the use of ANOVA methodology. We now turn to an example to flesh out the methods for estimating variance components associated with measurement errors.

2.9 Introduction to Ultraviolet and Visible Absorption Spectroscopy (Rouessac, 2000)

The interaction of electromagnetic radiation with matter in the domain ranging from the close ultraviolet to the close infrared, between 180 and 1,100 nm has been extensively studied. This portion of the electromagnetic spectrum, called UV/Visible because it contains radiation that can be seen by the human eye, provides little structural information except the presence of unsaturation sites in molecules. However, it has great importance in quantitative analysis. Absorbance calculations for compounds

absorbing radiation in the UV/Visible using Beer-Lambert's Law is the basis of the method known as colorimetry. This method is the workhorse in any analytical laboratory. It applied not only to compounds that possess absorption spectra in that spectral region, but to all compounds that lead to absorption measurements.

The spectral range of interest can be subdivided into three ranges: the near UV, the Visible and portions of the near Infrared (185-400, 400-700 and 700-1100 nm, respectively). Most commercial spectrometers have a spectral range of 185 to 900 nm. Absorption by materials in the atmosphere beginning at 185 nm is the limiting factor for the lower wavelength in this working range. About 10 to 20 nm can be gained at the shorter wavelength end by recording the spectrum under vacuum – the domain of the far UV.

These instruments allow a spectrum to be obtained which is a plot of absorbance (cf. 11.11) as a function of wavelength (Figure 2.6). Wavelengths are expressed in nanometers (nm), the recommended unit in this spectral domain.

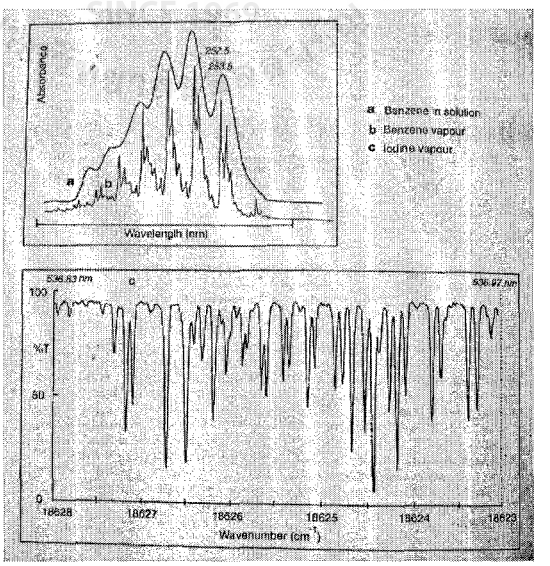

Figure 2.6. Three Different Aspects of Spectra Obtained in the UV/Visible Region.

2.10 UV/Visible spectrophotometers

A UV/VIS spectrophotometer consists of three components: the *source*, the *dispersive system* (combined in a *monochromator*) and a *detector*. These components, which can be used independently to design a system appropriate for a desired application, are typically integrated into the same instrument to make spectrophotometers for chemical analysis. The sample can be placed in the optical path before or after the dispersive system and recorded spectra can be treated using a number of different computer algorithms.

Because the spectra obtained from compounds in solution do not contain fine structure, it is not necessary to use spectrophotometers with high resolution. However, it is important to be able to precisely measure the absorbances over a range of several units. The simplest instruments, called spectrocolorimeters, are used for routine quantitative applications. Higher performance instruments designed for the best possible resolution are used in other areas besides analysis.

Light source

Two light sources are commonly used in this spectral domain. An *incandescent lamp* made from a tungsten filament housed in a glass envelope is used for the visible portion of the spectrum, above 350 nm. For that portion of the spectrum below this region, a medium pressure *deuterium arc lamp* is used (medium pressure must be applied to obtain an emission continuum).

(1) A deuterium arc lamp has two electrodes, bathed in an atmosphere of deuterium, between which a metallic screen pierced with a hole of 1 mm in diameter is placed. This discharge current creates an intense arc at the level of this hole, which is close to the anode. Under electron bombardment,

deuterium molecules dissociate, emitting a continuum of photons over the range of 160 to 400 nm (Figure 2.7).

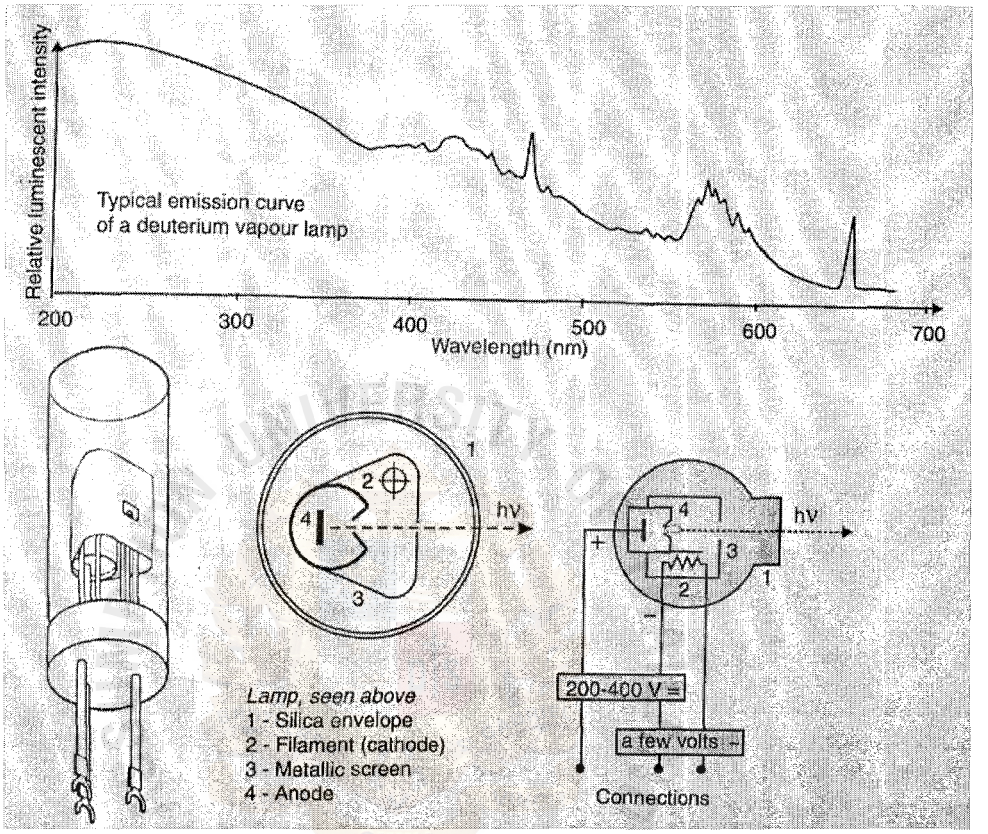

Figure 2.7. Emission Spectra of a Deuterium Lamp.

Dispersive systems and monochromators

Light emitted by the source is dispersed by a planar or concave grating with approximately 1200 lines per mm. For scanning spectrophotometers, the grating is integrated into an assembly called a monochromator, which extracts a narrow spectral band. The wavelength in these instruments is varied by pivoting the grating (Figure 2.8). Optical paths with long focal lengths (0.2 to 0.5 m) yield the best resolution.

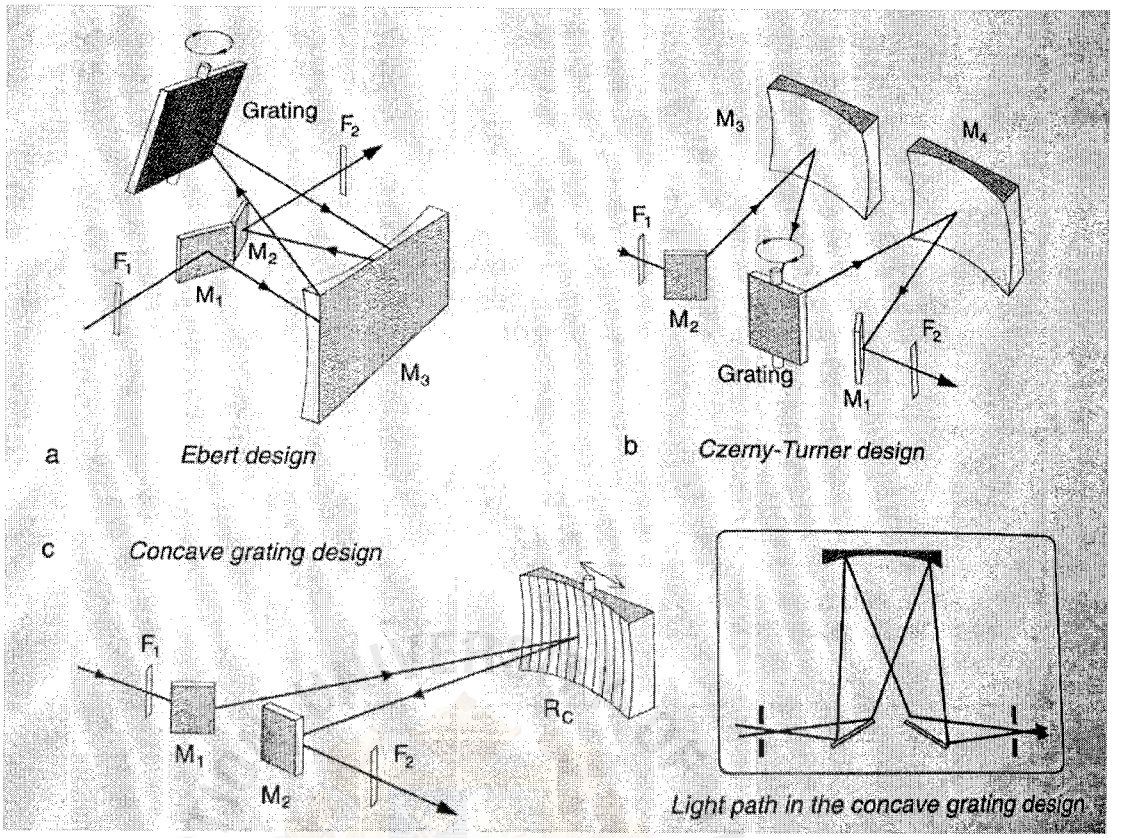

Figure 2.8. Grating Monochromators.

Detectors

The detector measures the light signal at a given wavelength. It is by nature a single channel device that converts the light intensity selected either by the monochromator exit or by the position, in the case of spectrograph, into an electrical signal. In the latter case, the use of a large number of detectors in the format of a *diode array* allows simultaneous multichannel detection. Two types of detectors exist: photomultiplier tubes and semiconductors (e.g. silicon photodiodes and charge transfer devices (CCD/CID).

The photomultiplier tube – a very sensitive device that has a linear response over seven decades – has for a long time been the most widely used detector in

spectrophotometers. Its efficiency depends on the yield of the photocathode, which varies with wavelength (e.g. 0.1e^-/photon at 750 nm), and with the signal gain provided by the dynode cascade (e.g. gain of 6 x 10^5). With such values, the impact of 10000 photons per second produces a current of 0.1 nA.

(1) As for the human eyes, it is difficult for a photomultiplier tube to precisely compare two light intensities, one from the reference beam and the other from the sample, when they are very different. For this reason, it is desirable to have the absorbance of solutions no higher than 1. On the other hand, for an instrument with a stray light of only 0.01% (measured in % transmittance), an increase in solution concentration will not create significant variations in the signal up to 4 absorbance units.

In routine spectrophotometers, photomultiplier tubes are replaced by photodiodes (Figure 2.9), which have excellent sensitivity, linearity and dynamic range. The photoelectric threshold, in the order of 1 eV, allows detection up to wavelengths of 1.1 μm. In *diode array* systems, each rectangular diode (15 μm x 2.5 mm) is associated with a capacitor. The electronic circuit sequentially samples the charge of each capacitor. While a photomultiplier tube measures the instant intensity in watts, a diode measures the emitted energy in joules over a time interval.

2.11 Quantitative analysis in the UV/Visible (Rouessac, 2000)

The spectral domain of the UV/Visible is well known because it includes the visible part of the spectrum and is widely used in quantitative analysis. Measurements are based on the Beer-Lambert law, which relates the absorption of light under certain conditions to the concentration of the compound.

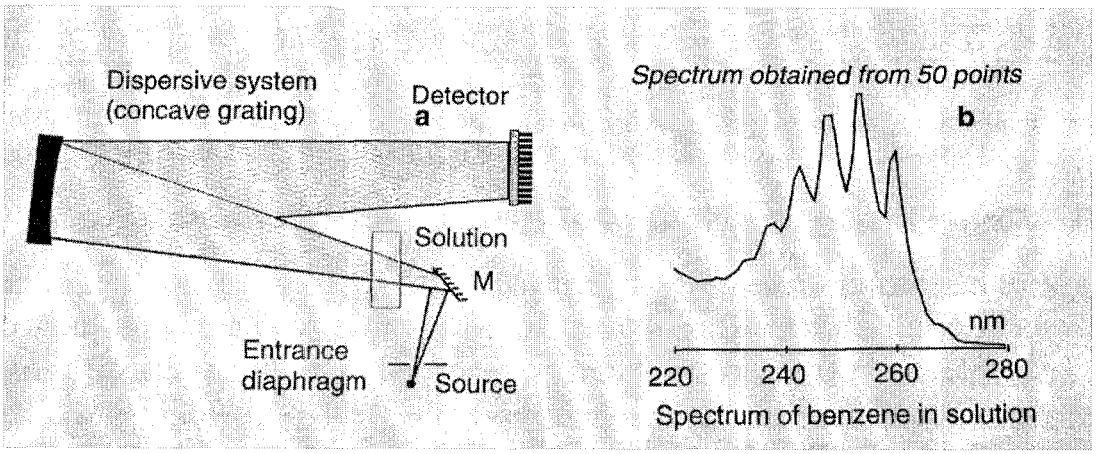

Figure 2.9. Multichannel Detection.

It is not necessary that the compound contain a chromophore as long as derivatisation is carried out before measurement to ensure absorption of the light. Through derivatisation, it becomes possible to quantify a chemical species that has no significant absorption because it is weak or, alternatively, because it lies in the same spectral domain as interferences.

To this effect, the measurement of absorbance is preceded by a chemical transformation (derivatisation) that has to be specific, total, rapid, reproducible and yield a UV/VIS absorbing derivative that is stable in solution. This is the principle of colorimetric tests.

(1) The term colorimetry comes from the fact that initial measurements in this spectral domain, well before the invention of spectrophotometers, were carried out with white light without any optical measurement. Visual comparison of the sample color with that of a reference solution of known concentration was then performed.

Two situations can be encountered with the use of this method (Figure 2.10):

(1) *The constituent A to be quantified is present in a mixture with a variable quantity of compound B that absorbs in the same spectral range*: direct measurement of the absorbance due solely to compound A is impossible because of the superposition of the spectra of A and B (Figure 10a). To remedy this situation, compound A is totally transformed by chemical reaction into compound C with an absorption band removed from that of B (Figure 2.10, curves a and b).

(2) Compound A does not possess a chromophore: here again a chromophore can be incorporated into A by transforming this substance into compound C, following the same principle (Figure 2.10, curves c and d).

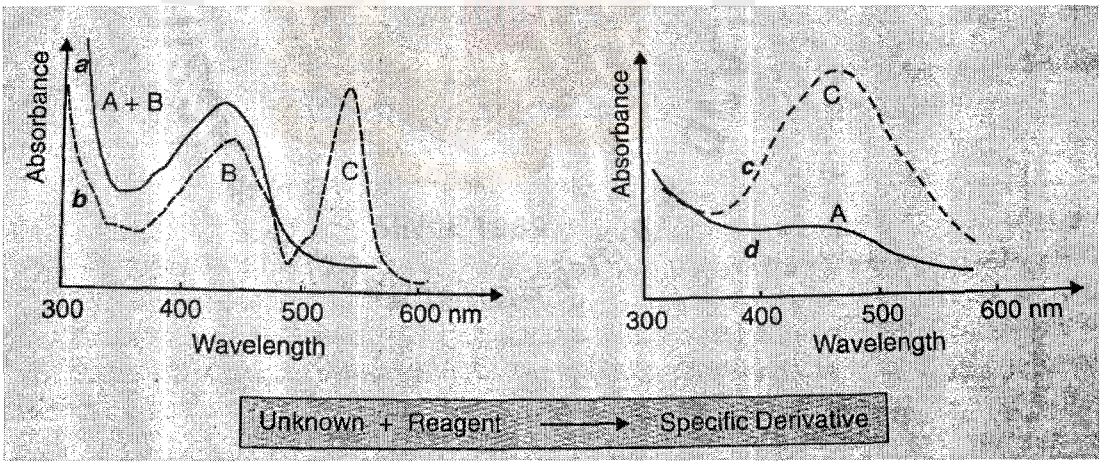

Figure 2.10. Two Situations Frequently Encountered in Colorimetry.

2.12 Absorbance measurements (Rouessac, 2000)

Light impinging on a sample can be transmitted, refracted, reflected scattered or absorbed. Beer-Lambert's law, which is only related to the fraction absorbed, is applicable under the following conditions:

(1) the light used must be monochromatic

(2) the concentration must be weak

(3) the solution must not fluoresce and must be homogeneous

(4) the solute must not undergo photochemical reactions

(5) the solute must not form variable associations with the solvent.

Experimentally, a calibration curve $A = f(C)$ is constructed using solutions of known concentration of the compound. The solutions undergo the same treatment as the sample. This curve is often a straight line for dilute solutions. It allows determination of the concentration C_X of the unknown sample.

In many instances, a single reference solution of concentration C_R can be used. This concentration is chosen such that the absorbance A_R is close to or slightly above that of the unknown solution A_X (see Figure 2.11).

The following formula permits calculation of C_X:

$$C_X = C_R \frac{A_x}{A_R}$$

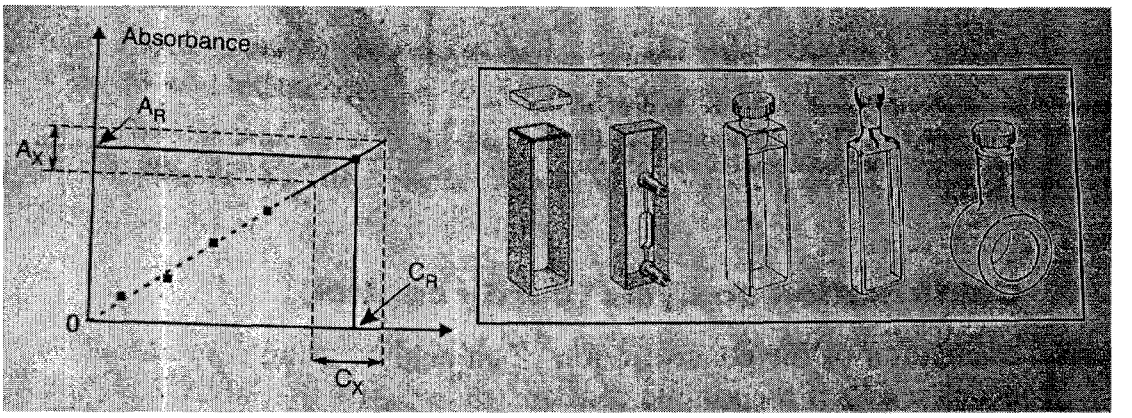

Figure 2.11. Colorimetric Calibration Curve and Classical Quartz Cells.

Beer-Lambert's law is additive. This implies that absorbance A, measured in a cell of thickness l for a mixture of two compounds 1 and 2 in solution in the same solvent, will be identical to the absorbance measured after light has passed through two cells of the same thickness l placed in series, the first containing compound 1 and the last containing the other compound, 2 (compounds must be at the same concentrations as in the initial mixture). By giving indices 1 and 2 to compounds 1 and 2 respectively, the following additive relation is obtained:

$$A = A_1 + A_2 = l(\varepsilon_1 C_1 + \varepsilon_2 C_2)$$

(1) **Isobestic points**. Consider compound A, which can be transformed by a first order reaction into compound B. Assume that the absorption spectra obtained under the same conditions of concentration cross over at a point I when they are superimposed (Figure 2.12). That is, the absorbances of the two solutions are the same for the wavelength at point I. Consequently, the coefficients A and B are identical. In this type of experiment, A is initially pure and at the end of the experiment B is pure. For all the intermediate solutions, mixtures of ε_A and ε_B can be prepared but the global concentration

does not change (C_A + C_B = constant). This leads to the following relationship:

$$A_1 = \varepsilon_A l C_A + \varepsilon_B l C_B = \varepsilon i (C_A + C_B) = \text{constant}$$

All spectra of the mixtures A + B will pass, over the course of time, through point I, called the isobestic point, where the absorbance of A will be constant. Families of concurrent curves are observed for colored indicators as a function of pH or as a function of reaction kinetics.

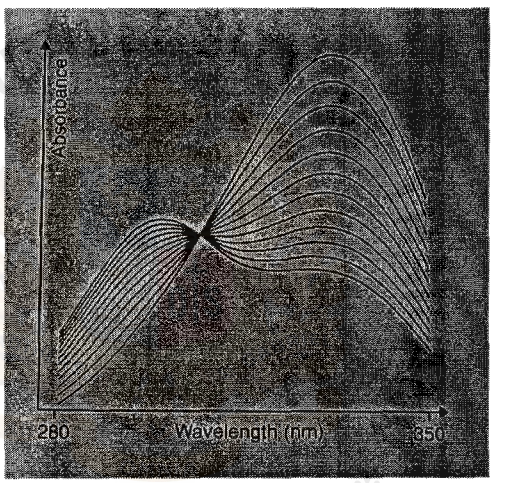

Figure 2.12. Isobestic Point.

III. PROJECT METHODOLOGY

3.1 Measurement System Analysis

Organizations frequently overlook the impact of not having quality measurement systems. Organizations sometimes do not even consider that their measurements might not be exact. Such presumptions and inadequate considerations can lead to questionable analyses and conclusions.

When appraisers do not measure a part consistently, the expense to a company can be very large when satisfactory parts are rejected and unsatisfactory are accepted. In addition, a poor measurement system can make the process capability assessment of a satisfactory process appear unsatisfactory. This can lead to lost sales and unnecessary expense while trying to fix a manufacturing or business process where the primary source of variability is from the measurement system.

This section presents procedural guidelines for the assessment of the quality of a measurement system. Mathematically, measurement systems analysis involves the understanding and quantification of measurement variance, as described in the following equation, to process variability and tolerance spread:

$$\sigma_T^2 = \sigma_p^2 + \sigma_m^2$$

where

σ_T^2 = Total variance

σ_p^2 = process variance

σ_m^2 = measurement variance

Measurement systems analysis assesses the statistical properties of repeatability, reproducibility, bias, stability, and linearity. Collectively, these techniques are sometimes referred to as "Gage R&R" (repeatability and reproducibility).

Focus is given to measurement systems where reading can be repeated on each part. The described gage R&R methodologies are applicable to both initial gage assessments and studies that help determine whether a measurement system is contributing a large amount to an unsatisfactory reported process capability index.

3.2 Terminology

(1) Bias is the difference between the observed average of measurements and the reference value. Bias is often referred to as accuracy.

(2) Repeatability is the variation in measurements obtained with one measurement instrument when used several times by on appraiser while measuring the identical characteristic on the same part.

(3) Reproducibility is the variation in the average of the measurements made by different appraisers using the same measuring instrument when measuring identical characteristics on the same part.

(4) Percent R&R is the percentage of process variation related to the measurement system for repeatability and reproducibility.

(5) Stability (or drift) is the total variation in the measurements obtained with measurement system on the same master or parts when measuring a single characteristic over an extended time period.

(6) Linearity is the difference in the bias values through the expected operating range of the gage.

(7) Percent of tolerance is the percentage of the part tolerance related to the measurement system for repeatability and reproducibility.

3.3 Gage R&R consideration

In a gage R&R study the following characteristics are essential

(1) The measurement must be in statistical control, which is referred to as statistical stability. This means that variation from the measurement system is from common causes only and not special cause.

(2) Variability of the measurement system must be small compared with both the manufacturing process and specification limit.

(3) Increments of measurement must be small relative to both process variability and specification limits. A common rule of thumb is that the increments should be no greater than one-tenth of the smaller of either the process variability or specification limits.

The purpose of a measurement system is to better understand the sources of variation that can influence the results produced by the system. A measurement is characterized by location and spread, which are impacted by the following metrics:

(a) *Location:* bias, stability, and linearity metrics

(b) *Spread:* repeatability and reproducibility

Bias assessments need an accepted reference value of a part. This can usually be done with tool room or layout inspection equipment. A reference value is derived from readings and compared with appraisers' observed averages. The following describes such as implementation method:

(a) Measure one part in a tool room

(b) Instruct one appraiser to measure the same part 10 times, using the gage being evaluated.

(c) Determine measurement system bias using the difference between the reference value and observed average.

(d) Express percent of process variation for bias as a ratio of bias to process variation multiplied by 100.

(e) Express percent of tolerance for bias as a ratio of bias to tolerance multiplied by 100.

Measurement system stability is the amount of total variation in system's bias over time on a give part or master part. One method of study in to plot the average and range of repeated master or master part readings on a regular basis. Care must be given to ensure that the master samples taken are representative (e.g., not just after morning calibration).

Linearity graphs are a plot of bias values throughout the expected operating range of the gage. Various measures of evaluating the acceptability of the measurement system spread are as follow:

(a) Percent of tolerance

(b) Percent of process variation

(c) Number of distinct data categories

Percent of population metrics equate to standard deviation units from an R&R study multiplied by a constant. This project uses a multiple of 5.15, where 5.15 multiple converts to 99% of the measurement for a normal distribution. Chrysler Corporation, Ford Motor Company, and General Motors Corporation use this percentage value in AIAG (1995a).

The discrimination of a measurement system is the concern when selecting or analyzing a measurement system. Discrimination or resolution of a measurement system is its capability to detect and faithfully indicate even small changes in the measured characteristic. Measurement systems cannot, because of economic and physical limitations, perceive infinitesimal separate or different in the measured

characteristic of parts or a process distribution. Measured values of a measured characteristic are instead grouped into data categories. For example, the incremental data categories using a rule might be 0.1 cm, while a micrometer might be 0.001 cm. Parts in the same data category have the same value for the measured characteristic.

When the discrimination of a measurement system is not adequate, the identification of process variation or individual part characteristic values is questionable. This situation warrants the investigation of improved measurement techniques. The recommended discrimination is at most one-tenth of six times the total process standard deviation.

Discrimination needs to be at an acceptable level of analysis and control. Discrimination needs to be able to both detect the process variation for analysis and control for the occurrence of special causes. The number of distinct data categories determined from a gage R&R study is useful for this assessment.

Unacceptable discrimination symptoms can also appear in a range chart, which describes the repeatability of operators within a gage R&R study. When, for example, the range chart shows only one, two, or three possible values for the range within the control limits, the discrimination for the measurements is inadequate. Another source of inadequate discrimination is when the range chart shows four possible values for the range within control limits, and more than one-fourth of the ranges are zero.

3.4 Preparation for a measurement system study

Sufficient planning and preparation should be done prior to conducting a measurement system study. Typical preparation prior to study is as follows:

(1) Plan the approach. For instance, determine by engineering judgment, visual observations, or gage study if there is an appraiser influence in calibrating or

using the instrument. Reproducibility can sometimes be considered negligible – for example, when pushing a button.

(2) Select number of appraisers, number of sample of parts, and number of repeat reading. Consider requiring more parts and/or trials for circle dimensions. Bulky or heavy parts may dictate fewer samples. Consider using at least two operators and ten samples where each operator measures each sample at least twice (all using the same device). Select appraisers who normally operate the instruments.

(3) Select sample parts from the process that represent its entire operating range. To achieve this, perhaps select one part daily. Number each part.

(4) Ensure that the instrument has a discrimination that is at least one-tenth of the expected process variation of the characteristic to be read. For example, if the characteristic's variation is 0.001, the equipment should be able to read a change of 0.0001.

Ensure that the measuring method of the appraiser and instrument is following the defined procedure. It is important to conduct the study properly. All analyses assume statistical independence of all readings. To reduce the possibility of misleading results, do the following:

(1) Execute measurements in random order to ensure that drift or changes that occur will be spread randomly throughout the study.

(2) Record readings to the nearest number obtained. When possible, make readings to nearest one-half of the smallest graduation (e.g., 0.00005 for 0.0001 graduations).

(3) Use an observer who recognizes the importance of using caution when conducting the study.

(4) Ensure that each appraiser uses the same procedure when taking measurements.

3.5 UV/Visible absorption spectroscopy measurement system study

3.5.1 Define Measurement System Analysis (MSA) of UV/Visible Instrument

UV/Visible model Cary100 is the instrument which uses to measure the absorption spectroscopy of the solutions such as %Valtron2275 or %Valtron97031 which use to clean the hard disk drive products. As a define section in Six Sigma methodologies, we set the problem statements as follows;

"The total Gage R&R of UV/Visible Instrument should be less than 7% of gage R&R Contribution."

Then, the hypothesis of this study is

H0: $\mu \leq 7$

H1: $\mu > 7$

3.5.2 Measure Phase of UV/Visible MSA

In this project, this instrument is selected to study and do the measurement analysis system. The specification ranges of %Valtron2275 and %Valtron97031 solutions are 0.5%-1.15% so 10 concentrations of solutions at range 0.5%-1.15% are prepared to study gage R&R which should represent the normal spread of %Valtron2275 or %Valtron97031 cleaning process. Four appraisers who normally do the measurement are chosen to participate in the study. Each part is measured two times by each appraiser. The designed table and data results table is shown in Table 3.1.

Table 3.1. Measurements for Gage R&R UV/Visible Absorption Spectroscopy.

Appraiser01										
Trials	Part01	Part02	Part03	Part04	Part05	Part06	Part07	Part08	Part09	Part10
1	0.473	0.907	0.798	0.760	0.917	1.162	0.703	1.072	0.976	0.602
2	0.473	0.908	0.798	0.759	0.917	1.162	0.704	1.074	0.977	0.602
Average	0.473	0.908	0.798	0.760	0.917	1.162	0.704	1.073	0.977	0.602
Range	0.000	0.001	0.000	0.001	0.000	0.000	0.001	0.002	0.001	0.000

Appraiser02										
Trials	Part01	Part02	Part03	Part04	Part05	Part06	Part07	Part08	Part09	Part10
1	0.485	0.911	0.806	0.777	0.929	1.172	0.705	1.089	0.987	0.607
2	0.483	0.918	0.807	0.775	0.932	1.170	0.708	1.082	0.991	0.604
Average	0.484	0.915	0.807	0.776	0.931	1.171	0.707	1.086	0.989	0.606
Range	0.002	0.007	0.001	0.002	0.003	0.002	0.003	0.007	0.004	0.003

Appraiser03										
Trials	Part01	Part02	Part03	Part04	Part05	Part06	Part07	Part08	Part09	Part10
1	0.468	0.910	0.791	0.761	0.914	1.155	0.705	1.067	0.969	0.605
2	0.462	0.900	0.797	0.759	0.916	1.157	0.707	1.070	0.977	0.610
Average	0.465	0.905	0.794	0.760	0.915	1.156	0.706	1.069	0.973	0.608
Range	0.006	0.010	0.006	0.002	0.002	0.002	0.002	0.003	0.008	0.005

Appraiser04										
Trials	Part01	Part02	Part03	Part04	Part05	Part06	Part07	Part08	Part09	Part10
1	0.464	0.911	0.806	0.775	0.925	1.169	0.707	1.084	0.979	0.611
2	0.472	0.906	0.798	0.776	0.924	1.170	0.707	1.083	0.986	0.602
Average	0.468	0.909	0.802	0.776	0.925	1.170	0.707	1.084	0.983	0.607
Range	0.008	0.005	0.008	0.001	0.001	0.001	0.000	0.001	0.007	0.009

3.5.3 Analyze Phase of UV/Visible MSA

We have finished the experiment and get the data from the measurement phase. Next step is to analyze the data from Table 3.1. There are 3 methods to analyze the data.

(1) **Range Method** is suitable for studying in short term experiment and no repeat measurement. The good point of this method is easy to analyze but you can not separate repeatability from reproducibility.

(2) **Average and Range Method** is suitable for studying in repeated measurement of each sample from each appraiser. That means each appraiser can measure the samples many times in the experiment. This method can separate repeatability from reproducibility but it can not separate

the variability between samples and appraisers (Interaction between samples and appraisers).

(3) **ANOVA** is suitable for studying in detail of samples and appraisers variability that are significant to each other or not. This method can separate the variability between samples and appraisers but it becomes too complicated when doing the calculation so the statistical computer software will help us at this point.

In this project, we use ANOVA method to study the measurement system analysis of UV/Visible. Minitab statistical software is used to analyze the data in this project. At this point, we can compare the analysis results to the specification that is called *Precision-to-Tolerance Ratio* or **P/T** for the measurement system that needs to identify the good or bad samples or we can compare the analysis results to the process variation that is called *Precision-to-Total Variation* or **P/TV** for measurement system that needs to capture variation in the process.

$$\text{P/T} = \frac{GR\&R}{USL - LSL} \times 100\%$$

$$\text{P/TV} = \frac{GR\&R}{\text{Process\_Variation}} \times 100\%$$

The project is only mentioned about P/T since the cleaning processes of the solutions are needed to classify and verify the good and bad samples.

Normally, the acceptance of repeatability and reproducibility is followed by below list;

P/T or P/TV< 10%	Accept the measurement system
10% ≤ P/T or P/TV < 30%	Accept the measurement system but it depends on the condition of the measurement system such as cost of the measurement or other factors.

P/T or P/TV > 30%	The measurement system is unacceptable, it needs to find the cause of the problem and reduce the variable of the measurement system.

3.5.4 Improve Phase of UV/Visible MSA

At this point, the results of the UV/Visible will be analyzed which are compared with the above acceptance guide lines. Many solutions are discussed in case P/T or P/TV are greater than 30%, the measurement system should be revised and re-do the test again to improve the quality of measurement. If P/T or P/TV is less than 10%, it might be better to find another way to improve the measurement system or improve the process since the results of the measurement is reliable. We will discuss this phase again in the next section (Results and Discussions).

3.5.5 Control Phase of UV/Visible MSA

Normally practice in control phase is needed to do the schedule or plan to confirm the steady process. The measurement could be planned to do the measurement at least semi-annually per year or quarterly per year. The important point is measurement verification could be scheduled. The schedule table is shown in the below Table 3.2.

Table 3.2. Schedule Table for Gage R&R Study.

Study Date	Gage Name	Reporter	Tolerance	%Gage Contribution	% Gage Tolerance (P/T)
1/Nov/2004	Gage R&R Study of UV/Visible	Polsak C.	0.65	0.10	5.43

IV. RESULTS AND DICUSSIONS

4.1 Measurement System Analysis Results

The results in Table 3.1 are done the statistical analysis by using Minitab software. The graphical computer output for a gage R&R study is shown in Figure 4.1and the computer for gage R&R study is shown next. An analysis discussion then follows in results and discussions section.

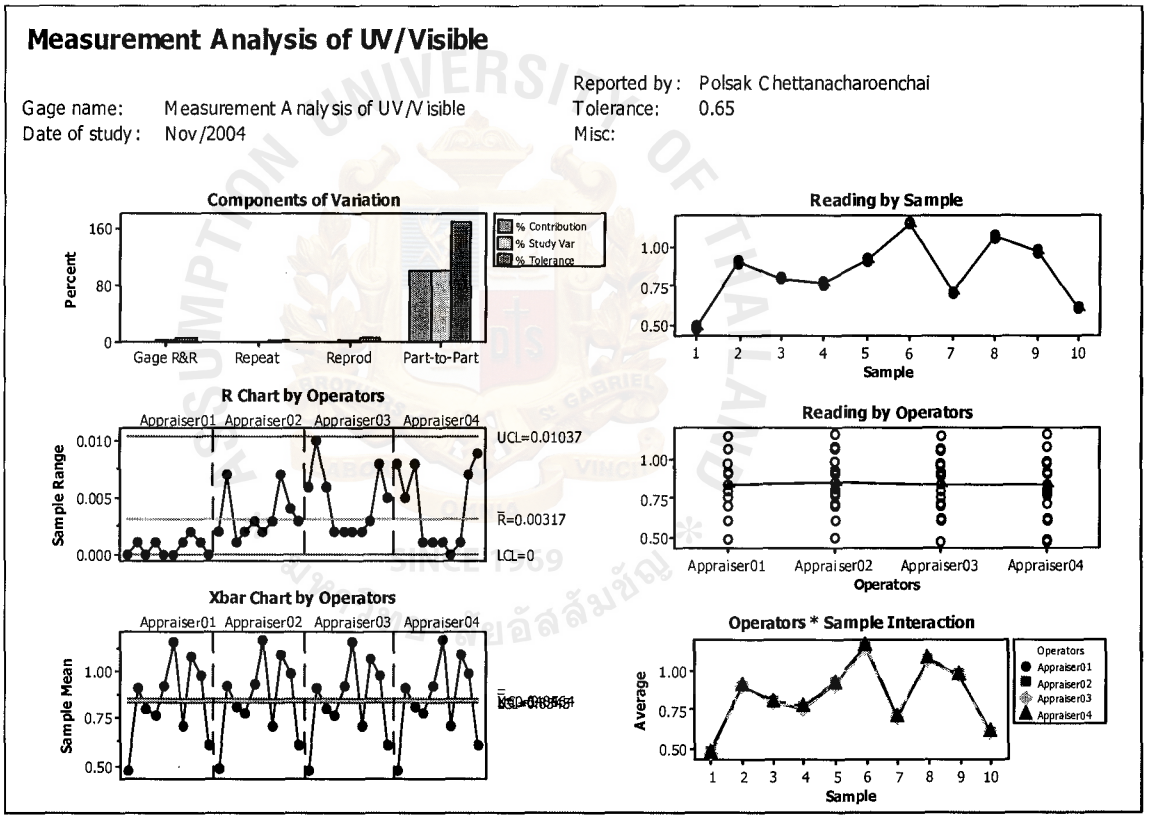

Figure 4.1. Gage R&R Graphical Output.

Gage R&R Computer Output

Two-Way ANOVA Table With Interaction

Source	DF	SS	MS	F	P
Sample	9	3.26304	0.362560	12225.1	0.000
Operators	3	0.00174	0.000581	19.6	0.000
Sample * Operators	27	0.00080	0.000030	3.2	0.000
Repeatability	40	0.00037	0.000009		
Total	79	3.26595			

Gage R&R

Source	VarComp	%Contribution (of VarComp)
Total Gage R&R	0.0000470	0.10
Repeatability	0.0000092	0.02
Reproducibility	0.0000378	0.08
Operators	0.0000276	0.06
Operators*Sample	0.0000102	0.02
Part-To-Part	0.0453163	99.90
Total Variation	0.0453633	100.00

Source	StdDev (SD)	Study Var (5.15 * SD)	%Study Var (%SV)	%Tolerance (SV/Toler)
Total Gage R&R	0.006855	0.03530	3.22	5.43
Repeatability	0.003031	0.01561	1.42	2.40
Reproducibility	0.006149	0.03166	2.89	4.87
Operators	0.005251	0.02704	2.47	4.16
Operators*Sample	0.003199	0.01648	1.50	2.53
Part-To-Part	0.212876	1.09631	99.95	168.66
Total Variation	0.212987	1.09688	100.00	168.75

Number of Distinct Categories = 43

4.2 Discussions of Measurement System Analysis

Gage analysis result from ANOVA shows 0.10% gage contribution which is less than our hypothesis tests. When gage is compared with the tolerance 0.65, the results are shown as 5.43% gage tolerance that is less than the acceptance of repeatability and reproducibility. In this project, it seems that there is no need to improve the gage study since the gage results are very good. Then, we should consider the schedule to do re-measurement again and record the data in Table 3.2. It is suggested to do at least twice per year.

The variance analysis considered four appraisers, sample and operators*samples interaction. From these analyses, appraisers, samples and operators*samples interaction were found to be significant because the probability of significance values (*P*) for appraisers, samples or operators*samples interaction were small. (e.g., not less than 0.05).

The recreation of the computer output calculations for the ratio variance component to total variance estimates is

$$\text{Variance component \%} = \frac{Variance\_Component}{Total\_Varinace} \text{ x } 100$$

$$\text{Gage variance component \%} = \frac{0.0000470}{0.0453633} \text{ x } 100 = 0.10\%$$

$$\text{Part-To-Part variance component \%} = \frac{0.0453163}{0.0453633} \text{ x } 100 = 99.90\%$$

These results indicate a good measurement system, because 0.10% of the total measured variance is not from repeatability and reproducibility of the gage.

The following shows a similar recreation of the previous computer output calculations, expect the ratio of variance component to total variance is now expressed in 99 percentile units:

$$\text{\%Study ratio} = \frac{5.15(s\tan dard\_deviation\_of\_component)}{(Total\_of\_5.15)(s\tan dard\_deviation\_of\_all\_components)} \text{ x } 100$$

$$\text{R\&R \% Study Var} = \frac{0.03530}{1.09688} \text{ x } 100 = 3.22$$

$$\text{Part-To-Part \% Var study} = \frac{1.09631}{1.09688} \text{ x } 100 = 99.95$$

From the results, there is no concern about measurement because it is estimated that about 3.22% of the 99% spread of variability is from the measurement system.

The gage R&R computer output shows 43 distinct categories, another indicator that the effectiveness of this gage is good. With many distinct categories, the data can be divided into many groups.

Graphical outputs associated with a gage R&R study can give additional insight to gage. In gage R&R study the $\bar{x}$ control chart address measurement variability relative to part-to-part variation. The control limits for these charts are based on repeatability inconsistencies, not part-to-part variations. The measurement system in this project is concluded to be adequate to detect part-to-part variations. An adequate measurement system is present when a majority of samples average fall outside the limits and appraisers agree on which parts fall outside the limits.

When *R* chart of a gage R&R study is in control, the inspection process by appraisers is similar. If one appraiser is out of control, his/her method differs from the others. If all appraisers have some out-of-control ranges, the measurement system is apparently sensitive to appraiser technique and needs improvement to obtain useful data. For this project there does not appear to be any inconsistency within and between operators.

Other output graphs from a gage R&R study can give additional insight to sources of variability (e.g. part-to-part, operators, operators*samples interaction, and components of variance). These charts, for this project, do not appear to contain any additional information that was already determined through other means.

V. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this project, UV/Visible was selected to study the measurement system analysis. We use Six Sigma methodologies to apply with measurement system analysis which are composed of Define-Measure-Analyze-Improve-Control (DMAIC) but we don't use all phases of the methodologies in this project. With the Six Sigma concept, we follow up DMAIC guide lines and apply the concept to the measurement system by defining the problem to get gage R&R less than 7%, measure the data by preparing the measurement system study, analyse the data by using Minitab software and control the measurement system by creating log book.

Four appraisers were used to study in UV/Visible measurement analysis system at measurement range 0.5-1.15% .The gage R&R results of this project show 0.1% gage contribution that is a very good gage R&R study when compared with the target (less than 7% gage contribution). The computer output shows graphical output and reading output. We should read the graphical output results before reading output since it is easier to look at overall gage R&R results than reading output. If you want more details of the gage study, you will read the reading output in the next step.

Many points are concerned when we were reading the results. The first one is gage R&R contribution. If the gage R&R is more than 7% gage contribution, we will need to review what happens with our measurement process and re-do again to improve the measurement process. Second is the interaction of samples, appraisers, and samples*appraisers. We can see this interaction from graphical output. The good one should be equal when doing the measurement. The project does not have any problem with the interaction. Third is the samples variation. It should cover all range of the measurement. In this project, the percentage concentration of the solvent is in range

0.5%-1.15% so this gage capability should cover all measurement range. The last one is the distinct categories of the measurement. At this point, we get 43 distinct categories that means the effectiveness of this gage is good. If you got distinct categories of only 2, it means you can measure it only good or bad, true or false, yes or no that is an attribute data.

One important thing to do with gage R&R study is approach of the study. If we don't have approach of the study and good plan, we could lose time and cost to study the measurement system since it needs to use the samples and man power to do the measurement system analysis. Best plans and good actions will get good results.

5.2 Recommendations

This project recommends to do gage R&R at least twice per year which can help us to reduce the measurement errors from the process. Another point to suggest is Six Sigma methodologies can be applied to any measurement system analysis to confirm our measurement system and errors by using the basic step that is provided in section 3.4.

For people who are interested in Six Sigma methodologies and want to apply the concept to your area work, there is a very important need to follow it step-by-step for Six Sigma methodologies, D.M.A.I.C tool., after, we confirm our measurement results; and gage R&R is less than 7%. We can do further study in another area which can help to improve the process such as the process capabilities/performance. The process capability/performance studies are to assess a process relative to specification criteria. A customer might set process capability/performance targets and then ask for their level of conformance to these targets which process capability/performance targets are sensitive to the input value for standard deviation. Some terms which are concerned to

process capabilities and process performance are inherent process variation, total process variation, process capability, and process performance.

5.3 Further Studies

The process capability is the studying of how the inherent variability in a process compares with the specifications or requirements for the product, as we confirm in our measurement system. Process capability is the next thing that we need to study in the process.

Process capability refers to the uniformity of the process. Obviously, the variability in the process is a measure of the uniformity of output. There are two ways to think of this variability:

(1) The natural or inherent variability at a specified time; that is, "instantaneous" variability.

(2) The variability over time.

Process capability analysis is a vital part of an overall quality-improvement program. Among the major uses of data from a process capability analysis are the following:

(1) Predicting how well the process will hold the tolerances.

(2) Assisting product developers/designers in selecting or modifying a process.

(3) Assisting establishing an interval between sampling for process monitoring.

(4) Specifying performance requirements for new equipment.

(5) Selecting between competing vendors.

(6) Planning the sequence of production processes when there is an interactive effect of processes on tolerances.

(7) Reducing the variability in a manufacturing process.

Thus, process capability analysis is a technique that has application in many segments of the product cycle, including product and process design, vendor sourcing, production or manufacturing planning and manufacturing.

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