# Reliability Analysis of GC-MS Instrument using Fault Tree Approach

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*partial fulfillment of the requirement for the award of degree of*

**Master of Engineering**
**in**
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# DECLARATION

*I hereby declare that the thesis entitled* ***"Reliability Analysis of GC-MS Instrument using Fault Tree Approach"*** *is an authentic record of my own work carried out as requirements for the award of degree of* ***Master of Engineering*** *in* ***Electronic Instrumentation & Control*** *at* ***Thapar University****, Patiala, under the guidance of supervisor* ***Dr. Yaduvir Singh*** *(Associate Professor, EIED) during January to June 2009.*

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# ABSTRACT

Gas chromatography-mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, pesticides detection and identification of unknown samples. GC/MS can also be used in airport security to detect substances in luggage or on human beings. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification.

A Polaris *Q* System includes the Polaris *Q* MS, the TRACE GC, and the Xcalibur for gas chromatography detection and analysis. It is optimally designed to eliminate ion molecule reaction. The Finnigan Polaris *Q* external source ion trap mass spectrometer makes high quality GC/MS affordable for every laboratory. The Polaris Q features benefitting people working in chemical industry industry—analysts, technicians, and chemists. So it is very necessary to analyze the reliability of Polaris Q system. The thesis is concentrated towards the analysis of reliability of Polaris Q system with the help of fault tree method.

A fault tree (FT) is constructed as a logical illustration of the events and their relationships that are necessary and sufficient to result in the undesired event, or top event. The data for every subpart is expressed in terms of their probability of failure which is the backbone of determining the reliability of the Polaris Q GC-MS instrument.

# ORGANISATION OF THESIS

The first chapter includes the introduction of the reliability which is defined as the probability that a product or system meets its specification over a given period of time. It also includes Reliability Block Diagram (RBD) that performed the system reliability and availability analyses on large and complex systems using block diagrams and also shown different network relationships. The second includes the review of literature. The third chapter includes the detailed description of the Gas Chromatography and Mass Spectrometry. The next chapter is based on Fault Tree which is a deductive, failure-based approach. Fault Tree has been used for the analysis of the reliability of Polaris Q. The fifth chapter includes the simulation and testing of the Polaris Q where various fault tree and tables are shown. The sixth chapter finally concludes the reliability of the instrument on the results obtained.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| **GC-MS** | Gas chromatography-mass spectrometry |
| **MS** | Mass Spectrometry |
| **RBD** | Reliability Block Diagram |
| **TSBU** | Transmission Systems Business Unit |
| **CBRE** | Component Based Reliabilty estimation |
| **BONES** | Block Oriented Network Simulator |
| **REST** | Reliability Estimation System Testbed |
| **SBIR** | Small Business Innovation Research |
| **FID** | flame ionization detector |
| **TCD** | Thermal Conductivity Detector |
| **DID** | Discharge Ionization Detector |
| **ECD** | Electron Capture Detector |
| **FPD** | Flame Photometric Detector |
| **HECD** | Hall Electrolytic Conductivity detector |
| **HID** | Helium Ionization Detector |
| **NPD** | Nitrogen Phosphorus Detector |
| **MSD** | Mass Selective Detector |
| **PID** | Photo-Ionization Detector |
| **PDD** | Pulsed Discharge Ionization Detector |
| **TCD** | Thermal Energy(Conductivity) Analyzer/Detector |
| **VOC** | Volatile Organic Compounds |
| **MSD** | Mass Selective Detector |
| **TOF** | Time of Flight |
| **SIM** | Selective Ion Monitoring |
| **EI** | Electron Ionization |
| **CI** | Chemical Ionization: |
| **SRM** | Single Reaction Monitoring |

| | |
|---|---|
| **MRM** | Multiple Reaction Monitoring |
| **ASTM** | American Society for Testing Materials |
| **FT** | Fault Tree |
| **FTA** | Fault Tree Approach |
| **MCS** | Minimal Cut Sets |
| **LOV** | Loss of Vehicle |
| **PRA** | Probabilistic Risk Assessment |
| **FMEA** | Failure Mode and Effects Analysis |

# CHAPTER 1

# INTRODUCTION

## 1.1 Overview

Gas chromatography-mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. GC/MS can also be used in airport security to detect substances in luggage or on human beings. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification. The GC-MS has been widely heralded as a "gold standard" for forensic substance identification because it is used to perform a specific test. A specific test positively identifies the actual presence of a particular substance in a given sample. A non-specific test merely indicates that a substance falls into a category of substances. Although a non-specific test could statistically suggest the identity of the substance, this could lead to false positive identification. The reliability analysis of such type of instrument is very necessary to check the failure mode of instrument.

## 1.2 Reliability

Reliability itself is defined as the probability that a product or system meets its specification over a given period of time. The word specification is of course very broad and a product might have several functions. One can calculate the reliability of each individual function or of all functions together which make up the specification. The term time can also be replaced by distance, or cycles or other units as appropriate. In other words it is very important to be clear when reliability is concerned as it can have different meanings to different people and in different situations. In a plant process availability, unavailability, probability of fail dangerous, success, fail safe, etc., can be calculated which are all aspects of, and related to, reliability. In general reliability deals with probability of failure of components, products and systems and is therefore at the heart of disciplines like hazard and risk analysis, loss prevention, maintenance programs, quality assurance and so on. Reliability engineering is thus the discipline of ensuring that a product or system will be reliable when operated in a specified manner. It is performed throughout the entire life cycle of a product or system, including design, development, test, manufacturing, operation, maintenance and repair. In process plants it is often a staff function where prime responsibility is to ensure that maintenance techniques are effective, that equipment is designed and modified to improve maintainability, that ongoing maintenance technical problems are investigated, and that appropriate corrective and improvement actions are taken. But in reality it is much broader than that. Reliability engineering deals with every aspect of a component or system from making a reliable design, to reviewing operating and maintenance procedures, or even to setup a reliability data collection program. In many plants reliability engineering is often also called maintenance engineering.

Reliability engineering heavily depends on probabilistic methods. In order to predict something, whether it is the reliability of a piece of equipment or a complete process plant, first a reliability model is needed. There are many different techniques and methods developed over time that be can used to make models. If models of (complex) systems are made for the purpose of prediction, then it depends on one or more techniques like:

1. Reliability block diagrams
2. Fault trees
3. Markov models
4. Monte Carlo simulation

Other techniques exist as well but these are very common ones.

### 1.2.1 Reliability Block Diagram

A Reliability Block Diagram (RBD) performs the system reliability and availability analyses on large and complex systems using block diagrams to show network relationships. The structure of the reliability block diagram defines the logical interaction of failures within a system that are required to sustain system operation. The rational course of a RBD stems from an input node located at the left side of the diagram. The input node flows to arrangements of series or parallel blocks that conclude to the output node at the right side of the diagram. A diagram should only contain one input and one output node. The RBD system is connected by a parallel or series configuration. A parallel connection is used to show redundancy and is joined by multiple links or paths from the Start Node to the End Node.

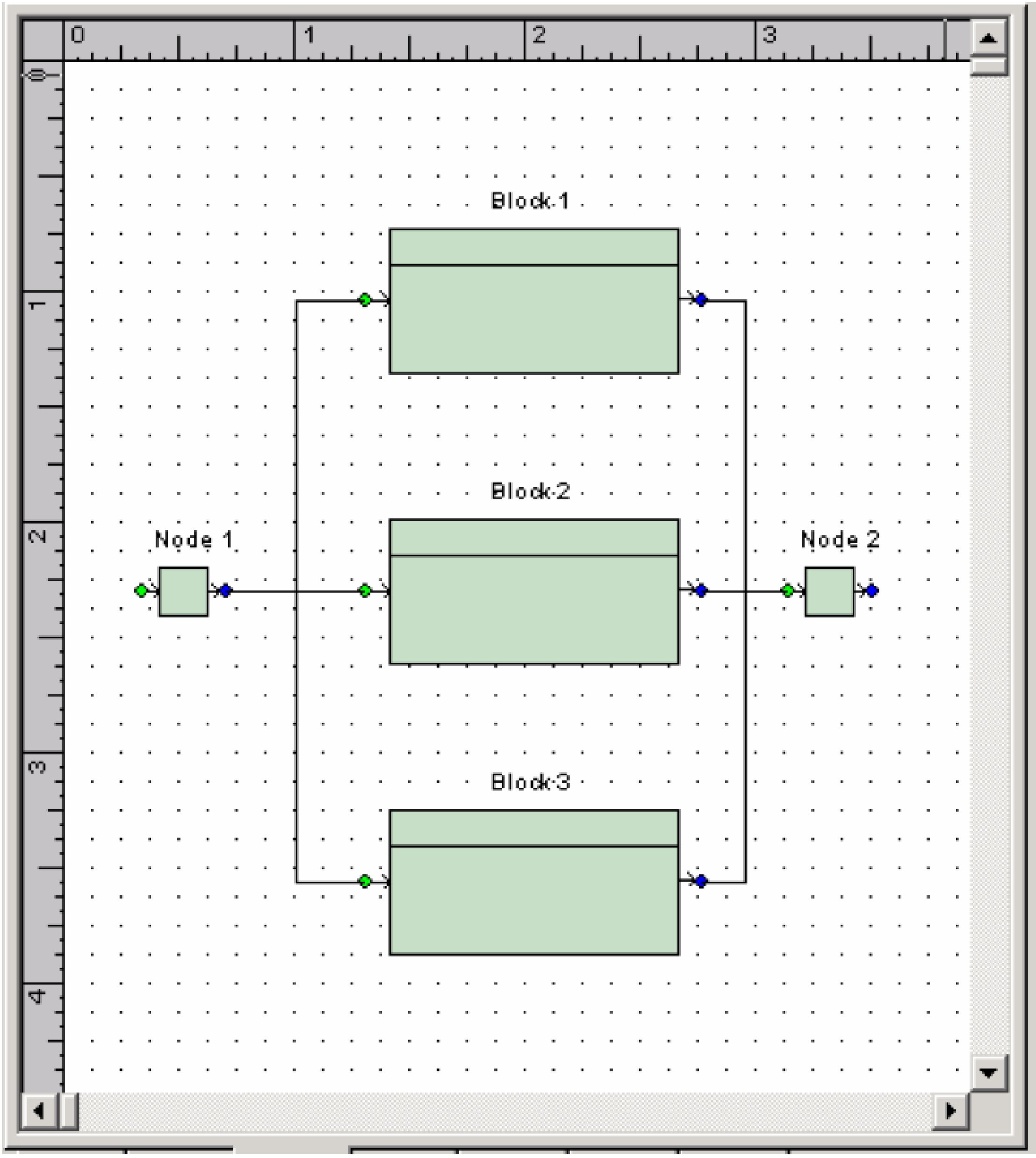


Figure 1.1 Reliability Block Diagram in parallel

A series connection is joined by one continuous link from the Start Node to the End Node.

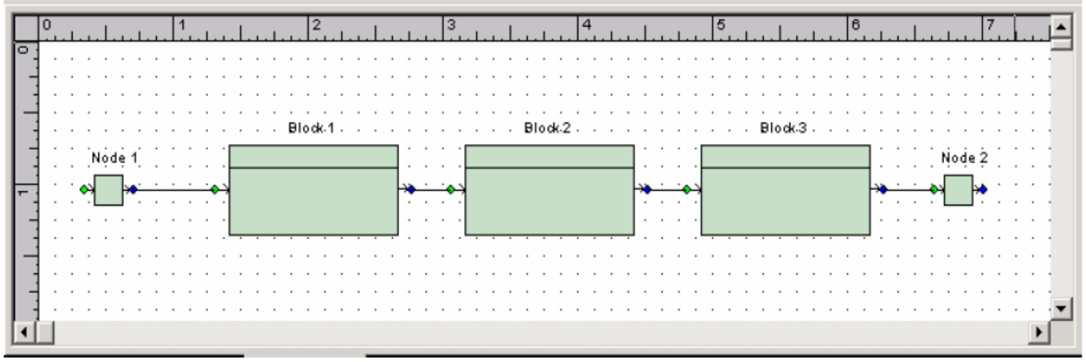


Figure 1.2 Reliability Block Diagram in series

A system can contain a series, parallel, or combination of series and parallel connections to make up the network. A reliability block diagram (RBD) is a drawing and calculation tool used to model complex systems. An RBD is a series of images (blocks) representing portions of a system. Once the images (blocks) are configured properly and image data is provided, the failure rate, MTBF, reliability, and availability of the system can be calculated. As the configuration of the diagram changes, the calculation results also change.

## 1.3 Fault Tree

FTA can be simply described as an analytical technique, whereby an undesired state of the system is specified (usually a state that is critical from a safety or reliability standpoint), and the system is then analyzed in the context of its environment and operation to find all realistic ways in which the undesired event (top event) can occur. The fault tree itself is a graphic model of the various parallel and sequential combinations of faults that will result in the occurrence of the predefined undesired event. The faults can be events that are associated with component hardware failures, human errors, software errors, or any other pertinent events which can lead to the undesired event. A fault tree thus depicts the logical interrelationships of basic events that lead to the undesired event, the top event of the fault tree. It is important to understand that a fault tree is not a model of all possible system failures or all possible causes for system failure.

A fault tree is tailored to its top event that corresponds to some particular system failure mode, and the fault tree thus includes only those faults that contribute to this top event. Moreover, these faults are not exhaustive—they cover only the faults that are assessed to be realistic by the analyst.

It is also important to point out that a fault tree is not in itself a quantitative model. It is a qualitative model that can be evaluated quantitatively and often is. This qualitative aspect ofcourse, is true of virtually all varieties of system models. The fact that a fault tree is a particularly convenient model to quantify does not change the qualitative nature of the model itself.

Intrinsic to a fault tree is the concept that an outcome is a binary event i.e., to either success or failure. A fault tree is composed of a complex of entities known as “gates” that serve to permit or inhibit the passage of fault logic up the tree. The gates show the relationships of events needed for the occurrence of a “higher” event. The “higher” event is the output of the gate; the “lower” events are the “inputs” to the gate. The gate symbol denotes the type of relationship of the input events required for the output event. Figure 1.3 shows a simple fault tree.

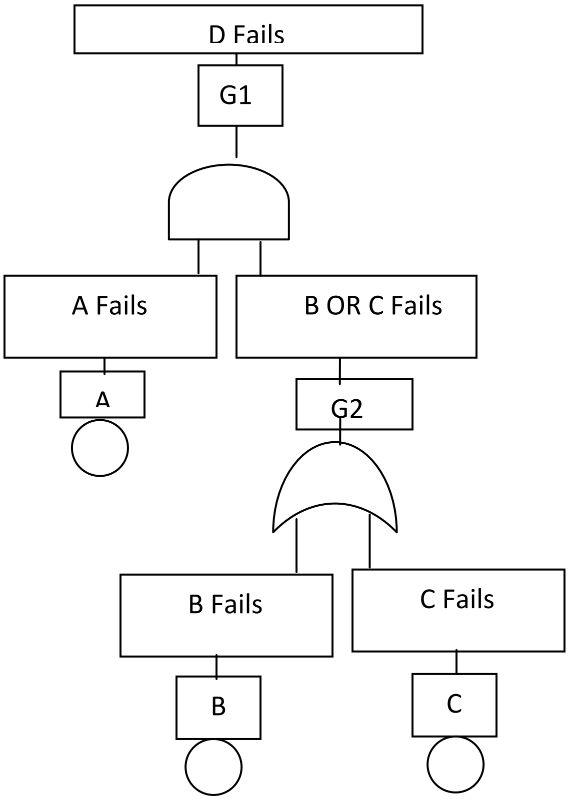


Figure 1.3 Simplified Fault Tree

## 1.4 Markov models

Markov models have traditionally been used to understand the reliability of storage systems. They provide intuition about the sensitivity of storage system reliability to changes in disk failure rates; rebuild rates, sector failure rates, scrubbing rates, and storage capacity. Unfortunately, as we move towards multi-disk fault tolerant storage systems, i.e., storage systems that tolerate two or more disk failures such as RAID 6, reliability estimates based on traditional Markov models become unreliable. Our concerns go beyond the recent demonstration that Weibull distributions need to be used instead of exponential distributions to accurately determine storage system reliability. The traditional construction of Markov models is flawed for multi-disk fault tolerant systems, and that their accuracy and utility decreases as the redundancy in the system increases. In this WIP, we will only discuss one of our concerns: modeling disk rebuild correctly. Two traditional Markov models are used to model two distinct storage rebuild policies. In a serial rebuild policy, a storage system rebuilds the first failed disk in its entirety before rebuilding the next failed disk, and so on. In a concurrent rebuild policy; a storage system begins rebuilding failed disks as they fail. Figure 1.4 illustrates the two traditional Markov models for an n disk system that tolerates m disk failures. The label of each state indicates the number of failed disks; state m + 1 is the data loss state. The transitions from left to right are disk failures, with being the failure rate. The transitions from right to left are disk rebuilds, with μ being the rebuild rate. For single disk fault tolerant systems, the serial and concurrent rebuild models are identical, and are correct. For multi-disk fault tolerant systems, both rebuild models are incorrect. The same modeling error is made in each case. The rebuild transitions for states 2 through m are incorrect: they model the rebuild of the disk that failed most recently, whereas reliability is dominated by the rebuild of the disk that failed earliest. In essence, traditional Markov models reset the rebuild time for all disks being rebuilt whenever another disk fails. The traditional serial rebuild Markov model thus models a rebuild policy in which each subsequent disk failure changes which disk is being rebuilt, and “re-fails” the disk currently being rebuilt. The traditional concurrent rebuild Markov model thus models a rebuild policy in which each subsequent disk failure restarts the rebuild of all failed disks.

The modeling error results in both traditional Markov models producing a similar, conservative reliability calculation. Different rebuild policies did not lead to noticeably different reliability calculations. Every additional disk of redundancy compounds the error due to incorrect Markov modeling of disk rebuild.

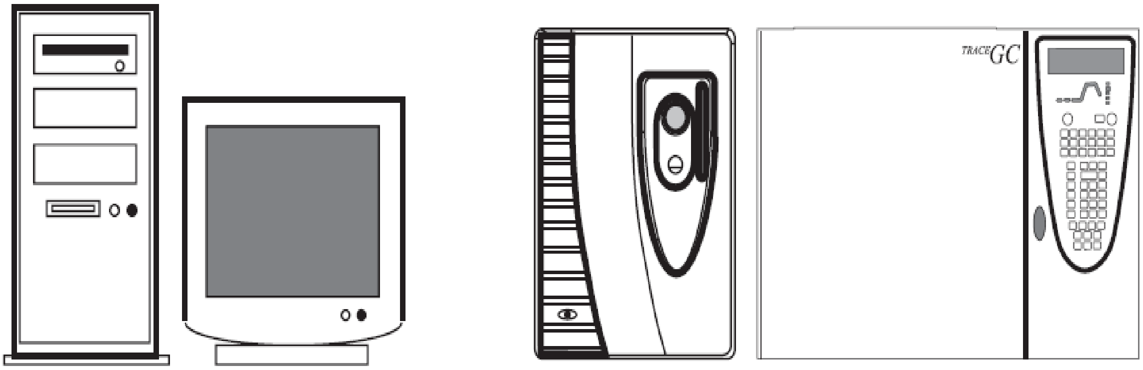
## 1.5 Monte Carlo Simulation

The Monte Carlo method of reliability prediction is useful when system complexity makes the formulation of exact models essentially impossible. The characteristics of the Monte Carlo method make it ideal for estimating the reliability of software systems. Unlike many other mathematical models, system complexity is irrelevant to the method. Not only can the structure of the system be dynamic, but the precise structure of the software system need not even be known. Instead, system components need only be tested for failure during operation, which ensures that components which are used more often contribute proportionally more to the overall reliability estimate. Combined with self-checking algorithms which respond to randomly generated inputs, the method obviates the need for valid, nontrivial input data and an external oracle. The reliability of each component is based on probability distributions, the reliability of each component in a system flow chart can be modeled by a set of random numbers. For instance, if the reliability of a component is 0.8, then successful operation of that component can be represented by the numbers from 0.0 through 0.79 and failure by the numbers from 0.8 through 0.99. By generating random numbers as the system flow chart is traced, it is possible to simulate the state of each component. These component states can then be combined using the structure function to determine the state of the system. Since “each execution of a simulation tells only whether a particular set of conditions did or did not” exist, the Monte Carlo method is an experimental problem-solving technique such that “many simulation runs have to be made to understand the relationships involved in the system”. Each repetition of the simulation results in another independent estimate of the reliability of the system. As the number of simulations increases, the sample mean of these independent estimates approaches the actual characteristics of the system.

The use of Monte Carlo methods to simulate the behavior of this system and thus can be used to estimate its reliability. The failure of one of the two components that form the series subsystem causes the failure of the entire subsystem. A given iteration of the subsystem is simulated by testing the state of the first component of the subsystem by generating a random number in the range [0,1]. If the first component does not fail, then the state of the second component is tested. If the series subsystem fails, then the parallel component is tested. If it too fails, then the entire system fails. After a number of these system simulations have been performed, the failure intensity of the system is calculated by dividing the number of observed failures by the total number of simulations. The actual failure intensity for this system is 0.01925.

## 1.6 Polaris Q

A Polaris*Q* System includes the Polaris*Q* MS, the TRACE GC, and the Xcalibur ver. 1.2 software for gas chromatography detection and analysis. It is optimally designed to eliminate ion molecule reaction. The Finnigan Polaris*Q* external source ion trap mass spectrometer makes high quality GC/MS affordable for every laboratory. It is available as an EI-only GC/MS configuration or as an MS/MS system with positive and negative chemical ionization, solids probes, and liquid or headspace autosampler. The Polaris*Q* truly offers the performance, versatility and reliability chemists are looking for.



PC (Xcalibur Data System)

*PolarisQ* Mass Spectrometer

*TRACE* Gas Chromatograph

Figure 1.4 Polaris Q MS System

The figure shows the various parts of Polaris Q. Xcalibur are the data system software used to configure instruments, calibrate the mass spectrometer, and setup instrument methods for data acquisition and data processing. A TRACE GC is the standard inlet solution for the Polaris*Q* Mass Spectrometer system. GCs connect to the Polaris*Q* by a capillary column inserted in the transfer line.

The Polaris Q features benefitting people working in chemical industry industry—analysts, technicians, and chemists. So it is very necessary to analyze the reliability of Polaris Q system. The thesis is concentrated towards the analysis of reliability of Polaris Q system with the help of fault tree method.

# CHAPTER 2

# LITERATURE REVIEW

This chapter provides brief overview of work done in this area:

William P.karas(1967) proposed the technique based on the production of electronic switching circuit evolved around electronic switching technique, such as electronic private branch exchange and electronic register sender, Solid state component parts which provide high reliability and simplified maintenance are utilized. This paper is used to produce commercial electronic switching systems to meet customer requirements. The advantages to the subscriber are additional services, increased flexibility, and high reliability with low maintenance cost. This paper is very useful to discuss the reliability and maintainability objectives, as applied in the design, before analyzing, here, Reliability and maintainability are expressed in numerical values and integrated into the system's performance specifications [1].

David J. Klinger et.al (1992) emphasized on reliability assurance with the help of quality assurance. This paper was mainly concentrated on reliability program activities, management responsibilities in managing reliability, and a reliability program team concept. The program includes reliability activities in all phases of the product life cycle, from product concept to deployment and field use. The discussion was highlighted width with a major example of reliability program management in the AT&T Transmission Systems Business Unit (TSBU). Transmission Systems has established goals to dramatically improve the quality and Reliability of transmission products, so that customer needs are met beyond the specified requirements. The concerns that reliability was not being sufficiently managed, major customers and suppliers of military systems, telecommunications systems, and computer systems have worked together to develop standards for reliability assurance programs and standards for the management of these programs. The challenge for these same customers and suppliers is to implement these standards for mutual benefit [2].

Christopher A. Lane et.al (1994) addressed the principles used to predict and attain reliability growth on real-time systems. System reliability modeling techniques that include Software reliability, maintenance effectiveness, and failure recovery are discussed in detail. The impact of maintenance effectiveness, which was a measure of the maintainer's skill and training levels, is shown. The need to develop and measure the robustness of failure recovery algorithms was emphasized in this paper. All of these factors were combined with the failure and repair characteristics of hardware to create comprehensive reliability growth models for real-time Systems. The effective failure recovery algorithms were the key to attaining highly reliable systems. The modeling and measurement techniques discussed in this paper provide the reliability practitioner with the methods to predict and achieve reliability growth resulting from improved software reliability and recovery algorithms. A fault tolerant system's ability to recover from hardware and software failures is gauged by a parameter called coverage. Coverage is the conditional probability of recovery given that a failure has occurred. Because of its huge impact on system reliability, the measurement of coverage was emphasized [3].

Saileshwar Krishnamurthy et.al (1997) evaluated a method, known as Component Based Reliabilty estimation (CBRE), for the estimation of reliability of a software system using reliabilities of its components. CBRE involves computing path reliability estimates based on the sequence of components executed for each test input. Path reliability estimates are averaged over all test runs to obtain an estimate of the system reliability. In the experiment reported, three components of a Unix utility were seeded with errors and the reliability of each component was measured. The faulty components were then introduced systematically into the utility, in various combinations, to produce several faulty versions of the utility. For each faulty version, test cases were drawn from an operational profile to measure the “component-based reliability”. The “true reliability” of the faulty version was estimated using the frequency count approach. The goodness of CBRE was assessed in terms of the accuracy and efficiency of the estimates with respect to the “true reliability.” Results from this experiment suggest that CBRE yields reasonably accurate results at an efficient rate. However, the accuracy and efficiency of CBRE is sensitive to the dependency among successive calls to a component [4].

Jon G. Elerath et.al (1999) proposed a reliability program for the commercial computer industry. The program diligently applied reliability principles throughout the design, manufacture and field use of our products. Our process establishes reliability goals that, in turn, drive change and improved product reliability. It described not only the assemblies design but also but also the reliability of those purchased from outside Suppliers. An effective field reliability data collection and analysis process have developed that allows us to measure the increase in reliability and identify potential future problems. The designs have been impacted by providing analyses that optimize cost while achieving the high system availability that our customers expect. The evidence of the effectiveness of our efforts came through the field data that shows decreased failure rates and sustained high levels of customer satisfaction [5].

Yusen Lin, Sourav Bhattacharyya(1999) proposed Reliability based software development process and an end-to-end reliability estimation of a multi module software system have been presented in this paper Development of an end-to-end software system requires comprehensive reliability-driven treatment. Therefore, all phases of system engineering life-cycle require adequate treatment from the reliability perspective. Research in software engineering also indicates that early removal of faults is critical to the success of a reliable software system. A combined treatment of reliability engineering and software life-cycle can provide the capability of reliability estimation td designers to help them clarify, analyze and verify the reliability requirement in the early phases of the life-cycle.the broad goal of research was to provide a computer Aided Reliability program(CARE).The end-to-end reliability estimation analyzed the reliability parameters of each module (or components) as well as the data and control flows among them to provide accurate reliability parameters of the software system. The reliability information can be used in high level design phases as well as in testing. We propose a multi-module based reliability estimation approach that, by using a resolution function, can model the fault propagation amongst the modules and links. This approach, includes both data and control flow structure of the program, as well as provision for looping structure in the program [6].

David M. Nicol et.al (1999) proposed a new graphical reliability estimation tool Reliability Performance Module (RPM) RPM combines the features of a powerful reliability tool, Reliability Estimation System Testbed (REST), developed at NASA Langley, with the convenient graphical modeling and simulation capabilities of an off-the-shelf commercial software package, Block Oriented Network Simulator (BONes'), from the Alta Group of Cadence Design Systems. In order to estimate the reliability of a system, the built-in bones graphics capabilities are used to describe the system, and the embedded REST execution engine produces a reliability analysis automatically. An additional benefit of this approach is that a detailed failure modes and effects analysis can be derived by using the simulation capabilities of the tool. as compared to our current design process, RPM promises to reduce overall modeling and analysis time, provide better documentation, make trade studies easier, create reusable modeling components and subsystems, and provide the integration of reliability and timing analysis necessary to guarantee the safety of critical real-time systems [7].

Ronald E. Giuntini (2000) proposed a mathematical reliability methodology for estimating the contribution of the human operator in a human-machine system. The methodology consists of a mathematical probabilistic conceptual approach for the analytical characterization of human reliability for multi-task system operation. From a system perspective, reliability for a system includes three different reliability elements: (1) hardware reliability, (2) software reliability, and (3) human reliability. Therefore, the reliability of a system is just as constrained by the reliability of the human operator as it is by the reliability of the hardware and software. Seldom is the human component considered in the mix when the total reliability of a system is being planned. This is tantamount to the assumption that the human reliability is 1.0 or perfect. The methodology is applicable to high value, high risk human-machine operations where failures can be catastrophic and costly such as rendezvous and docking of a space craft at the International Space Station, landing of a new generation of space vehicles, the operation of piloted dynamic flight simulators, critical control activities in a nuclear power plant, and other potentially risky human machine interfaces [8].

Katerina Goseva (2003) worked towards the developing of software reliability modeling framework that can consider the phenomena of failure correlation and to study its effects on the software reliability measures. This paper described that the classical software reliability theory can be extended to consider a sequence of possibly –dependent software runs, viz, failure correlation. It does not deal with inference nor with predictions, per se.

1. Detailed assumptions about the nature of the overall reliability growth.
2. The way modeling-parameters change as a result of the fault-removal attempts [9].

D. David Dylis Rome et.al (2001) proposed a new methodology includes new component-level reliability prediction models (RACRates) as well as a process for assessing the reliability of systems due to non-component variables which are major contributors to electronic system reliability. This new methodology factors in all available test and/or field reliability data as it becomes available on a program to form the best estimate of field reliability. The work was mainly concentrated here for reliability of electronic systems with the help of software tool PRISM. Features of this methodology were that it:

1. Models reliability based upon observed failure mode distributions.
2. Incorporates RAC's new component reliability models RACRates incorporates software reliability.
3. Models component reliability growth based upon observed industry trends.
4. Whether tailorable is based upon user failure experience data or not [10].

A.O.Charles Elegbede, et.al (2003) proposed the allocation of reliability and redundancy to parallel-series systems, while minimizing the cost of the system. It is proven that under usual conditions satisfied by cost functions, a necessary condition for optimal reliability allocation of parallel-series systems is that the reliability of the redundant components of a given subsystem are identical. This paper proved that the components in each stage of a parallel-series system must have identical reliability, under some nonrestrictive condition on the component's reliability cost functions. An algorithm, ECAY, was proposed for the design of systems with parallel-series architecture, which allows the allocation of both reliability and redundancy to each subsystem for a target reliability for minimizing the system cost. ECAY has the added advantage of allowing the optimal reliability allocation in a very short time. A benchmark is used to compare the ECAY performance to LM-based algorithms. For a given reliability target, ECAY produced the lowest reliability costs and the optimum redundancy levels in the successive reliability allocation for all cases studied. Thus ECAY, as compared with LM-based algorithms, yields a less costly reliability allocation within a reasonable computing time on large systems, and optimizes the weight and space-obstruction in system design throughout an optimal redundancy allocation [11].

Om P. Yadav et.al (2003) proposed a simple and practical two-stage approach of system reliability growth modeling considering components, functions, and failure modes. The consideration of these three dimensions will help in uncovering the weak spots in design responsible for low system reliability. In a product development process, to develop appropriate design validation and verification program for reliability assessment, one has to understand the functional behavior of the system, role of components in achieving required functions and failure modes if component/sub-system fails to perform required function. The integration of these three issues will help design and reliability engineers in identify in weak spots in design and planning future actions and testing program. The existing system-level reliability predictions are generally developed based on a system model and component level reliability prediction. These prediction methods are not of much help in pinpointing the exact location and nature of problem. Since time and budgetary constraints limit the extent of analysis and testing needed to estimate component reliability, it is necessary to utilize prior information available. System-reliability predictions should be updated iteratively as the design evolves and more information becomes available [12].

Fashandi (2003) discussed the essential requirements for establishing concise and effective reliability specifications, and proposed a method to define equipment failure. While product reliability has become a major concern to most organizations, many have overlook developing good reliability specifications. This oversight can result in ambiguous and purposeless reliability testing during validation phase of the product development. Effective reliability testing requires well-defined reliability specification. After all, the prime objective of a reliability engineering program is to test and assess product reliability. A common element that was vastly ignored hut rather critical to a sound reliability specification is definitions of equipment failure. Even the most vigorous reliability-testing program is of little use if the product being tested has poorly defined failure parameters. Product specifications are no longer limited to just meeting functionality measures (i.e., speed, capacity, range, etc) because for products with poor reliability and seldom available for use, functionality measures are meaningless. Reliability specification is the backbone of a reliability program and it is a prerequisite for reliability testing. Without this, the implementation of a reliability program will be difficult and frustrating process. Typical equipment reliability specification includes performance indices such MTBF and it must always be accompanied with clear definition if failure. Effective reliability testing heavily binges on clear definition of equipment failure. Without this definition as a baseline, any reliability discussions become meaningless [13].

Manthos Economou (2004) presented the merits and limitations of reliabilitypredictions as contrasted to reliability testing and assurance techniques from a product development standpoint. Every method offers a certain benefit at a certain cost, is limited by a time element. No single answer exists in accurately predicting and demonstrating reliability. Balancing cost, benefit and time, the essential elements of a new product reliability & quality assurance program, provide a framework for selecting the methods. Specific, theoretical and practical examples will be used to demonstrate the concepts and illustrate the methods that have been successfully used with encouraging results. In addition, useful interpretations of reliability predictions will be presented, since it appears many popular misconceptions exist in the electronics industry. MIL-based reliability prediction methods are consistent, mathematically simple, but inherently inaccurate, usually erring on the conservative side. This limitation may be overcome with the use of historical data and appropriate correction factors rendering reliability predictions quite accurate on a practical level. The reliability predictions should not be taken at face value, but as a figure of merit or adequate baseline towards comparative studies of design alternatives, evaluation of competitive products, or early forecasting of the total lifecycle cost of a product. The value of these methods is very high at the early stages of the product development where no physical product exists, but the value decreases rapidly as prototypes become available for testing [14].

Milena Krasich, et.al (2004) proposed and compared two models - one motivated by the practical engineering process (the Modified Power Law) and the other by extending the reasoning of statistical reliability growth modeling (the Modified IBM). The commonalities and differences between these models are explored through an assessment of their logic and an application. The choice of model depends on the growth process being modeled. Key drivers are the type of system design and the project management of the growth process. When the design activities are well understood and project workloads can be managed evenly, leading to predictable and equally spaced modifications each of which having a similar effect on the reliability of the item, then the Modified Power Law is a more appropriate model [15].

Preston R. et.al (2006) presented the results of the recent Small Business Innovation Research (SBIR) Phase II PROTOCOL program carried out for the US Army Aviation and Missile Research, Development, and Engineering Center (AMRDEC) at Redstone Arsenal, Alabama. PROTOCOL provides tailorable reliability decision recommendations, analysis tools, rules-of-thumb, checklists, and lessons-learned coupled with the program specific constraints/schedule, requirements, and results tracking in a web based environment. PROTOCOL has been developed primarily to serve the reliability engineer, but it can also be used as a management aid to track the progress of development efforts and to ensure consistency among reliability approaches across a reliability organization with varying experience levels. Access to various portions of PROTOCOL can also be provided to interested parties outside the primary reliability organization. PROTOCOL has been designed to be a reliability knowledge environment that grows over time. Users continually add knowledge as new data/information sources, new definitions, new lessons-learned, new rules-of-thumb and the like, all while tracking the reliability. Progress of products/systems that have been developed. PROTOCOL “learns” from informed decisions as it is used, as a means to improve the organization’s reliability decision-making processes [16].

Ilse M. de Visser et.al (2006) illustrated the risks of applying qualitative reliability prediction methods in practice and make suggestions for improving the application of these methods. This illustration is based on a complete reliability prediction approach named ROMDA. This ROMDA approach adopts FMEA to predict product reliability and will be presented in the second section. Subsequently this ROMDA approach is applied in a practical situation after which the reliability predictions are evaluated. Based on this evaluation, general conclusions and recommendations are described in order to improve the application of qualitative reliability prediction methods in practice. In current business processes qualitative reliability prediction methods are often applied toestimate the reliability risks present in products and processes. An example of a popular qualitative reliability prediction method is the so-called Failure Mode and Effects Analysis (FMEA) [17].

John Nierwinski Jr (2006) validates a reliability sampling methodology using simulation, and re-sampling; and which incorporates unit-to-unit variation in the determination of significant sample sizes for analytically intractable reliability cases. This sample size determination is very important because the reliability of the sampled vehicles should represent the reliability of the entire fleet. Smaller-than-required sample sizes may lead to an incorrect representation of the reliability of the fleet, which may mislead the Army to make poor decisions, such as deploying a fleet that may not be reliable. These type II errors can be minimized by incorporating a more realistic sampling methodology, as developed in this research [18].

Dr. Michel Houtermans et.al (2007) tried to implement reliability programs to improve plant safety while trying to maintain plant availability. These programs can vary significantly in size and complexity. Any kind of reliability program, like a preventive maintenance (PM) program, consists always of one or more reliability models and reliability data to execute these models. It is needless to say that the actual successful implementation and utilization of these reliability programs heavily depends on the accuracy of the reliability models and the availability of realistic data, or at least as close as possible data [19].

Milena Krasich (2007) discussed the dependency of the reliability estimates or requirements on the use environments, including the details of reliability changes of electronic and mechanical components as a function of environmental and operational stresses as well as of their duty cycle. He also provided a discussion of the fundamental differences between the product validation and reliability demonstration or assessment. He also showed how the same product used in a different location of a system, e.g. vehicle, or in merely different orientation that affected its natural heat transfer that had different reliability estimates. For that reason, the reliability requirements or goals need to be tailored for the product actual expected use. The reliability details such as dependency on the product use cannot be numerically tailored at all times for all locations and details of use, especially contractually. Therefore specification of reliability requirements in a form of a reliability range in average and or a minimum reliability in the harshest use profile is needed rather than as a fixed numerical value [20].

Christian Tanguy (2007) calculated the network reliability in a probabilistic Context that had long been an issue of practical and academic importance. Conventional approaches (determination of bounds, sums of disjoint products algorithms, Monte Carlo evaluations, studies of the reliability polynomials, etc.) only provide approximations when the network's size increases, even when nodes do not fail and all edges have the same reliability p.He considered the directed, generic graph of arbitrary size mimicking real-life long-haul communication networks, and gave the exact, analytical solution for the two-terminal reliability. This solution involved a product of transfer matrices, in which individual reliabilities of edges and nodes are taken into account. The special case of identical edge and node reliabilities were addressed. He considered a case study based on a commonly-used configuration, and assessed the influence of the edges being directed (or not) on various measures of network performance. While the two-terminal reliability, the failure frequency and the failure rate of the connection were quite similar, the locations of complex zeros of the two-terminal reliability polynomials exhibited strong differences [21].

Mihir R. Choudhury (2009) proposed the reliability analysis of logic circuits which was computationally complex because of the exponential number of inputs, combinations, and correlations in gate failures. He presented three accurate and scalable algorithms for reliability analysis of logic circuits. The first algorithm, called observability-based reliability analysis, provides a closed form expression for reliability and is accurate when single gate failures are dominant in a logic circuit. The second algorithm, called single-pass reliability analysis, computes reliability in a single topological walk through the logic circuit. It computes the exact reliability for circuits without reconvergent fan-out, even in the presence of multiple gate failures. The algorithm can also handle circuits with reconvergent fan-out with high accuracy using correlation coefficients as described in this paper. The third algorithm, called maximum-k gate failure reliability analysis, allows a constraint on the maximum number (k) of gates that can fail simultaneously in a logic circuit. Simulation results for several benchmark circuits demonstrated the accuracy, performance, and potential applications of the proposed algorithms [22].

# CHAPTER 3

# GAS CHROMATOGRAPHY –MASS SPECTROMETRY

## 3.1 Introduction

The use of a mass spectrometer as the detector in gas chromatography was developed during the 1950s by Roland Gohlke and Fred McLafferty. These sensitive devices were bulky, fragile, and originally limited to laboratory settings. The development of affordable and miniaturized computers has helped in the simplification of the use of this instrument, as well as allowed great improvements in the amount of time it takes to analyze a sample. In 1996 the top-of-the-line high-speed GC-MS units completed analysis of fire accelerants in less than 90 seconds, whereas first-generation GC/MS would have required at least 16 minutes. This has led to their widespread adoption in a number of fields.

Gas chromatography coupled with mass spectrometry is a powerful, quick, and convenient tool for organic analysis. An unknown sample of volatile gases is injected into a gas chromatograph producing a separation the basic individual gases with respect to time versus the absorption the gases. Next, these isolated gases are injected into a mass spectrometer where they pass through an ion source, mass analyzer, and ion detector to produce a spectrum of elemental mass versus the abundance of the elements.

## 3.2 Gas Chromatography

Gas Chromatography is the separation of a mixture of compounds (solutes) into separate components, which then can me analyzed by a Mass Spectrometer to give us detailed empirical molecular information regarding the chemistry of the samples. In gas chromatography (GC), the sample is vaporized and injected onto chromatographic columns and then separate into many components. The elution is brought about by the flow of an inert gaseous mobile phase. Carrier gases, which compose the mobile phase of GC, include helium, argon, and nitrogen. And the stationary phase of GC is a solid or liquid with a large surface where the absorption of the solutes takes place.

The basic components of the GC include the carrier gas supply, the sample introduction system, and the detection system. GC has a gaseous mobile phase, the carrier gas, a column containing the stationary phase and a injector for sample introduction by syringe injection. The detectors generate a signal current requiring an amplifier for output to produce the chromatogram.

## 3.3 Mass Spectrometry

Mass spectrometers measure the mass-to-charge ratio of individual molecules that have been converted into ions and this information is then used to determine the masses of the molecules. In mass spectroscopy, the sample (liquid, solid, solution, or vapor) enters the vacuum chamber through an inlet and depending on the sample, it may be ionized if it already isn’t. The ions are sorted in the mass analyzer according to their mass-to-charge ratios and then collected by a detector where the ion flux is converted to a proportional electrical current that is used to produce a mass spectrum.

### 3.3.1 Functionality

GC/MS will be used on Mars in an effort to explore the chemistry of the subsurface. It is one of the intermediate steps in the search for life where interesting samples will be analyzed to determine is further testing on the sample is necessary and useful as determined by the scientists on Mars and standard protocols.

The GC/MS system will be stationed in the laboratory habitat on Mars and if possible on at least one LMR. Weight of GC/MS*:* approximately 70-140 kg

## 3.4 Gas-liquid chromatography

Gas-liquid chromatography (GLC), or simply gas chromatography (GC), is a common type of chromatography used in organic chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound. In microscale chemistry, GC can be used to prepare pure compounds from a mixture.

In gas chromatography, the moving phase (or "mobile phase") is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a piece of glass or metal tubing called a column. The instrument used to perform gas chromatography is called a gas chromatograph (or "aerograph", "gas separator").

Figure 3.1 Gas chromatograph with a headspace sampler

The gaseous compounds being analyzed interact with the walls of the column, which is coated with different stationary phases. This causes each compound to elute at a different time, known as the retention time of the compound. The comparison of retention times is what gives GC its analytical usefulness. Gas chromatography is in principle similar to column chromatography (as well as other forms of chromatography, such as HPLC, TLC), but has several notable differences. Firstly, the process of separating the compounds in a mixture is carried out between a liquid stationary phase and a gas moving phase, whereas in column chromatography the stationary phase is a solid and the moving phase is a liquid. (Hence the full name of the procedure is "Gas-liquid chromatography", referring to the mobile and stationary phases, respectively.) Secondly, the column through which the gas phase passes is located in an oven where the temperature of the gas can be controlled, whereas column chromatography (typically) has no such temperature control. Thirdly, the concentration of a compound in the gas phase is solely a function of the vapor pressure of the gas.

Gas chromatography is also similar to fractional distillation, since both processes separate the components of a mixture primarily based on boiling point (or vapor pressure) differences. However, fractional distillation is typically used to separate components of a mixture on a large scale, whereas GC can be used on a much smaller scale (i.e. microscale).

## 3.5 GC analysis

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time. Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, and the temperature.

In a GC analysis, a known volume of gaseous or liquid analyst is injected into the "entrance" (head) of the column, usually using a micro syringe (or, solid phase microextraction fibers, or a gas source switching system). As the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified (qualitatively) by the order in which they emerge (elute) from the column and by the retention time of the analyte in the column.

## 3.6 Physical component

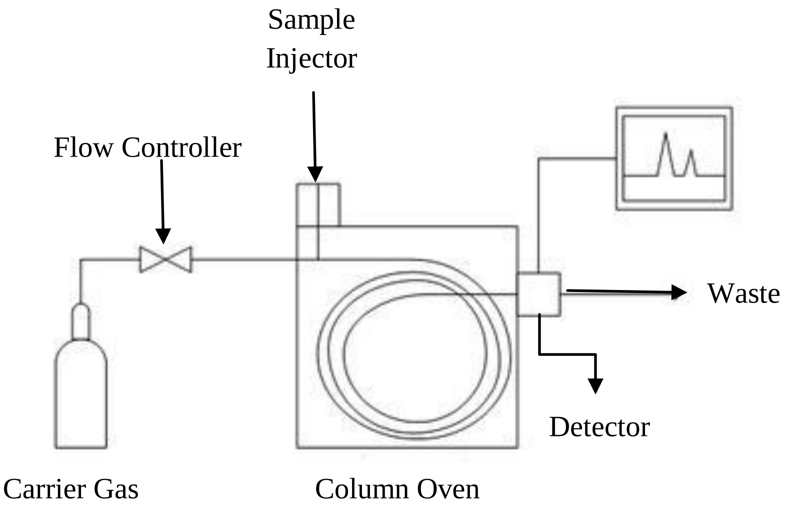


Figure 3.2 Diagram of a gas chromatograph

### 3.6.1 Autosamplers

The autosampler provides the means to introduce a sample automatically into the inlets. Manual insertion of the sample is possible but is no longer common. Automatic insertion provides better reproducibility and time-optimization.

Different kinds of autosamplers exist. Autosamplers can be classified in relation to sample capacity (auto-injectors vs. autosamplers, where auto-injectors can work a small number of samples), to robotic technologies (XYZ robot vs. rotating/SCARA-robot – the most common), or to analysis:

1. Liquid
2. Static head-space by syringe technology
3. Dynamic head-space by transfer-line technology
4. Solid phase microextraction (SPME)

Traditionally autosampler manufacturers are different from GC manufacturers and currently no GC manufacturer offers a complete range of auto samplers. Historically, the countries most active in autosampler technology development are the United States, Italy, and Switzerland.

### 3.6.2 Inlets

The column inlet provides the means to introduce a sample into a continuous flow of carrier gas. The inlet is a piece of hardware attached to the column head.

Common inlet types are:

1. **S/SL (Split/Splitless) injector;** a sample is introduced into a heated small chamber via a syringe through a septum - the heat facilitates volatilization of the sample and sample matrix. The carrier gas then either sweeps the entirety or a portion of the sample into the column. In split mode, a part of the sample/carrier gas mixture in the injection chamber is exhausted through the *split vent*. Split injection is preferred when working with samples with high analyte concentrations (>0.1%) whereas splitless injection is best suited for trace analysis with low amounts of analytes. (<0.01%)
2. **On-column inlet**; the sample is here introduced in its entirety without heat.
3. **PTV injector**; Temperature-programmed sample introduction was first described by Vogt in 1979. Originally Vogt developed the technique as a method for the introduction of large sample volumes (up to 250 µL) in capillary GC. Vogt introduced the sample into the liner at a controlled injection rate. The temperature of the liner was chosen slightly below the boiling point of the solvent. The low-boiling solvent was continuously evaporated and vented through the split line. Based on this technique, Poy developed the Programmed Temperature Vaporising injector; PTV. By introducing the sample at a low initial liner temperature many

of the disadvantages of the classic hot injection techniques could be circumvented.

4. **Gas source inlet** or **gas switching valve**; gaseous samples in collection bottles are connected to what is most commonly a six-port switching valve. The carrier gas flow is not interrupted while a sample can be expanded into a previously evacuated sample loop. Upon switching, the contents of the sample loop are inserted into the carrier gas stream.
5. **P/T (Purge-and-Trap) system**; an inert gas is bubbled through an aqueous sample causing insoluble volatile chemicals to be purged from the matrix. The volatiles are 'trapped' on an absorbent column (known as a trap or concentrator) at ambient temperature. The trap is then heated and the volatiles are directed into the carrier gas stream. Samples requiring preconcentration or purification can be introduced via such a system, usually hooked up to the S/SL port.
6. **SPME** (solid phase microextraction) offers a convenient, low-cost alternative to P/T systems with the versatility of a syringe and simple use of the S/SL port.

### 3.6.3 Columns

Two types of columns are used in GC:

1. **Packed columns** are 1.5 - 10 m in length and have an internal diameter of 2 - 4 mm. The tubing is usually made of stainless steel or glass and contains a packing of finely divided, inert, solid support material (eg. diatomaceous earth) that is coated with a liquid or solid stationary phase. The nature of the coating material determines what type of materials will be most strongly adsorbed. Thus numerous columns are available that are designed to separate specific types of compounds.
2. **Capillary columns** have a very small internal diameter, on the order of a few tenths of millimeters, and lengths between 25-60 meters are common. The inner column walls are coated with the active materials (WCOT columns), some columns are quasi solid filled with many parallel micropores (PLOT columns). Most capillary columns are made of fused-silica with a polyimide outer coating. These columns are flexible, so a very long column can be wound into a small coil.

3. **New developments** are sought where stationary phase incompatibilities lead to geometric solutions of parallel columns within one column. Among these new developments are:
    a) Internally heated microfast columns, where two columns, an internal heating wire and a temperature sensor are combined within a common column sheath (micro FAST);
    b) Micro packed columns (1/16" OD) are column-in-column packed columns where the outer column space has a packing different from the inner column space, thus providing the separation behaviour of two columns in one. They can easily fit to inlets and detectors of a capillary column instrument.

The temperature-dependence of molecular adsorption and of the rate of progression along the column necessitates a careful control of the column temperature to within a few tenths of a degree for precise work. Reducing the temperature produces the greatest level of separation, but can result in very long elution times. For some cases temperature is ramped either continuously or in steps to provide the desired separation. This is referred to as a temperature program. Electronic pressure control can also be used to modify flow rate during the analysis, aiding in faster run times while keeping acceptable levels of separation.

The choice of carrier gas is important, with hydrogen being the most efficient and providing the best separation. However, helium has a larger range of flowrates that are comparable to hydrogen in efficiency, with the added advantage that helium is non-flammable, and works with a greater number of detectors. Therefore, helium is the most common carrier gas used.

### 3.6.4 Detectors

A number of detectors are used in gas chromatography. The most common are the flame ionization detector (FID) and the thermal conductivity detector (TCD). Both are sensitive to a wide range of components, and both work over a wide range of concentrations.

While TCDs are essentially universal and can be used to detect any component other than the carrier gas (as long as their thermal conductivities are different from that of the carrier gas, at detector temperature), FIDs are sensitive primarily to hydrocarbons, and are more sensitive to them than TCD. However, an FID cannot detect water. Both detectors are also quite robust. Since TCD is non-destructive, it can be operated in-series before an FID (destructive), thus providing complementary detection of the same analytes.

Other detectors are sensitive only to specific types of substances, or work well only in narrower ranges of concentrations. They include:

1. Discharge Ionization Detector (DID), which uses a high-voltage electric discharge to produce ions.
2. Electron Capture Detector (ECD), which uses a radioactive Beta particle (electron) source to measure the degree of electron capture.
3. Flame Photometric Detector (FPD)
4. Flame Ionization Detector (FID)
5. Hall Electrolytic Conductivity detector (HECD)
6. Helium Ionization Detector (HID)
7. Nitrogen Phosphorus Detector (NPD)
8. Mass Selective Detector (MSD)
9. Photo-Ionization Detector (PID)
10. Pulsed Discharge Ionization Detector (PDD)
11. Thermal Energy(Conductivity) Analyzer/Detector (TEA/TCD)

Some gas chromatographs are connected to a mass spectrometer which acts as the detector. The combination is known as GC-MS. Some GC-MS are connected to an NMR spectrometer which acts as a backup detector. This combination is known as GC-MS-NMR. Some GC-MS-NMR is connected to an infrared spectrophotometer which acts as a back up detector. This combination is known as GC-MS-NMR-IR. It must, however, be stressed this is very rare as most analyses needed can be concluded via purely GC-MS.

## 3.7 Methods of Processing

It is the collection of conditions in which the GC operates for a given analysis. Method development is the process of determining what conditions are adequate and/or ideal for the analysis required.

Conditions which can be varied to accommodate a required analysis include inlet temperature, detector temperature, column temperature and temperature program, carrier gas and carrier gas flow rates, the column's stationary phase, diameter and length, inlet type and flow rates, sample size and injection technique. Depending on the detector(s) (see below) installed on the GC, there may be a number of detector conditions that can also be varied. Some GCs also include valves which can change the route of sample and carrier flow. The timing of the opening and closing of these valves can be important to method development.

Figure 3.3 Interior of GC-MS

This image above shows the interior of a GeoStrata Technologies Eclipse Gas Chromatograph that runs continuously in three minute cycles. Two valves are used to switch the test gas into the sample loop. After filling the sample loop with test gas, the valves are switched again applying carrier gas pressure to the sample loop and forcing the sample through the Column for separation.

### 3.7.1 Carrier gas selection and flow rates

Typical carrier gases include helium, nitrogen, argon, hydrogen and air. Which gas to use is usually determined by the detector being used, for example, a DID requires helium as the carrier gas. When analyzing gas samples, however, the carrier is sometimes selected based on the sample's matrix, for example, when analyzing a mixture in argon, an argon carrier is preferred, because the argon in the sample does not show up on the chromatogram. Safety and availability can also influence carrier selection, for example, hydrogen is flammable, and high-purity helium can be difficult to obtain in some areas of the world. The purity of the carrier gas is also frequently determined by the detector, though the level of sensitivity needed can also play a significant role. Typically, purities of 99.995% or higher are used. Trade names for typical purities include "Zero Grade," "Ultra-High Purity (UHP) Grade," "4.5 Grade" and "5.0 Grade."

The carrier gas flow rate affects the analysis in the same way that temperature does (see above). The higher the flow rate the faster the analysis, but the lower the separation between analytes. Selecting the flow rate is therefore the same compromise between the level of separation and length of analysis as selecting the column temperature.

With GCs made before the 1990s, carrier flow rate was controlled indirectly by controlling the carrier inlet pressure, or "column head pressure." The actual flow rate was measured at the outlet of the column or the detector with an electronic flow meter, or a bubble flow meter, and could be an involved, time consuming, and frustrating process. The pressure setting was not able to be varied during the run, and thus the flow was essentially constant during the analysis. The relation between flow rate and inlet pressure is calculated with Poiseuille's equation for compressible fluids.Many modern GCs, however, electronically measure the flow rate, and electronically control the carrier gas pressure to set the flow rate. Consequently, carrier pressures and flow rates can be adjusted during the run, creating pressure/flow programs similar to temperature programs.

### 3.7.2 Inlet types and flow rates

The choice of inlet type and injection technique depends on if the sample is in liquid, gas, adsorbed, or solid form, and on whether a solvent matrix is present that has to be vaporized. Dissolved samples can be introduced directly onto the column via a COC injector, if the conditions are well known; if a solvent matrix has to be vaporized and partially removed, a S/SL injector is used (most common injection technique); gaseous samples (e.g., air cylinders) are usually injected using a gas switching valve system; adsorbed samples (e.g., on adsorbent tubes) are introduced using either an external (on-line or off-line) desorption apparatus such as a purge-and-trap system, or are desorbed in the S/SL injector (SPME applications).

## 3.8 Sample size and injection technique

The sample size and injection techniques are explained below:

### 3.8.1 Sample injection

The real chromatographic analysis starts with the introduction of the sample onto the column. The development of capillary gas chromatography resulted in many practical problems with the injection technique. The technique of on-column injection, often used with packed columns, is usually not possible with capillary columns. The injection system, in the capillary gas chromatograph, should fulfil the following two requirements:

1. The amount injected should not overload the column.
2. The width of the injected plug should be small compared to the spreading due to the chromatographic process. Failure to comply with this requirement will reduce the separation capability of the column. As a general rule, the volume injected, $V_{inj}$, and the volume of the detector cell, $V_{det}$, should be about 1/10 of the volume occupied by the portion of sample containing the molecules of interest (analytes) when they exit the column.

Some general requirements, which a good injection technique should fulfill, are:

1. It should be possible to obtain the column’s optimum separation efficiency.
2. It should allow accurate and reproducible injections of small amounts of representative samples.
3. It should induce no change in sample composition. It should not exhibit discrimination based on differences in boiling point, polarity, concentration or thermal/catalytic stability.
4. It should be applicable for trace analysis as well as for undiluted samples.

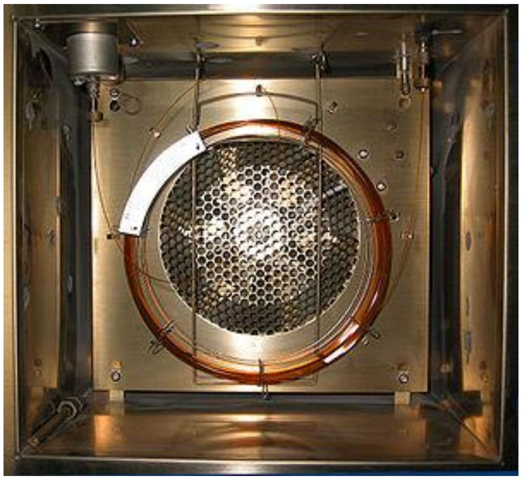


Figure 3.4 Gas chromatography oven, open to show a capillary column

The column(s) in a GC are contained in an oven, the temperature of which is precisely controlled electronically. (When discussing the "temperature of the column," an analyst is technically referring to the temperature of the column oven. The rate at which a sample passes through the column is directly proportional to the temperature of the column. The higher the column temperature, the faster the sample moves through the column. However, the faster a sample moves through the column, the less it interacts with the stationary phase, and the less the analytes are separated.

In general, the column temperature is selected to compromise between the length of the analysis and the level of separation. A method which holds the column at the same temperature for the entire analysis is called "isothermal." Most methods, however, increase the column temperature during the analysis, the initial temperature, rate of temperature increase (the temperature "ramp") and final temperature is called the "temperature program."

A temperature program allows analytes that elute early in the analysis to separate adequately, while shortening the time it takes for late-eluting analytes to pass through the column.

## 3.9 Data reduction and analysis

There are two types of data reduction techniques which are explained below:

**1. Qualitative analysis:** Generally chromatographic data is presented as a graph of detector response (y-axis) against retention time (x-axis), which is called a chromatogram. This provides a spectrum of peaks for a sample representing the analyses present in a sample eluting from the column at different times. Retention time can be used to identify analytes if the method conditions are constant. Also, the pattern of peaks will be constant for a sample under constant conditions and can identify complex mixtures of analytes. In most modern applications however the GC is connected to a mass spectrometer or similar detector that is capable of identifying the analytes represented by the peaks.

**2. Quantitive analysis:** The area under a peak is proportional to the amount of analyte present in the chromatogram. By calculating the area of the peak using the mathematical function of integration, the concentration of an analyte in the original sample can be determined. Concentration can be calculated using a calibration curve created by finding the response for a series of concentrations of analyte, or by determining the relative response factor of an analyte. The relative response factor is the expected ratio of an analyte to an internal standard (or external standard) and is calculated by finding the response of a known amount of analyte and a constant amount of internal standard (a chemical added to the sample at a constant concentration, with a distinct retention time to the analyte).

In most modern GC-MS systems, computer software is used to draw and integrate peaks, and match MS spectra to library spectra.

### 3.9.1 Application

In general, substances that vaporize below ca. 300 °C (and therefore are stable up to that temperature) can be measured quantitatively. The samples are also required to be salt-free; they should not contain ions. Very minute amounts of a substance can be measured, but it is often required that the sample must be measured in comparison to a sample containing the pure, suspected substance.

Various temperature programs can be used to make the readings more meaningful; for example to differentiate between substances that behave similarly during the GC process.

Professionals working with GC analyze the content of a chemical product, for example in assuring the quality of products in the chemical industry; or measuring toxic substances in soil, air or water. GC is very accurate if used properly and can measure picomoles of a substance in a 1 ml liquid sample, or parts-per-billion concentrations in gaseous samples.

In practical courses at colleges, students sometimes get acquainted to the GC by studying the contents of Lavender oil or measuring the ethylene that is secreted by Nicotiana benthamiana plants after artificially injuring their leaves. These GC analyses hydrocarbons (C2-C40+). In a typical experiment, a packed column is used to separate the light gases, which are then detected with a TCD. The hydrocarbons are separated using a capillary column and detected with an FID. A complication with light gas analyses that include $H_2$ is that He, which is the most common and most sensitive inert carrier (sensitivity is proportional to molecular mass) has an almost identical thermal conductivity to hydrogen (it is the difference in thermal conductivity between two separate filaments in a Wheatstone Bridge type arrangement that shows when a component has been eluted). For this reason, dual TCD instruments are used with a separate channel for hydrogen that uses nitrogen as a carrier are common. Argon is often used when analyzing gas phase chemistry reactions such as F-T synthesis so that a single carrier gas can be used rather than 2 separate ones. The sensitivity is less but this is a tradeoff for simplicity in the gas supply.

### 3.10 Instrumentation used in GC-MS.

The insides of the GC-MS, with the column of the gas chromatograph in the oven on the right. The GC-MS is composed of two major building blocks: the gas chromatograph and the mass spectrometer. The gas chromatograph utilizes a capillary column which depends on the column's dimensions (length, diameter, film thickness) as well as the phase properties (e.g. 5% phenyl polysiloxane). The difference in the chemical properties between different molecules in a mixture will separate the molecules as the sample travels the length of the column.

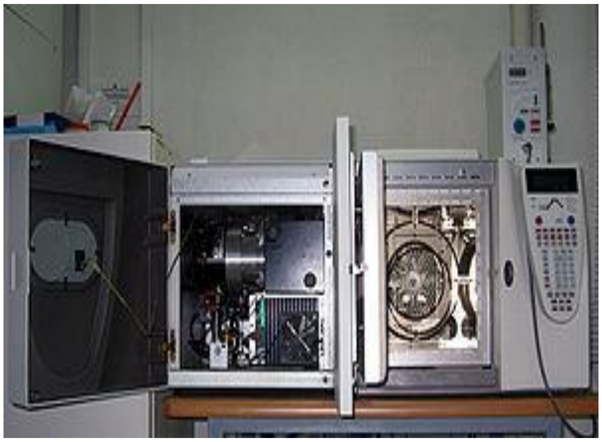


Figure 3.5 Instrumentation used in GC-MS

The difference in the chemical properties between different molecules in a mixture will separate the molecules as the sample travels the length of the column. The molecules take different amounts of time (called the retention time) to come out of (elute from) the gas chromatograph, and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio.

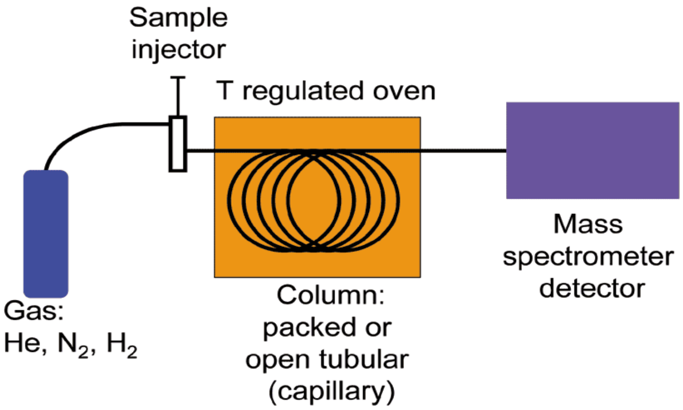


Figure 3.6 GC-MS schematic diagram

These two components, used together, allow a much finer degree of substance identification than either unit used separately. It is not possible to make an accurate identification of a particular molecule by gas chromatography or mass spectrometry alone. The mass spectrometry process normally requires a very pure sample while gas chromatography using a traditional detector (e.g. Flame Ionization Detector) detects multiple molecules that happen to take the same amount of time to travel through the column (*i.e.* have the same retention time) which results in two or more molecules to co-elute. Sometimes two different molecules can also have a similar pattern of ionized fragments in a mass spectrometer (mass spectrum). Combining the two processes makes it extremely unlikely that two different molecules will behave in the same way in both a gas chromatograph and a mass spectrometer. Therefore when an identifying mass spectrum appears at a characteristic retention time in a GC-MS analysis, it typically lends to increased certainty that the analyte of interest is in the sample.

### 3.10.1 Split/Splitless GC-MS inlets

Samples are introduced to the column via an inlet. This inlet is typically injection through a septum. Once in the inlet, the heated chamber acts to volatilize (vaporize) the sample. In a split system, a constant flow of carrier gas moves through the inlet. A portion of the carrier gas flow acts to transport the sample into the column. Another portion of the carrier gas flow gets directed to purge the inlet of any sample following injection (septum purge). Yet another portion of the flow is directed through the split vent in a set ratio known as the split ratio. In a split less system, the advantage is that a larger amount of sample is introduced to the column. However, a split system is preferred when the detector is sensitive to trace amounts of analyte and there is concern about overloading the column.

### 3.10.2 Purge and Trap GC-MS

For the analysis of volatile compounds a Purge and Trap (P&T) concentrator system may be used to introduce samples. The target analytes are extracted and mixed with water and introduced into an airtight chamber. An inert gas such as Nitrogen ($N_2$) is bubbled through the water; this is known as purging. The volatile compounds move into the headspace above the water and are drawn along a pressure gradient(caused by the introduction of the purge gas) out of the chamber. The volatile compounds are drawn along a heated line onto a 'trap'. the trap is a column of adsorbent material at ambient temperature that holds the compounds by returning them to the liquid phase. The trap is then heated and the sample compounds are introduced to the GC-MS column via a volatiles interface, which is a split inlet system. P&T GC-MS is particularly suited to volatile organic compounds (VOCs) and BTEX compounds (aromatic compounds associated with petroleum).

### 3.10.3 Types of Mass Spectrometer Detectors

The most common type of mass spectrometer (MS) associated with a gas chromatograph (GC) is the quadrupole mass spectrometer, sometimes referred to by the Hewlett-Packard trade name "Mass Selective Detector" (MSD). Another relatively common detector is the ion trap mass spectrometer. Additionally one may find a magnetic sector mass spectrometer, however these particular instruments are expensive and bulky and not typically found in high-throughput service laboratories. Other detectors may be encountered such as time of flight (TOF), tandem quadrupoles (MS-MS) (see below), or in the case of an ion trap $MS^n$ where n indicates the number mass spectrometry stages.

## 3.11 Analysis of Mass Spectrometry

A mass spectrometer is typically utilized in one of two ways:

1. Full Scan
2. Selective Ion Monitoring (SIM)

The typical GC/MS instrument is capable of performing both functions either individually or concomitantly, depending on the setup of the particular instrument.

### 3.11.1 Full scan MS

When collecting data in the full scan mode, a target range of mass fragments is determined and put into the instrument's method. An example of a typical broad range of mass fragments to monitor would bem/z 50 to m/z 400. The determination of what range to use is largely dictated by what one anticipates in being in the sample while being cognizant of the solvent and other possible interferences. A MS should not be set to look for mass fragments too low or else one may detect air (found as *m/z* 28 due to nitrogen), carbon dioxide (*m/z* 44) or other possible interferences. Additionally if one is to use a large scan range then sensitivity of the instrument is decreased due to performing fewer scans per second since each scan will have to detect a wide range of mass fragments.

Full scan is useful in determining unknown compounds in a sample. It provides more information than SIM when it comes to confirming or resolving compounds in a sample. During instrument method development it may be common to first analyze test solutions in full scan mode to determine the retention time and the mass fragment fingerprint before moving to a SIM instrument method.

### 3.11.2 Selective Ion Monitoring

In Selective Ion Monitoring (SIM) certain ion fragments are entered into the instrument method and only those mass fragments are detected by the mass spectrometer. The advantages of SIM are that the detection limit is lower since the instrument is only looking at a small number of fragments (e.g. three fragments) during each scan. More scans can take place each second. Since only a few mass fragments of interest are being monitored, matrix interferences are typically lower. To additionally confirm the likelihood of a potentially positive result, it is relatively important to be sure that the ion ratios of the various mass fragments are comparable to a known reference standard.

### 3.11.3 Types of Ionization

After the molecules travel the length of the column, pass through the transfer line and enter into the mass spectrometer they are ionized by various methods with typically only one method being used at any given time. Once the sample is fragmented it will then be detected, usually by an electron multiplier diode, which essentially turns the ionized mass fragment into an electrical signal that is then detected.

The ionization technique chosen is independent of using Full Scan or SIM.

#### 3.11.3.1 Electron Ionization

By far the most common and perhaps standard form of ionization is electron ionization (EI). The molecules enter into the MS (the source is a quadrupole or the ion trap itself in an ion trap MS) where they are bombarded with free electrons emitted from a filament, not much unlike the filament one would find in a standard light bulb. The electrons bombard the molecules causing a hard ionization that fragments the molecule, and the way in which a molecule fragment is usually typical for all EI techniques.

### 3.11.3.2 Chemical Ionization

In chemical ionization a reagent gas, typically methane or ammonia is introduced into the mass spectrometer. Depending on the technique (positive CI or negative CI) chosen, this reagent gas will interact with the electrons and analyte and cause a 'soft' ionization of the molecule of interest. A softer ionization fragments the molecule to a lower degree than the hard ionization of EI. One of the main benefits of using chemical ionization is that a mass fragment closely corresponding to the molecular weight of the analyte of interest is produced.

1. Positive Chemical Ionization: In this, the reagent gas interacts with the target molecule, most often with a proton exchange. This produces the species in relatively high amounts.
2. Negative Chemical Ionization: In this, the reagent gas decreases the impact of the free electrons on the target analyte. This decreased energy typically leaves the fragment in great supply.

The primary goal of instrument analysis is to quantify an amount of substance. This is done by comparing the relative concentrations among the atomic masses in the generated spectrum. Two kinds of analysis are possible, comparative and original. Comparative analysis essentially compares the given spectrum to a spectrum library to see if its characteristics are present for some sample in the library. This is best performed by a computer because there are a myriad of visual distortions that can take place due to variations in scale. Computers can also simultaneously correlate more data (such as the retention times identified by GC), to more accurately relate certain data.

Another method of analysis measures the peaks in relation to one another. In this method, the tallest peak is assigned 100% of the value, and the other peaks being assigned proportionate values. All values above 3% are assigned. The total mass of the unknown compound is normally indicated by the parent peak. The value of this parent peak can be used to fit with a chemical formula containing the various elements which are believed to be in the compound. The isotope pattern in the spectrum, which is unique for elements that have many isotopes, can also be used to identify the various elements present. Once a chemical formula has been matched to the spectrum, the molecular structure and bonding can be identified, and must be consistent with the characteristics recorded by GC/MS. Typically, this identification done automatically by programs which come with the instrument, given a list of the elements which could be present in the sample.

A “full spectrum” analysis considers all the “peaks” within a spectrum. Conversely, selective ion monitoring (SIM) only monitors selected peaks associated with a specific substance. This is done on the assumption that at a given retention time, a set of ions is characteristic of a certain compound. This is a fast and efficient analysis, especially if the analyst has previous information about a sample or is only looking for a few specific substances. When the amount of information collected about the ions in a given gas chromatographic peak decreases, the sensitivity of the analysis increases. So, SIM analysis allows for a smaller quantity of a compound to be detected and measured, but the degree of certainty about the identity of that compound is reduced.

### 3.12 GC-MS/MS

When a second phase of mass fragmentation is added, for example using a second quadrupole in a quadrupole instrument, it is called MS/MS or Tandem MS. Tandem mass spectrometry (MS/MS) is a more powerful technique to quantitate low levels of target compounds in the presence of a high sample matrix background.

The first quadrupole (Q1) is connected with a collision cell (q2) and another quadrupole (Q3). Both quadrupoles can be used in scanning or static mode, depending on the type of MS/MS analysis being performed. Types of analysis include product ion scan, precursor ion scan, Single Reaction Monitoring (SRM) and Multiple Reaction Monitoring (MRM) and Neutral Loss Scan. For example: When Q1 is in static mode (looking at one mass only as in SIM), and Q3 is in scanning mode, one obtains a so-called product ion spectrum (also called "daughter spectrum"). From this spectrum, one can select a prominent product ion which can be the product ion for the chosen precursor ion. The pair is called a "transition" and forms the basis for SRM (MRM is sometimes used as term). SRM is highly specific and virtually eliminates matrix background.

## 3.13 Applications

Following are the applications of the GC-MS:

### 3.13.1 Environmental Monitoring and Cleanup

GC-MS is becoming the tool of choice for tracking organic pollutants in the environment. The cost of GC-MS equipment has decreased significantly, and the reliability has increased at the same time, which has contributed to its increased adoption in environmental studies. There are some compounds for which GC-MS is not sufficiently sensitive, including certain pesticides and herbicides, but for most organic analysis of environmental samples, including many major classes of pesticides, it is very sensitive and effective.

### 3.13.2 Criminal Forensics

GC-MS can analyze the particles from a human body in order to help link a criminal to a crime. The analysis of fire debris using GC-MS is well established, and there is even an established American Society for Testing Materials (ASTM) standard for fire debris analysis. GCMS/MS is especially useful here as samples often contain very complex matrices and results, used in court, needs to be highly accurate.

### 3.13.3 Law Enforcement

GC-MS is increasingly used for detection of illegal narcotics, and may eventually supplant drug-sniffing dogs. It is also commonly used in forensic toxicology to find drugs and/or poisons in biological specimens of suspects, victims, or the deceased.

### 3.13.4 Security

A post-September 11 development, explosive detection systems have become a part of all US airports. These systems run on a host of technologies, many of them based on GC-MS. There are only three manufacturers certified by the FAA to provide these systems one of which is Thermo Detection (formerly Thermedics), which produces the EGIS, a GC-MS-based line of explosives detectors. The other two manufacturers are Barringer Technologies, now owned by Smith's Detection Systems and Ion Track Instruments, part of General Electric Infrastructure Security Systems.

### 3.13.5 Food, Beverage and Perfume Analysis

Foods and beverages contain numerous aromatic compounds, some naturally present in the raw materials and some forming during processing. GC-MS is extensively used for the analysis of these compounds which include esters, fatty acids, alcohols, aldehydes, tarpons' etc. It is also used to detect and measure contaminant from spoilage or adulteration which may be harmful and which is often controlled by governmental agencies, for example pesticides.

### 3.13.6 Medicine

In combination with isotopic labeling of metabolic compounds, the GC-MS is used for determining metabolic activity. Most applications are based on the use of $^{13}C$ as the labeling and the measurement of $^{13}C/^{12}C$ ratios with an isotope ratio mass spectrometer (IRMS); an MS with a detector designed to measure a few select ions and return values as ratios.

## 3.14 GCs in popular culture

Movies, books and TV shows tend to misrepresent the capabilities of gas chromatography and the work done with these instruments. In the U.S. TV show CSI, for example, GCs are used to rapidly identify unknown samples. In fact, a typical GC analysis takes much more time; sometimes a single sample must be run more than an hour according to the chosen program; and even more time is needed to "heat out" the column so it is free from the first sample and can be used for the next. Equally, several runs are needed to confirm the results of a study - a GC analysis of a single sample may simply yield a result per chance.

Also, GC does not positively identify most samples; and not all substances in a sample will necessarily be detected. All a GC truly tells you is at which relative time a component eluted from the column and that the detector was sensitive to it. To make results meaningful, analysts need to know which components at which concentrations are to be expected; and even then a small amount of a substance can hide itself behind a substance having both a higher concentration and the same relative elution time. Last but not least it is often needed to check the results of the sample against a GC analysis of a reference sample containing only the suspected substance.

A GC-MS can remove much of this ambiguity, since the mass spectrometer will identify the component's molecular weight. But this still takes time and skill to do properly.
Similarly, most GC analyses are not push-button operations. You cannot simply drop a sample vial into an auto-sampler's tray, push a button and have a computer tell you everything you need to know about the sample. According to the substances one expects to find the operating program must be carefully chosen.

A push-button operation can exist for running similar samples repeatedly, such as in a chemical production environment or for comparing 20 samples from the same experiment to calculate the mean content of the same substance.

# CHAPTER 4

# FAULT TREE

## 4.1 Introduction

Fault Tree is a deductive, failure-based approach. As a deductive approach, FTA starts with an undesired event, such as failure of a main engine, and then determines causes using a systematic, backward-stepping process. In determining the causes, a fault tree (FT) is constructed as a logical illustration of the events and their relationships that are necessary and sufficient to result in the undesired event, or top event. The symbols used in a FT indicate the type of events and type of relationships that are involved. The FT is a qualitative model that provides extremely useful information on the causes of the undesired event. The FT can also be quantified to provide useful information on the probability of the top event occurring and the importance of all the causes and events modeled in the FT.

In addition to FTA, inductive approaches are also used in safety analysis and in risk and reliability analysis. In contrast to the deductive approach used in FTA, inductive approaches are forward-stepping approaches that begin with a basic cause or initiating event and then investigate (induce) the end effects. Both FTA and inductive approaches are failure-based.

A FT can be transformed into its logical complement, a success tree (ST) that shows the specific ways the undesired event can be prevented from occurring. The ST provides conditions that, if assured, guarantee that the undesired event will not occur. The ST is a valuable tool that provides equivalent information to the fault tree, but from a success viewpoint. Techniques for transforming the FT to its ST are described along with uses of the ST. The uses of FTA to assist decision-making are described in this AFTH. FTA provides critical information that can be used to prioritize the importance of the contributors to the undesired event. The contributor importance provided by FTA vividly shows the causes that are dominant and that should be the focus of any safety or reliability activity. More formal risk-benefit approaches can also be used to optimally allocate resources to minimize both resource expenditures and the occurrence probability of the undesired event. These risk benefit approaches are useful for allocating resource expenditures, such as safety upgrades to complex systems like the Space Shuttle. FTA can be applied to both an existing system and to a system that is being designed. When it is applied to a system being designed for which specific data do not exist, FTA can provide an estimate of the failure probability and the important contributors using generic data to bracket the design components or concepts. FTA can also be used as an important element in the development of a performance-based design. When applied to an existing system, FTA can be used to identify weaknesses and to evaluate possible upgrades. It can also be used to monitor and predict behavior. Furthermore, FTA can be used to diagnose causes and potential corrective measures for an observed system failure. The approaches and tools to obtain this information and the applications of this information in decision-making are important topics of the AFTH.

## 4.2 The Fault Tree Approach

FTA can be simply described as an analytical technique, whereby an undesired state of the system is specified (usually a state that is critical from a safety or reliability standpoint), and the system is then analyzed in the context of its environment and operation to find all realistic ways in which the undesired event (top event) can occur. The fault tree itself is a graphic model of the various parallel and sequential combinations of faults that will result in the occurrence of the predefined undesired event. The faults can be events that are associated with component hardware failures, human errors, software errors, or any other pertinent events which can lead to the undesired event. A fault tree thus depicts the logical interrelationships of basic events that lead to the undesired event, the top event of the fault tree. It is important to understand that a fault tree is not a model of all possible system failures or all possible causes for system failure. A fault tree is tailored to its top event that corresponds to some particular system failure mode, and the fault tree thus includes only those faults that contribute to this top event. Moreover, these faults are not exhaustive they cover only the faults that are assessed to be realistic by the analyst.

It is also important to point out that a fault tree is not in itself a quantitative model. It is a qualitative model that can be evaluated quantitatively and often is. This qualitative aspect, of course, is true of virtually all varieties of system models. The fact that a fault tree is a particularly convenient model to quantify does not change the qualitative nature of the model itself. Intrinsic to a fault tree is the concept that an outcome is a binary event i.e., to either success or failure. A fault tree is composed of a complex of entities known as "gates" that serve to permit or inhibit the passage of fault logic up the tree. The gates show the relationships of events needed for the occurrence of a "higher" event. The "higher" event is the output of the gate; the "lower" events are the "inputs" to the gate. The gate symbol denotes the type of relationship of the input events required for the output event. Figure 1-1 shows a simple fault tree.

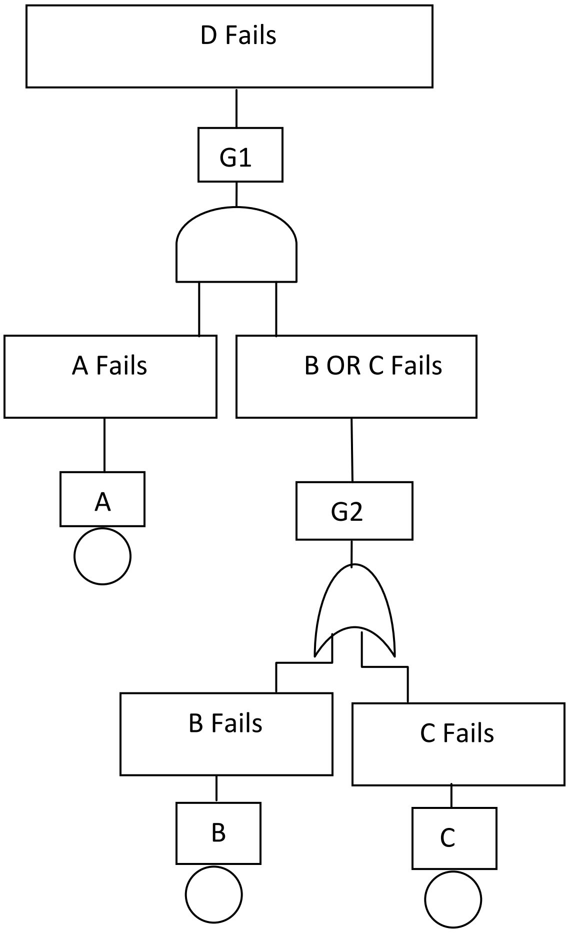


Figure 4.1 Simplified Fault Tree

## 4.3 Qualitative and Quantitative Evaluations of a Fault Tree

Both qualitative and quantitative evaluations can be performed on an FT. The FT itself is a qualitative assessment of the events and relationships that lead to the top event. In constructing the FT, significant insights and understanding are gained concerning the causes of the top event. Additional evaluations serve to further refine the information that the FT provides. The qualitative evaluations basically transform the FT logic into logically equivalent forms that provide more focused information. The principal qualitative results that are obtained are the minimal cut sets (MCSs) of the top event. A cut set is a combination of basic events that can cause the top event. An MCS is the smallest combination of basic events that result in the top event. The basic events are the bottom events of the fault tree. Hence, the minimal cut sets relate the top event directly to the basic event causes. The set of MCSs for the top event represent all the ways that the basic events can cause the top event. A more descriptive name for a minimal cut set may be “minimal failure set.” The set of MCSs can not only be obtained for the top event, but for any of the intermediate events (e.g., gate events) in the FT.

A significant amount of information can be obtained from the structure of MCSs. Any MCS with one basic event identifies a single failure or single event that alone can cause the top event to occur. These single failures are often weak links and are the focus of upgrade and prevention actions. Examples of such single failures are a single human error or single component failure that can cause a system failure. An MCS having events with identical characteristics indicates a susceptibility to implicit dependent failure, or common cause that can negate a redundancy. An example is an MCS of failures of identical valves. A single manufacturing defect or single environmental sensitivity can cause all the valves to simultaneously fail.

The quantitative evaluations of a FT consist of the determination of top event probabilities and basic event importance. Uncertainties in any quantified result can also be determined. Fault trees are typically quantified by calculating the probability of each minimal cut set and by summing all the cut set probabilities. The cut sets are then sorted by probability. The cut sets that contribute significantly to the top event probability are called the dominant cut sets. While the probability of the top event is a primary focus in the analysis, the probability of any intermediate event in the fault tree can also be determined. Different types of probabilities can be calculated for different applications. In addition to a constant probability value that is typically calculated, time-related probabilities can be calculated providing the probability distribution of the time of first occurrence of the top event. Top event frequencies, failure or occurrence rates, and availabilities can also be calculated. These characteristics are particularly applicable if the top event is a system failure.

In addition to the identification of dominant cut sets, importance of the events in the FT are some of the most useful information that can be obtained from FT quantification. Quantified importances allow actions and resources to be prioritized according to the importance of the events causing the top event. The importance of the basic events, the intermediate events, and the minimal cut sets can be determined. Different importance measures can be calculated for different applications. One measure is the contribution of each event to the top event probability. Another is the decrease in the top event probability if the event were prevented from occurring. A third measure is the increase in the top event probability if the event were assured to occur. These importance measures are used in prioritization, prevention activities, upgrade activities, and in maintenance and repair activities. Later sections describe in further detail the rich amount of qualitative and quantitative information that can be obtained from a FT.

## 4.4 Logical Complement of the Fault Tree

Since success and failure are related, the FT can be transformed into its equivalent ST. In the FT context, success in a success tree is specifically defined as the top event not occurring.. The ST is a logical complement of the FT, with the top event of the ST being the complement of the top event of the FT. For example, if the top event of the FT is “Occurrence of LOV,” LOV implying Loss of Vehicle, then the ST will have as a top event “Nonoccurrence of LOV.” The ST therefore defines the logic for the failure top event not occurring. Moreover, the ST identifies the minimal sets of basic events that need to be prevented in order to assure that the failure top event will not occur. These minimal sets of events that prevent the failure top event are termed the minimal path sets. A more descriptive name may be “minimal prevention sets” since they indicate how to prevent the occurrence of the failure top event and achieve success in terms of its nonoccurrence. The minimal path sets provide valuable information on the means by which the failure top event can be prevented even without quantification. Moreover, the ST can be quantified to provide the probability of success, i.e., nonoccurrence of the failure top event. Additionally, each of the minimal path sets can be quantified to prioritize the most effective methods for prevention (often in terms of cost to ensure prevention). Ability to analyze the top event from both a failure (occurrence) and success (nonoccurrence) standpoint increases the scope of information that can be obtained from these logic trees.

## 4.5 Role of FTA in Decision Making

A variety of information is provided by FTA to assist decision-making. An overview some of the major uses of FTA is presented here to give an appreciation of the breadth of applications of FTA in decision-making. This section includes some information already provided in previous sections for the benefit who want to focus on the FTA role in decision making.

1. Use of FTA to understand of the logic leading to the top event. FTA provides a visual, logic model of the basic causes and intermediate events leading to the top event. Typically, fault trees are not limited to a single system, but cross system boundaries. Because of this, they have shown great benefit in identifying system interactions that impact redundancy. The combination of failures and events that propagate through a system are clearly shown. The minimal cut sets can be organized and prioritized according to the number of events involved and their nature. For example, if there are minimal cut sets that contain only one component failure then this shows that single component failures can cause failure of the system. A failure path of only human errors shows that human errors alone can cause system failure. the qualitative information obtained from an FTA is of equal importance to the quantitative information provided.

2. Use of FTA to prioritize the contributors leading to the top event. One of the most important types of information from FTA is the prioritization of the contributors to the top event. If a FT is quantified, the failures and basic events that are the causes of the top events can be prioritized according to their importance. In addition, the intermediate faults and events leading to the top event can also be prioritized. Different prioritizations and different importance measures are produced for different applications. One of the valuable conclusions from FTAs is that generally only a few contributors are important to the top event. Often only 10% to 20% of the basic events contribute significantly to the top event probability. Moreover, the contributors often cluster in distinct groupings whose importance differs by orders of magnitude. The prioritizations obtained from FTA can provide an important basis for prioritizing resources and costs. Significant reductions in resource expenditures can be achieved with no impact to the system failure probability. For a given resource expenditure, the system failure probability can be minimized by allocating resources to be consistent with contributor importance. The importance measures obtained from a FTA are as important as the top event probability or the ranked cut set lists obtained from the analysis.

3. Use of FTA as a proactive tool to prevent the top event. FTA is often used to identify vulnerable areas in a system. These vulnerable areas can be corrected or improved before the top event occurs. Upgrades to the system can be objectively evaluated for their benefits in reducing the probability of the top event. The evaluation of upgrades is an important use of the FTA. Advocates of different corrective measures and upgrades will often claim that what they are proposing provides the most benefit and they may be correct from their local perspective. However, FTA is a unique tool that provides a global perspective through a systematic and objective measure of the impact of a benefit on the top event. The probability of the top event an be used to determine the criticality of carrying out the upgrades. The probability of the top event can be compared to acceptability criteria or can be used in cost benefit evaluations. Advances in cost benefit

methodology allow uncertainties and risk aversion to be incorporated as well as the probabilities. Furthermore, success paths provided from FTA can be used to identify specific measures that will prevent the top event. The proactive use of FTA has been shown to be one of its most beneficial uses.

4. Use of FTA to monitor the performance of the system. The use of the FT as a monitoring tool is a specific proactive use that has been identified because of its special features. When monitoring performance with regard to the top event, FTA can account for updates in the basic event data as well as for trending and time dependent behaviors, including aging effects. Using systematic updating techniques, the fault tree can be re-evaluated with new information that can include information on defects and near failures. Actions can then be identified to maintain or replace necessary equipment to control the failure probability and risk. This use of FTA as a monitoring tool is common in the nuclear industry.

5. Use of FTA to minimize and optimize resources. This particular use of FTA is sometimes overlooked but it is one of the most important uses. Through its various importance measures, a FTA identifies not only what is important but also what is unimportant. For those contributors that are unimportant and have negligible impact on the top event, resources can be relaxed with negligible impact on the top event probability. In fact, using formal allocation approaches, resources can be re-allocated to result in the same system failure probability while reducing overall resource expenditures by significant amounts. In various applications, FTA has been used to reduce resource burdens by as much as 40% without impacting the occurrence probability of the top event. Software has been developed to help carry out these resource re-allocations for large systems.

6. Use of FTA to assist in designing a system. When designing a system, FTA can be used to evaluate design alternatives and to establish performance-based design requirements. In using FTA to establish design requirements, performance requirements are defined and the FTA is used to determine the design alternatives that satisfy the performance requirements. Even though system specific data are

not available, generic or heritage data can be used to bracket performance. This use of FTA is often overlooked, but is important enough to be discussed further in a subsequent section.

7. Use of FTA as a diagnostic tool to identify and correct causes of the top event. This use of FTA as a diagnostic tool is different from the proactive and preventative uses described above. FTA can be used as a diagnostic tool when the top event or an intermediate event in the fault tree has occurred. When not obvious, the likely cause or causes of the top event can be determined more efficiently using the FTA power to prioritize contributors. The chain of events leading to the top event is identified in the fault tree, providing valuable information on what may have failed and the areas in which improved mitigation could be incorporated. When alternative corrective measures are identified, FTA can be used to objectively evaluate their impacts on the top event re-occurrence. FTA can also be an important aid to contingency analysis by identifying the most effective actions to be taken to reduce the impact of a fault or failure. In this case, components are set to a failed condition in the fault tree and actions are identified to minimize the impact of the failures. This contingency analysis application is often used to identify how to reconfigure a system to minimize the impact of the component failures. Allowed downtimes and repair times can also be determined to control the risk incurred from a component failure. As can be seen from the above, FTA has a wide variety of uses and roles it can play in decision-making. FTA can be used throughout the life cycle of the system from design through system implementation and improvement. As the system proceeds to the end of life, its performance can be monitored to identify trends before failure occurs. When consciously used to assist decision-making, the payoffs from FTA generally far outweigh the resources expended performing the analysis.

## 4.6 Role of Fault Trees in a PRA

A Probabilistic Risk Assessment, or PRA, models sequences of events that need to occur in order for undesired end states to occur. A sequence of events is usually called an accident sequence. An example of an accident sequence is a fire that leads to catastrophic consequences because mitigation systems fail to operate. A model of a simple event sequence in a PRA is shown below.

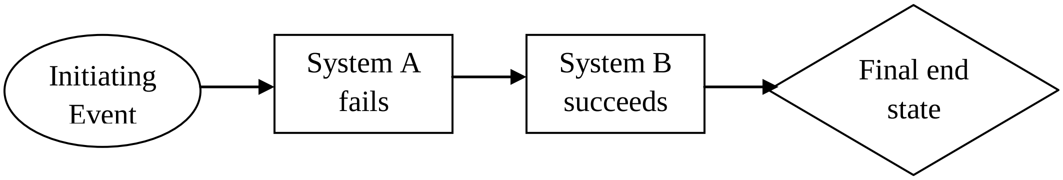


Figure 4.2 Event Sequence Model

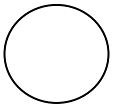
Notice that in the above event sequence model, success of a system as well as failure of another system appears. Which particular systems fail and which succeed determine the type of end state and its associated consequences. To quantify the accident sequence, a probability for each event in the event sequence, other than the end state, needs to be determined. The probability of each event is conditional on the previous events in the sequence (e.g., the probability of system A failing is the probability of A failing given the initiating event occurs, the probability of system succeeding is the probability of B succeeding given A fails and the initiating event occurs). If an event is independent of others in the sequence and failure data exist, the probability can be directly estimated from the data. For more complex events in the sequence, that do not have directly applicable data or that may have dependencies on other events in the sequence, such as for a system failure, a fault tree is usually constructed. The fault tree is developed to a level that encompasses the dependencies between systems or to a level where failure data exist for the basic events, whichever is lower. The fault tree is then evaluated to determine the probability of the system failure. Each event sequence is a logical intersection (an AND gate) of the initiating event and the subsequent events other than the end state. Available PRA software automatically carries out the operations involving this intersection using all the fault trees that are input to an event sequence.

Depending upon the level of resolution, a complex PRA such as for the Space Shuttle can have tens of thousands of accident sequences involving hundreds of different fault trees. In a large analysis, the fault trees (AND gates) of each sequence are combined into a single OR gate to generate accident sequence cut sets for the entire PRA in a single analysis run. When several different end states are defined the fault trees for each individual end state are combined.

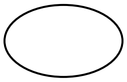
## 4.7 Software for Fault Tree Analysis

A number of software applications exist for FTA and new applications are continually being developed. It is not the purpose of this document to serve as reference for FT-related software; it is not possible to describe all FT software that is currently available and it is clearly not possible to describe software that may be available in the future

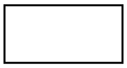
## 4.8 Basic Elements of Fault Tree



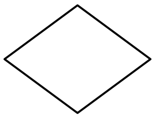
**BASIC EVENT—**A basic initiating fault requiring no further development.



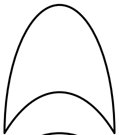
**CONDITIONING EVENT—**A specific conditions or restrictions that apply to any logic gate



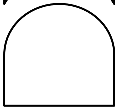
**INTERMEDIATE EVENT—**A fault event that occurs because of one or more antecedent causes acting through logic gates



**UNDEVELOPED EVENT—**An event which is not further developed



**OR GATE—**Output fault occurs if at least one of the input faults occurs



**AND GATE—**Output fault occurs if all of the input faults occurs

## 4.9 System Logical Modeling Approaches

There are various approaches for logical modeling which are as follows:

### 4.9.1 Success vs. Failure Approaches

The operation of a system can be considered from two standpoints: the various ways for system success can be enumerated or the various ways for system failure can be enumerated. Such an enumeration would include completely successful system operation and total system failure, as well as intermediate conditions such as minimum acceptable success. Figure 4.3 depicts the Failure/Success space concept.

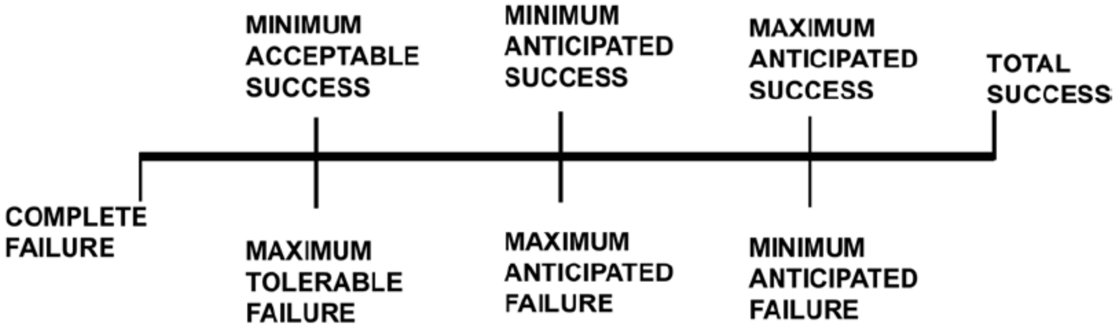


Figure 4.3 Failure Space-Success Space Concept

It is interesting to note that certain identifiable points in success space coincide with certain analogous points in failure space. Thus, for instance, “maximum anticipated success” in success space can be thought of as coinciding with the “minimum anticipated failure” in failure space. Although the first inclination might be to select the optimistic view of our system (success) rather than the pessimistic one (failure) when considering system operation, this is not necessarily the most advantageous perspective to take. From an analytical standpoint, there are several overriding advantages that accrue from the failure space perspective. First of all, it is generally easier to attain concurrence on what constitutes failure than it is to agree on what constitutes success. An aircraft might be desired to fly high and fast, travel far without refueling and carry a big load. When the final version of this aircraft rolls off the production line, some of these features may have been compromised in the course of making design trade-offs. Whether the vehicle is a "success" or not may very well be a matter of controversy. On the other hand, if the aircraft crashes, there will be little argument that this event constitutes system failure. Success tends to be associated with the efficiency of a system, the amount of output, the degree of usefulness, and production and marketing features. These characteristics are describable by continuous variables that are not easily modeled in terms of simple discrete events, such as “valve does not open,” which characterize the failure space (partial failures, i.e., a valve opens partially, are also difficult events to model because of their continuous possibilities). Thus, the event “failure,” or in particular, “complete failure,” is generally easy to define, whereas the event “success” may be much more difficult to tie down. This fact makes the use of failure space in analysis much more valuable than the use of success space.

Another point in favor of the use of failure space is that, although theoretically the number of ways in which a system can fail and the number of ways in which a system can succeed are both infinite, from a practical standpoint there are generally more ways to success than there are to failure. Thus, purely from a practical point of view, the size of the population in failure space is less than the size of the population in success space. In analysis, therefore, it is generally more efficient to make calculations on the basis of failure space.

A final point in favor of the use of failure space is the nature of the mathematics involved in the quantification of failure models. Most failure probabilities are small (less than 0.1), which allows the use of accurate approximations when combining failure probabilities. Since success probabilities are usually close to 1.0, these approximations cannot be used, necessitating the use of complex calculations when combining success probabilities. The solution of success models is therefore much more different than the solution of failure models.

The advantageous use of the failure space when analyzing system operation has been demonstrated on numerous occasions in the past. The drawing of logic diagrams for a complex system is an expensive and time-consuming operation. When failures are considered, it may be necessary to construct only one or two system models, such as fault trees, that cover all the significant failure modes. When successes are considered, it may become necessary to construct several hundred system models covering various definitions of success. A good example of the parsimony of events characteristic of failure space was the Minuteman missile analysis. Only three fault trees were drawn corresponding to the three undesired events: inadvertent programmed launch, accidental motor ignition, and fault launch. It was found that careful analysis of just these three events provided a complete overview of the complex Minuteman system.

Consider the “mission” in Figure 4.4 referring to the transport of person X by automobile from home to the office. The desired arrival time is 8:30, but the mission will be considered marginally successful if X arrives at the office by 9:00. Arrival at 8:30 is labeled “minimum anticipated failure.”

Below “minimum anticipated failure” lie a number of possible incidents that constitute minor annoyances, but which do not prevent X from arriving at the desired time. Arrival at 9:00 is labeled “maximum anticipated failure.” Between this point and “minimum anticipated failure” lie a number of occurrences that cause X’s arrival time to be delayed half an hour or less. It is perhaps reasonable to let the point “maximum tolerable failure” coincide with some accident that causes some damage to the car and considerable delay but no personal injury. Above this point lie incidents of increasing seriousness terminating in complete failure or death.

Note that an event such as “windshield wipers inoperative” will be positioned along the line according to the nature of the environment at that time.

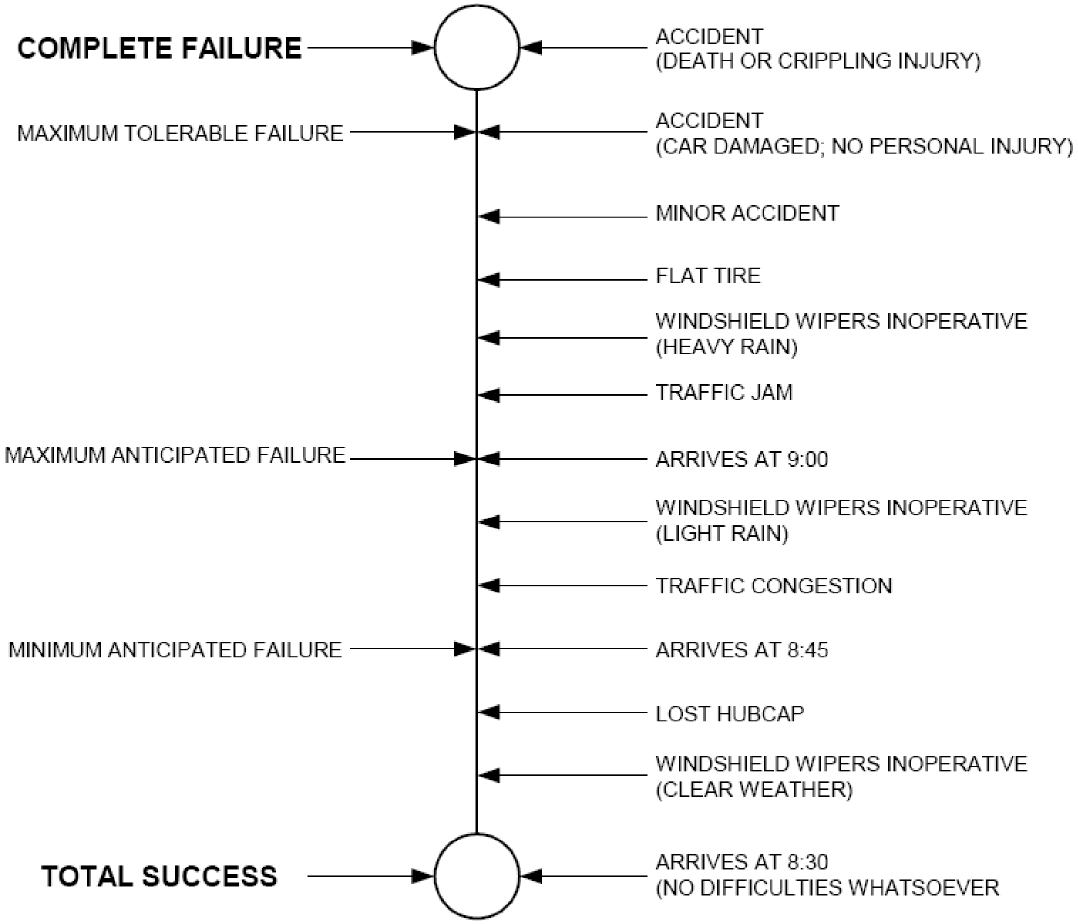


Figure 4.4 Use of Failure Space in Transport Example

## 4.10 Deductive Methods and FTA

Deduction constitutes reasoning from the general to the specific. In a deductive system analysis, it is postulated that the system itself has failed in a certain way, and an attempt is made to find out what modes of system or subsystem (component) behavior contribute to this failure. In common parlance this approach might be referred to as a “Sherlock Holmes” approach.

Holmes, faced with given evidence, has the task of reconstructing the events leading up to the crime. Indeed, all successful detectives and other types of investigators are experts in deductive analysis. Typical deductive analyses in real life are accident investigations.

## 4.11 Inductive Methods

Induction involves reasoning from individual cases to a general conclusion. If, in the consideration of a certain system, a particular fault or initiating condition is postulated and an attempt to ascertain the effect of that fault or condition on system operation is made, an inductive system analysis is being conducted. Thus, an inquiry might be made into how the loss of some specified control surface affects the flight of an aircraft or into how the elimination of some item in the budget affects the overall operation of a school district. More formally, the process consists of assuming particular states for components, generally failed states, and then analyzing the effects on the system. More generally, a given initiating event is assumed, such as a pipe rupture, and the consequences of the event are analyzed.

Inductive approaches are also termed bottom-up approaches that start at the bottom, i.e., at the failure initiators and basic event initiators, and then proceed upwards to determine the resulting system effects of a given initiator. Inductive approaches thus start at a possible basic cause and then analyze the resulting effects. A set of possible causes are analyzed for their effects.

### 4.11.1 Reliability Block Diagram (RBD)

A reliability block diagram is an inductive model wherein a system is divided into blocks that represent distinct elements such as components or subsystems. These elemental blocks are then combined according to system-success pathways. RBDs are generally used to represent active elements in a system, in a manner that allows an exhaustive search for and identification of all pathways for success. Dependencies among elements can be explicitly addressed.

Initially developed top-level RBDs can be successively decomposed until the desired level of detail is obtained. Alternately, series components representing system trains in detailed RBDs can be logically combined, either directly or through the use of FTs, into a super component that is then linked to other supercomponents to form a summary model of a system. Such a representation can sometimes result in a more transparent analysis.

An example RBD for the fuel system depicted in Figure 4.3 is shown in Figure 4.4. Separate blocks representing each system element (fuel supply, block valves, control valves and motor) are structurally combined to represent both potential flow paths through the system. The model is solved by enumerating the different success paths through the system and then using the rules of Boolean algebra to continue the blocks into an overall representation of system success.

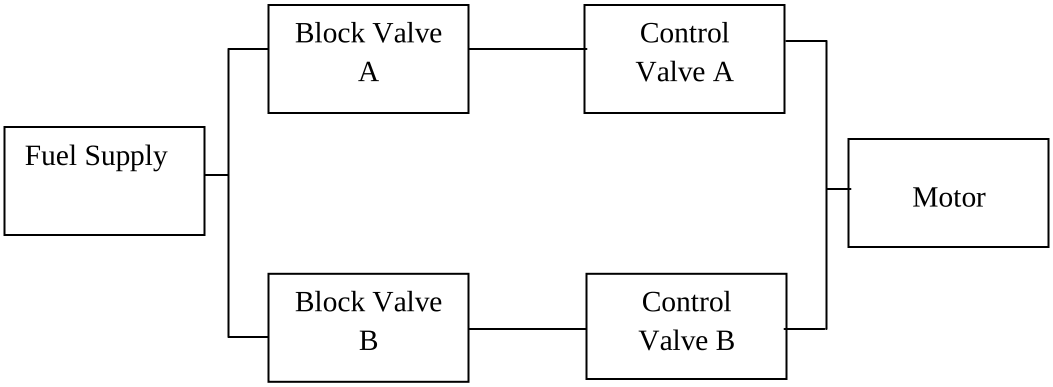


Figure 4.5 Reliability Block Diagram of a Fuel System

Software exists to convert RBDs into FTAs and vice versa. While these conversions result in logically equivalent models, the logical representation in the conversion may not be as clear as in the original model.

## 4.12 Fault Tree Analysis

The steps for analyzing fault tree is explained in the next topic.

### 4.12.1 Steps in Carrying Out a Fault Tree Analysis

A successful FTA requires the following steps be carried out:

The first five steps involve the problem formulation for an FTA. The remaining steps involve the actual construction of the FT, the evaluation of the FT, and the interpretation of the FT results.

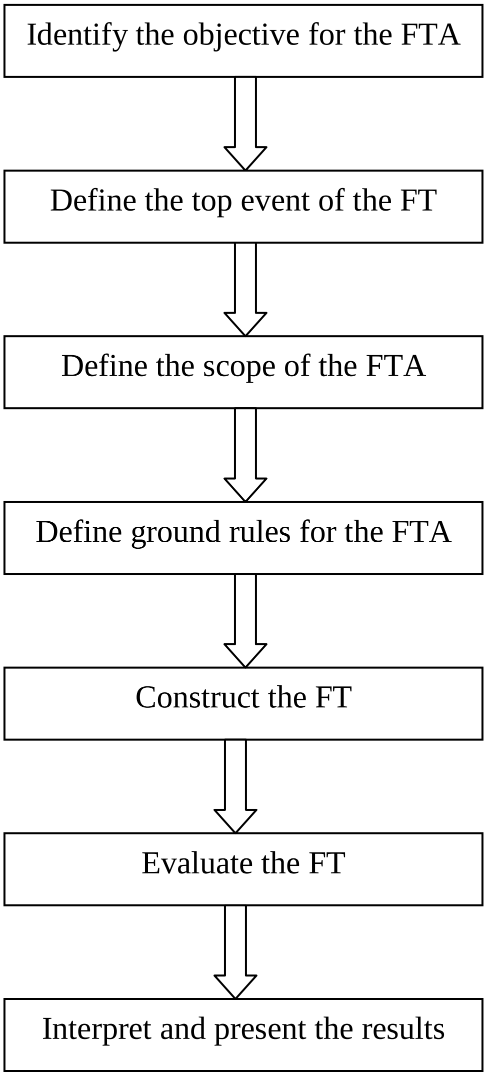


Figure 4.6 Fault Tree Analyses

While most of the steps are performed sequentially, steps 3-5 can proceed concurrently. It is not uncommon for steps 4 and 5 to be modified during steps 6 and 7.

## 4.13 Failure Mechanism, Failure Mode, and Failure Effect

The definitions of system, subsystem, and component are relative, and depend upon the context of the analysis. A “system” is the overall structure being considered, which in turn consists of subordinate structures called “subsystems,” which in turn are made up of basic building blocks called “components.”

For example, in a fault tree of the Space Shuttle Solid Rocket Booster (SRB) the Thrust Vector Control (TVC) may be referred to as a system. A subsystem is then, for example, the Auxiliary Power Unit (APU) of the TVC. A component is then the Fuel Pump of the APU. In a particular analysis, definitions of system, subsystem, and component are generally made for convenience in order to provide a hierarchy for and boundaries to the problem. These definitions are also used in the naming scheme developed for the fault tree. A key aspect of FTA is that the elements of a system are viewed in terms of their function—artificial systems boundaries are largely ignored.

In constructing a fault tree, the basic concepts of failure effects, failure modes, and failure mechanisms are important in determining the proper interrelationships among the events. When failure effects are addressed, the concern is why a particular failure is of interest, i.e., what are its effects (if any) on the system. When the failure modes are detailed, exactly what aspects of component failure are of concern. When failure mechanisms are listed, how can a particular failure mode occur. Failure mechanisms are thus the means by which failure modes occur, which in turn are the effects of more basic causes. Alternatively, failure mechanisms produce failure modes, which, in turn, have certain effects on system operation.

The subsystem of interest consists of a valve and a valve actuator. Various events that can occur can be classified from the system, subsystem, or component perspective. Some of the events are given in the left-hand column of the table below. For example, “valve unable to open” is a mechanism of subsystem failure, a mode of valve failure, and an effect of actuator failure.

# CHAPTER 5
# SIMULATION AND TESTING

## 5.1 Troubleshooting of Polaris Q

The failure of the following symptoms of the Polaris Q results in its failure:

### 5.1.1 Communication Symptoms

Communication symptoms likely involve links between the data system and the mass spectrometer, the gas chromatograph, and the autosampler.

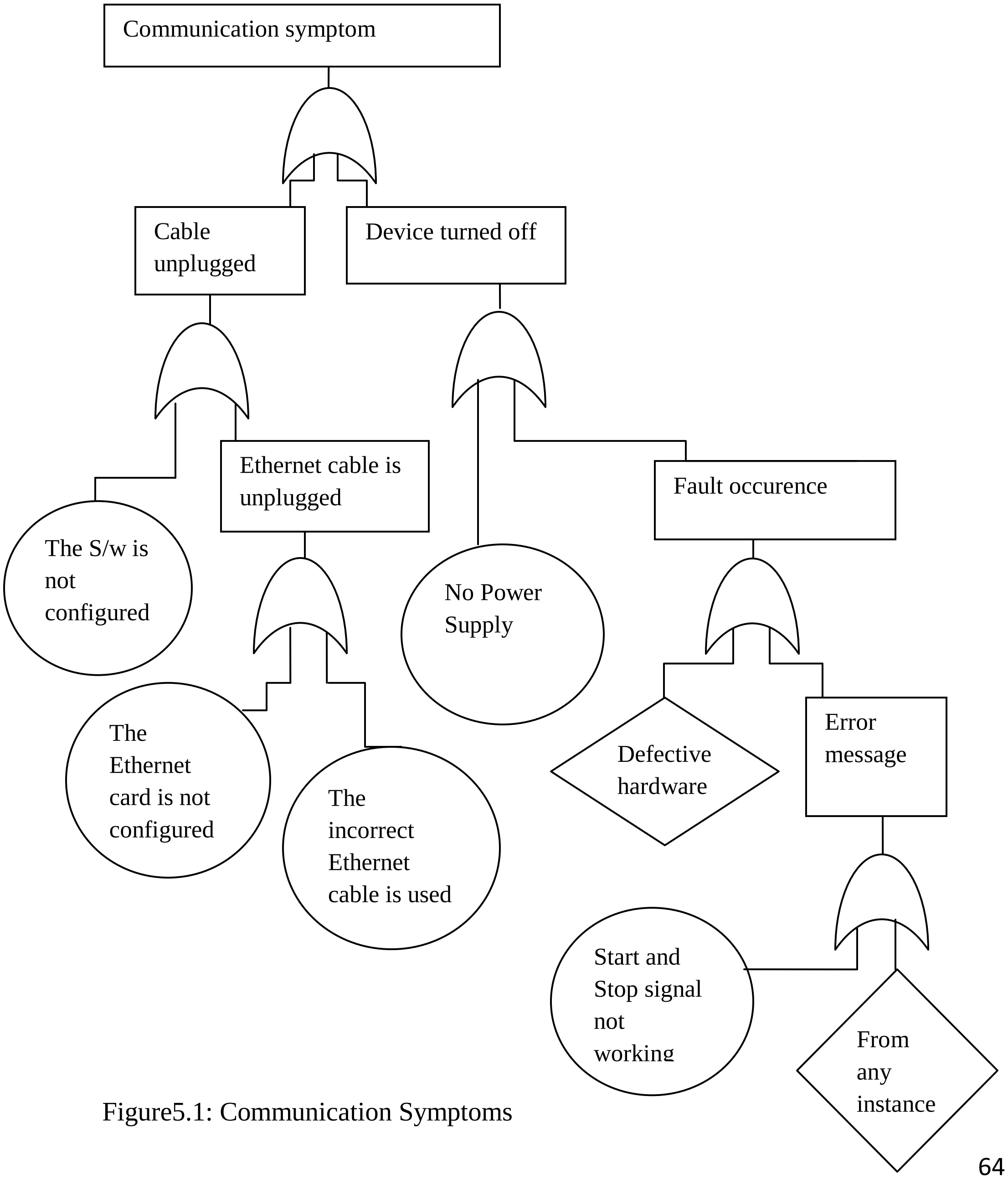


Figure5.1: Communication Symptoms

Communication symptoms may occur during:

1. Data transfer between the mass spectrometer and the data system
2. Mass spectrometer, gas chromatograph and autosampler current status feedbacks.
3. Instrument control, method downloading and uploading.
4. Start, stop, pause and initialize functions

### 5.1.2 Contamination Symptoms

hemical noise is always present in any mass spectrometer. As a result, the high sensitivity of the ion trap can cause new users to confuse background with a contamination problem. The spectra shown in Xcalibur Tune and Real-Time Display are auto-normalized, which

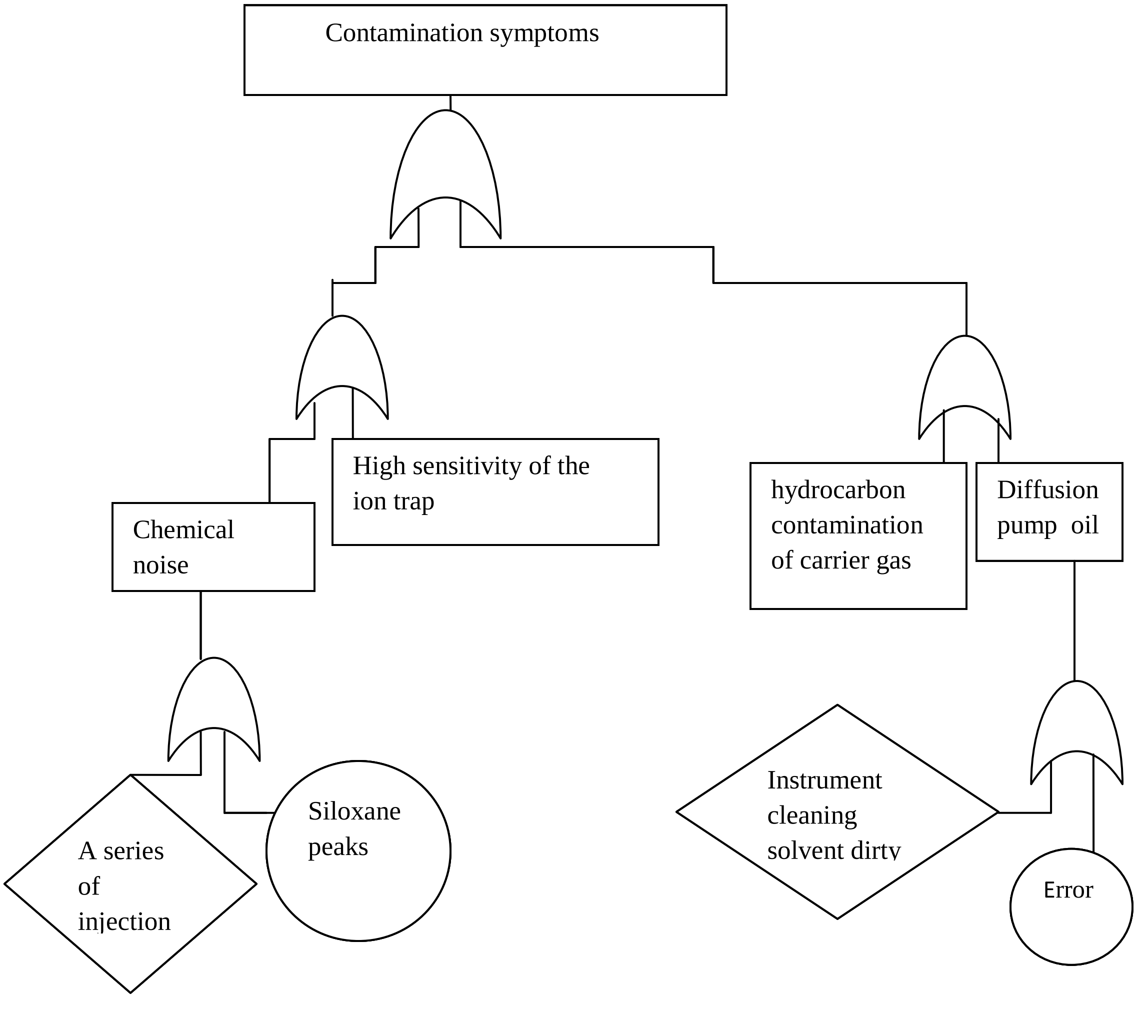


Figure 5.2: Contamination Symptoms

### 5.1.3 Filament and Lens Control Symptoms

The lifetime of a filament depends on its exposure to oxygen and solvent vapors. The filament assembly protects the filament and increases its lifetime for many months. Xcalibur Diagnostics tests the filament for continuity and current regulation. Testing the filament for continuity before each acquisition ensures that an open filament condition will stop an autosampler sequence and generate an error message.

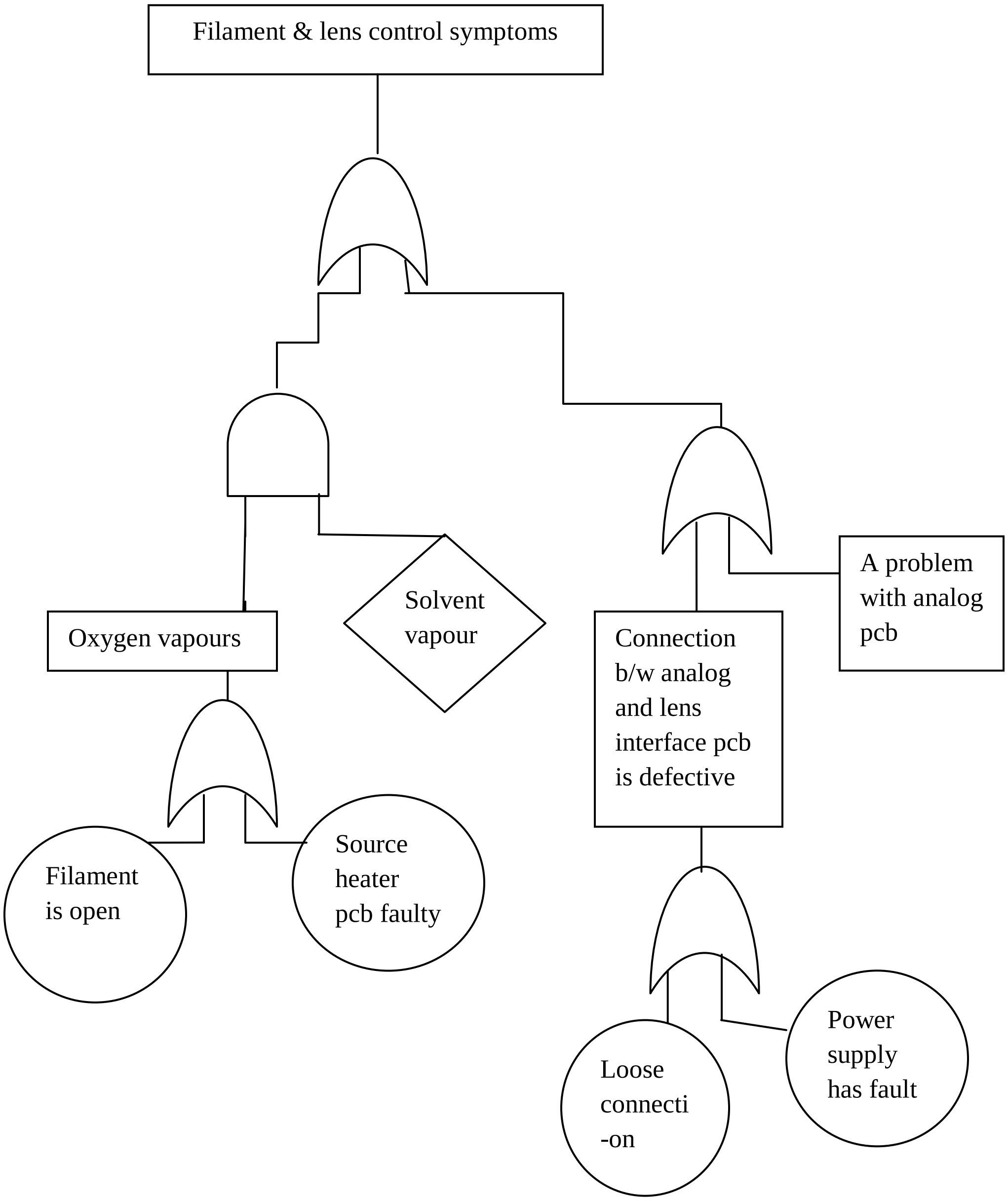


Figure 5.3: Filament and Lens Control Symptoms

### 5.1.4 Heated Zone Symptoms

The Ion Source and Transfer Line are heated zones related to the Polaris*Q*. The ion source heater is controlled by the Polaris*Q* and the transfer line heater is controlled by the Aux1 heated zone of the TRACE GC. Often, a heated zone problem is the result of downloading a method to the

Polaris*Q* that has a different setpoint from the current setting, causing a delay while the heated zone heats or cools. Component failures are less common, but can occur. These are usually related to open circuits in heater cartridges or faulty temperature sensors.

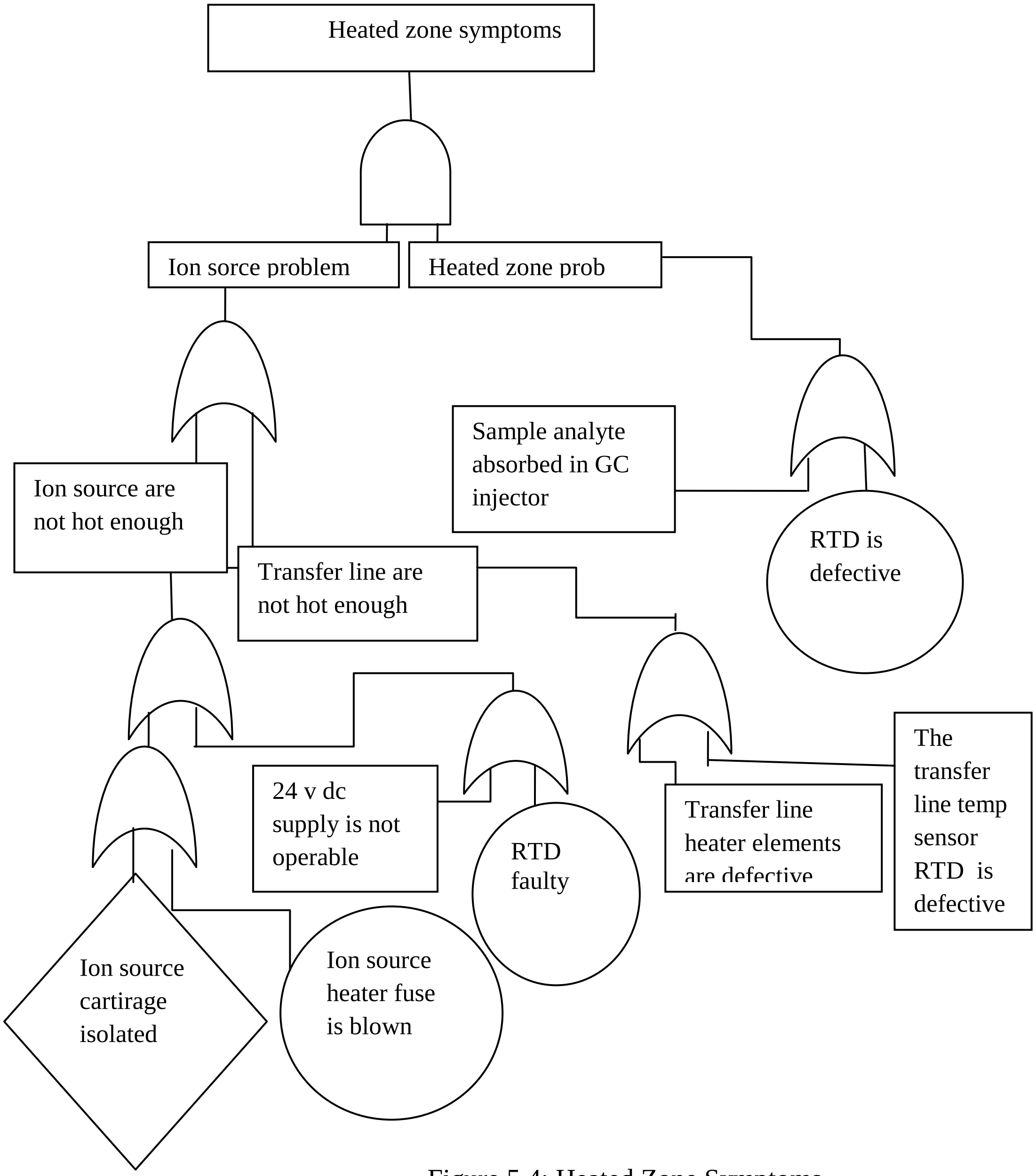


Figure 5.4: Heated Zone Symptoms

### 5.1.5 High Vacuum Symptoms

High Vacuum problems can manifest themselves in two ways. First, an intermittent vacuum condition (the vacuum pressure in the vacuum manifold fluxuates intermittently) can cause chromatographic signals to drop out, or, if the pressures exceed the maximum allowed pressures by Xcalibur, then the MS can automatically shut down.

Second, if the vacuum is consistent enough to where it does not exceed the maximum allowed pressure and avoids the Xcalibur automatic shutdown, non-reproducible false chromatographic peaks can be generated in the chromatogram.

Typical forepressure readbacks are 30-40 mTorr (in EI mode), and typical manifold pressure (ion gauge readback) is 1-5 x 10-5 Torr. For CI mode, forepressure is usually 60-90 mTorr, with anifold pressures no greater than 9 x 10-4 Torr.

The most reliable way to find vacuum leaks is to spray a gas around the vacuum manifold and looking for the characteristics ions in full-scan EI. Argon produces m/z 40. Alternatively, compressed electronic dusting spray containing an HFC can be used. For example, Falcon, Dust-Off and MicroCare Micro-Blast contain tetrafluoroethane which produce ions at m/z 69 and 83.

Vacuum system components lower the pressure within the Polaris*Q*. The principal components include: the convectron gauge, high vacuum pump, ion gauge, rotary-vane pump (and expansion volume), and the vacuum manifold.

This also includes valves, gauges, and associated electronic and other control devices. All but the rotary-vane pump and expansion volume are located around the vacuum manifold. These components maintain low pressure necessary for the ion source, ion trap, and ion detector system to operate properly. The vacuum manifold, which houses the ion source, ion trap, and ion detector system, is pumped (or evacuated) by the high vacuum pump.

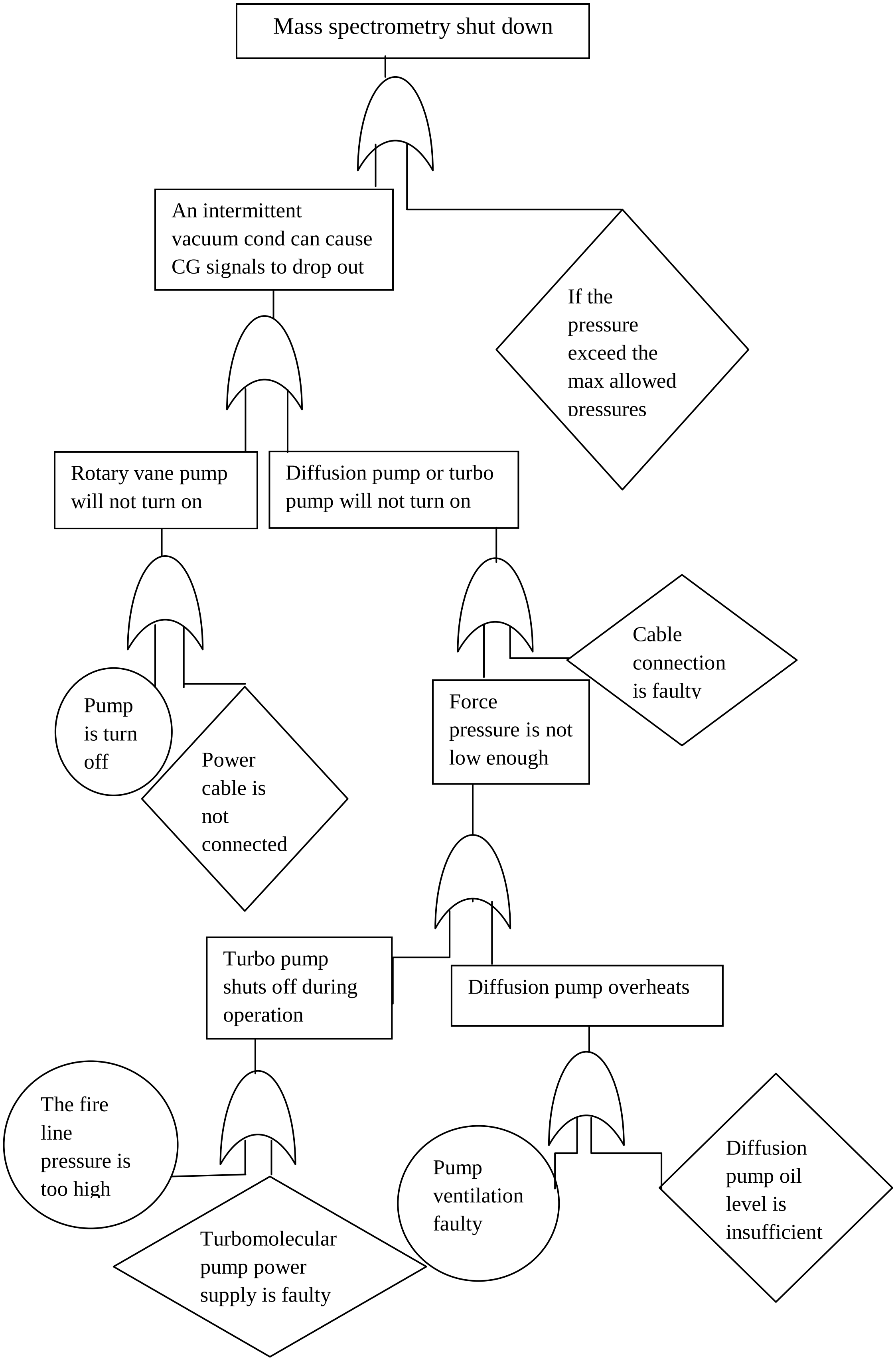


Figure 5.5: High Vacuum Symptoms

### 5.1.6 Linearity Symptoms

Linearity symptoms are when a plot of intensity versus concentration of a known compound are not uniform throughout the curve, or vary from their expected peaks. Poor instrument operating conditions can cause linearity problems. Additionally, certain compounds do not give a desired linear response due to chromatographic activity. A well-maintained instrument will provide good linear response over a wide range of concentration for most compounds. Like any instrument, however, the Polaris*Q* has a saturation point.

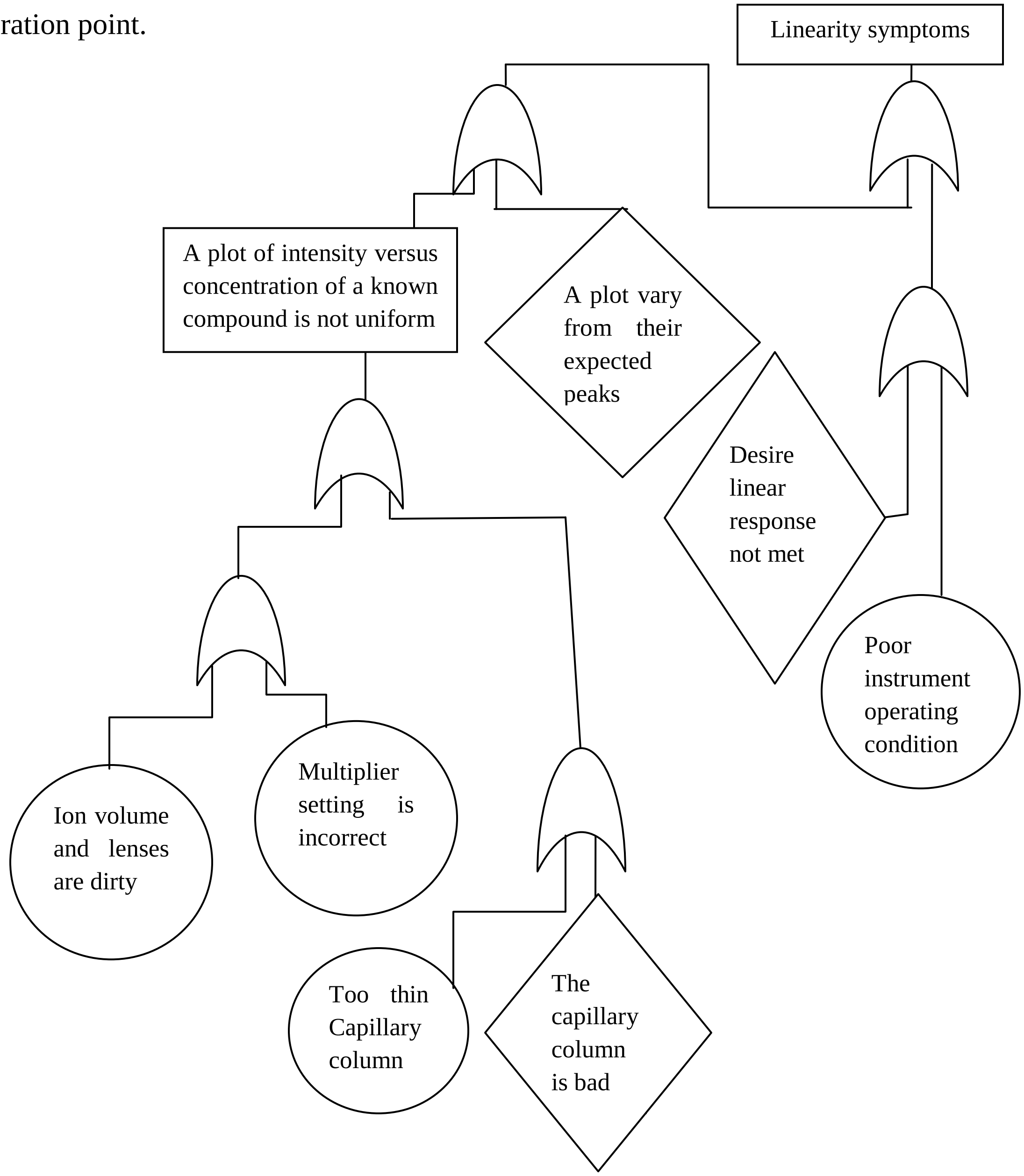


Figure 5.6: Linearity Symptoms

### 5.1.7 Power Supply Symptoms

Xcalibur Diagnostics detects most power supply symptoms. Power supply problems often involve a blown fuse, faulty electronic components, or even something as simple as a disconnected cable. Use extreme care when you replace a fuse or electronic component. Turn the Polaris*Q* off and unplug the instrument before removing the covers.

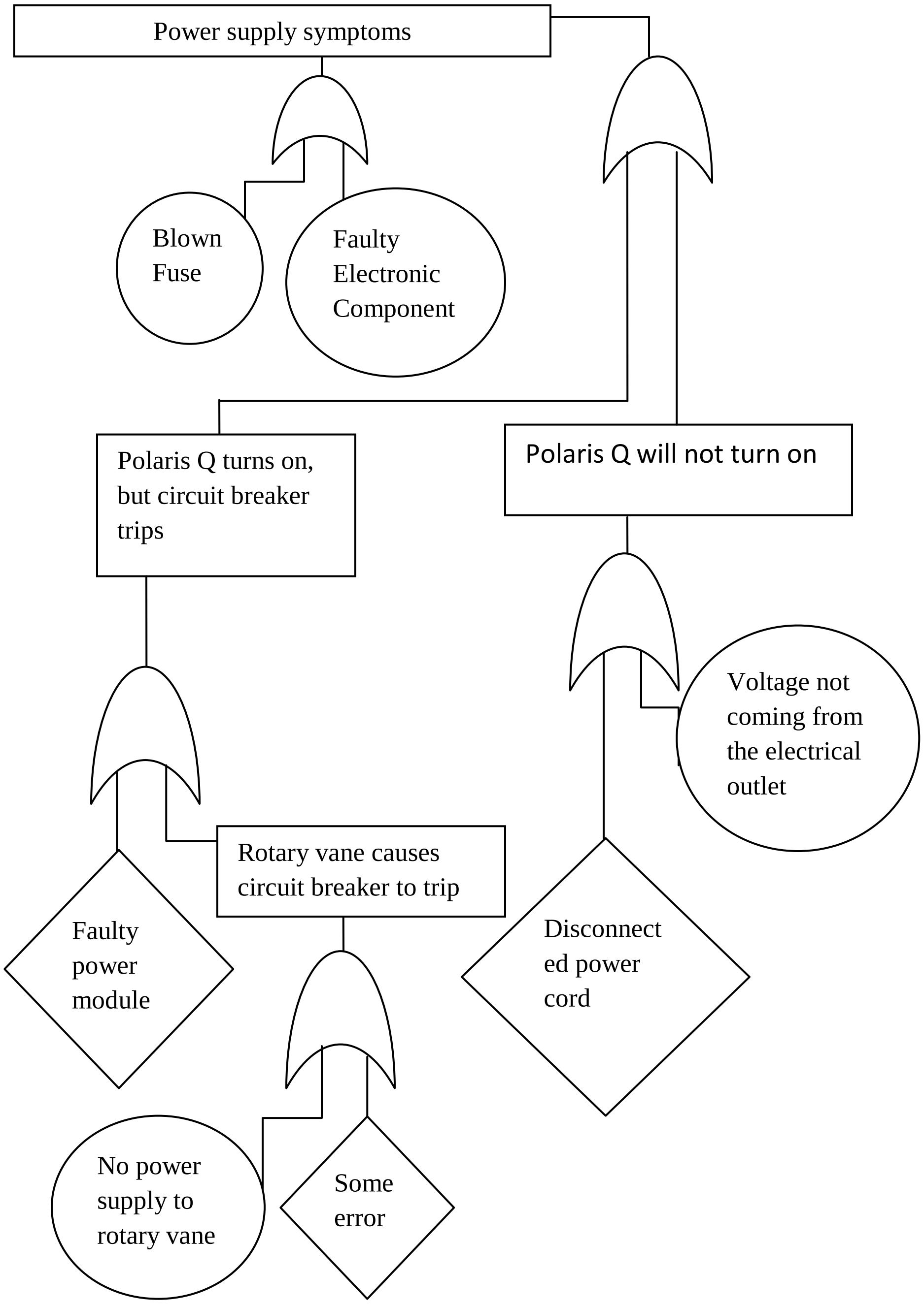


Figure 5.7: Power Supply Symptoms

### 5.1.8 RF Control Symptoms

Automatic RF frequency calibration or RF dip and gain problems can be caused by several things. Begin troubleshooting ion trap control problems by using Xcalibur Diagnostics.

Diagnostics helps you identify whether the fault is due to a power supply problem, a break in the RF signal path, or a faulty component. Diagnostics Flowchart, is an excellent resource to begin troubleshooting RF control problems.

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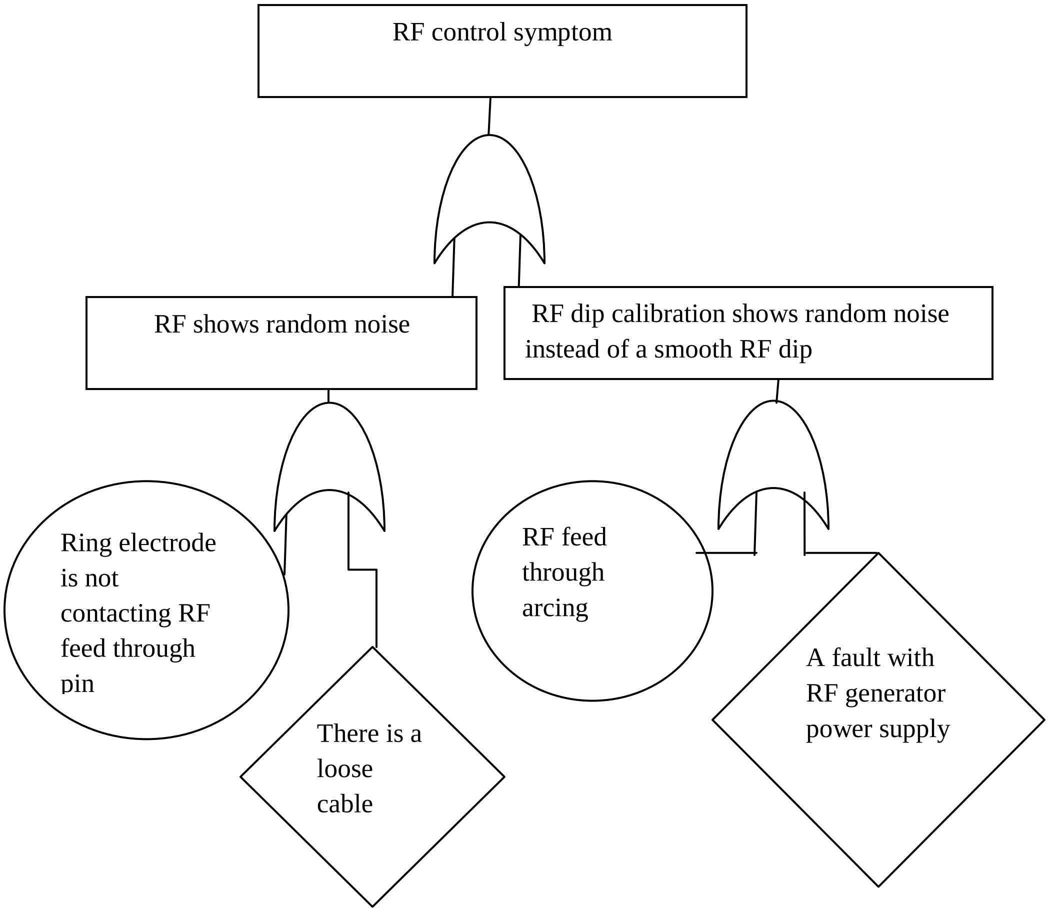

Figure 5.8: RF Control Symptoms

### 5.1.9 Sensitivity Symptoms

If you observe a drop in instrument sensitivity, you should determine if the sensitivity drop was sudden or if it occurred gradually. A sudden loss of sensitivity can be the result of sudden component failure or an unnoticed change in the analytical method. Simple errors such as a plugged autosampler syringe or too low sample level in the sample vial can give the appearance of instrument failure. Gradual drops in sensitivity are usually the result of source or lens contamination, and are easily remedied by cleaning the ion volume or lenses. The Electron Multiplier influences sensitivity and has a limited lifetime. Eventually it will need to be replaced.

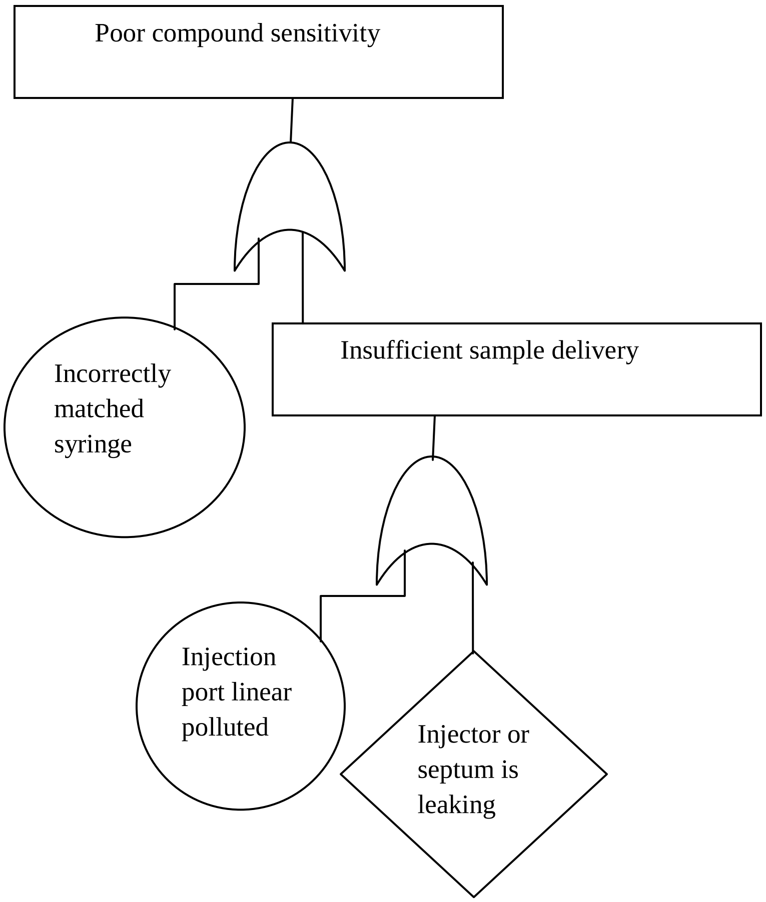

Figure 5.9: Sensitivity Symptoms

### 5.1.10 Stability Symptoms

Stability problem symptoms are concerned with consistent instrument precision and the reproducibility of accurate results. Good operating conditions for the mass spectrometer, gas chromatograph, and autosampler contribute to instrument stability. Sample preparation, spiking errors, sample injection errors, and lack of routine maintenance on the instruments may cause false stability symptoms.

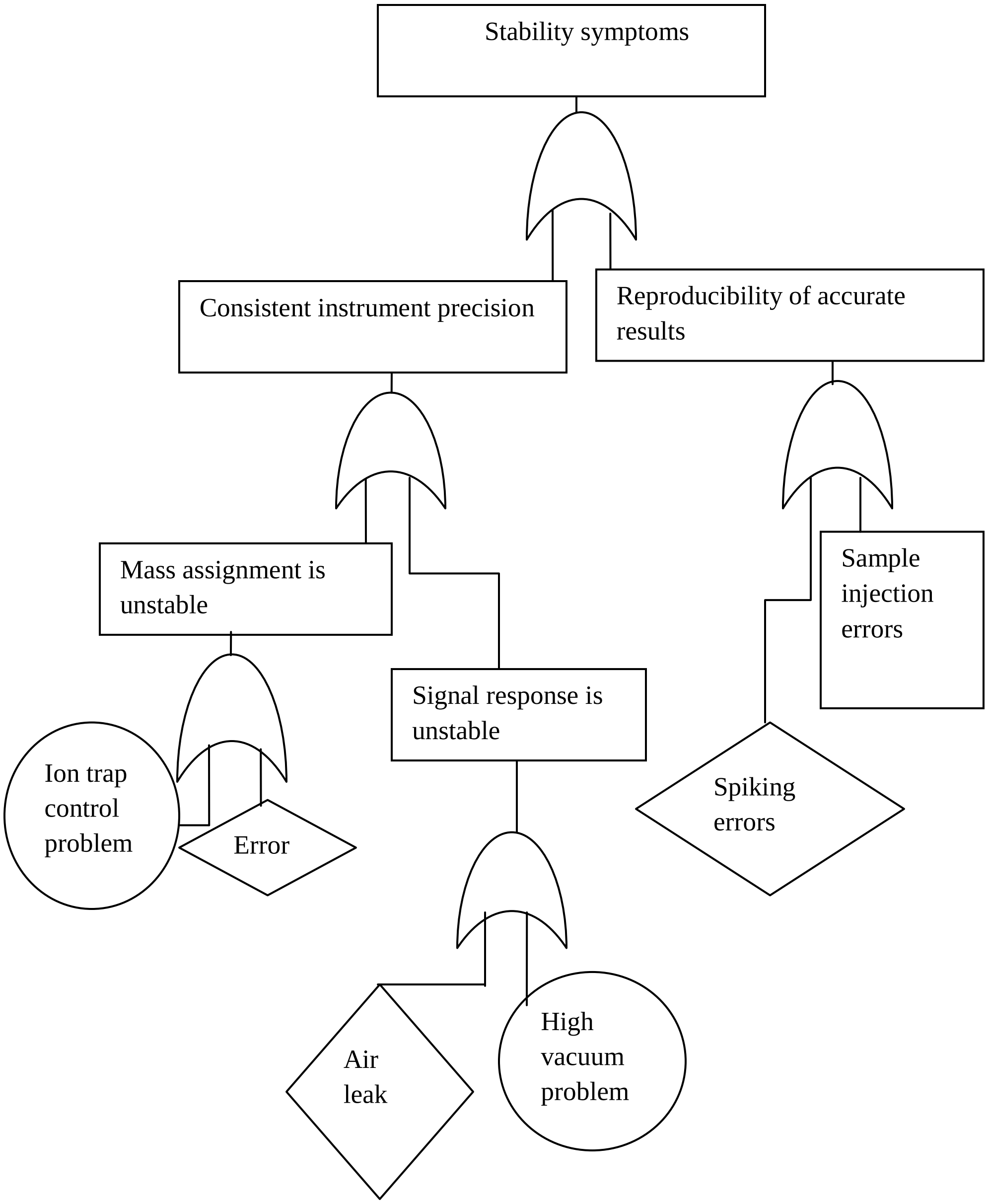

Figure 5.10: Stability Symptoms

### 5.1.11 Tuning Symptoms

Symptoms when tuning the ion trap and lens may be the result of a misadjusted manual control parameter. Suspect a tuning problem when Xcalibur Autotune fails. Autotune performs several functions, and symptoms or error messages indicate different problems. A tuning symptom can usually be found in Diagnostics.

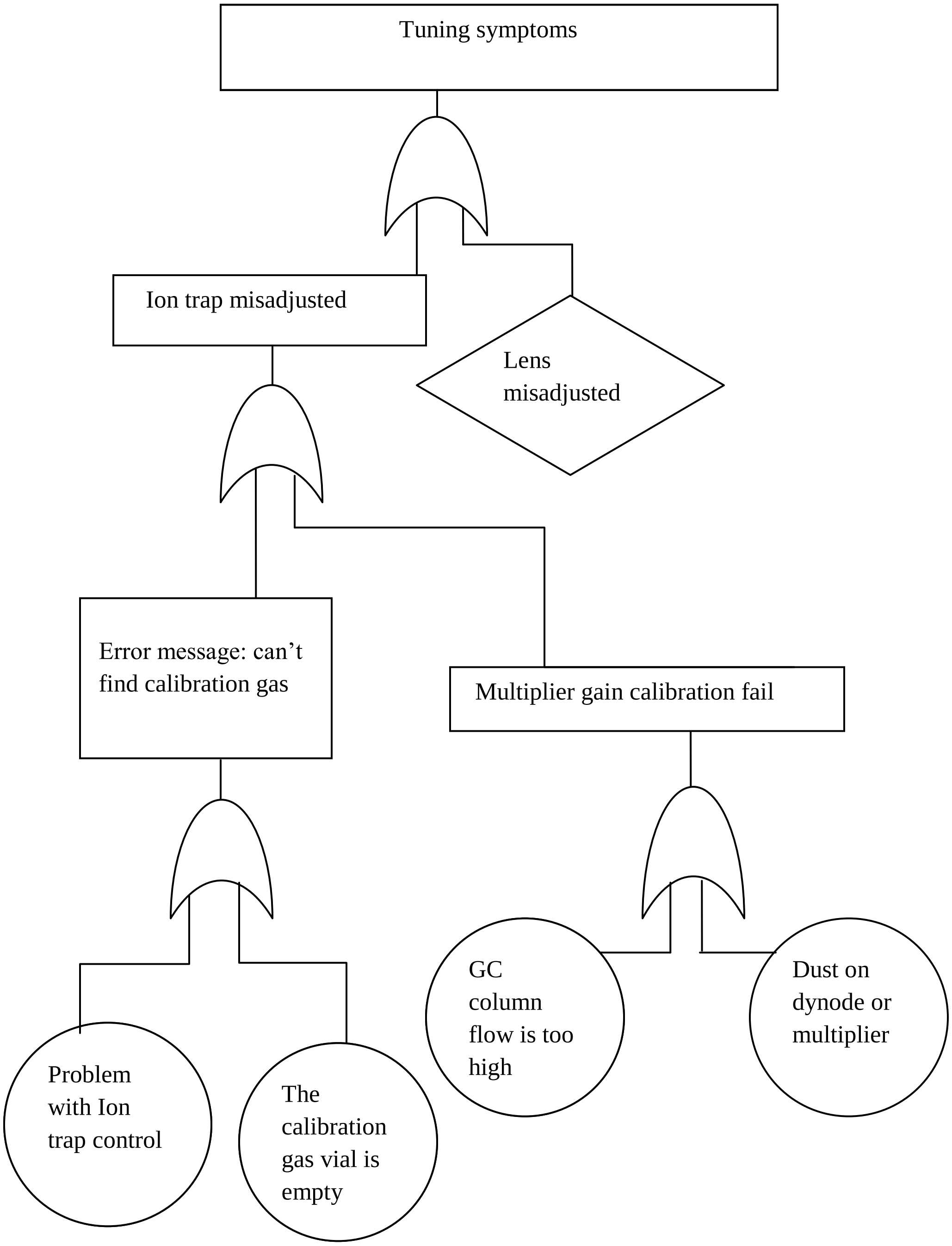

Figure 5.11: Tuning Symptoms

## 5.2 Tabular Formation of various Symptoms

Following are the tabular representation of basic events and failure of probability of various symptoms of the Polaris Q.

### 5.2.1 Communication Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.1 proved the probability of failure of the system which is 0.16 due to the occurrence of Communication Symptoms.

**Table 5.1: Probability due to which Communication Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Start signal not working | 0.10 |
| 2 | Fault from any instance | 0.15 |
| 3 | Error message | 0.23 |
| 4 | Defective hardware | 0.20 |
| 5 | Fault Occurrence | 0.38 |
| 6 | No Power Supply | 0.10 |
| 7 | Device Turned Off | 0.44 |
| 8 | Incorrect Ethernet Cable | 0.10 |
| 9 | Ethernet Cable Not Configured | 0.20 |
| 10 | Ethernet Cable Unplugged | 0.28 |
| 11 | Software Not Configured | 0.05 |
| 12 | Cable Unplugged | 0.31 |

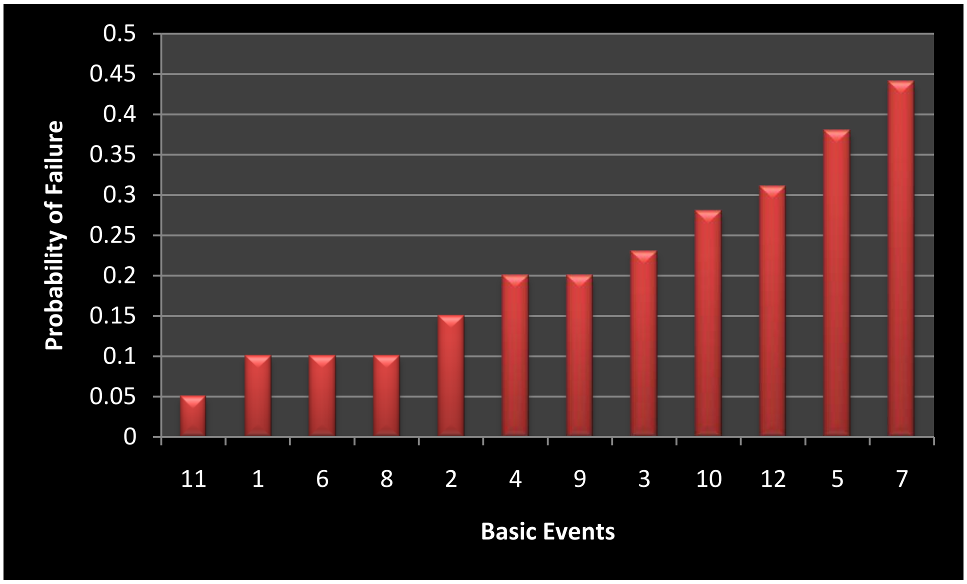

Figure 5.12: Graph between Probability of Failure and Basic Events of Communication Symptoms

From the above graph, it is observed that the probability of failure of event due to turning off the device is maximum in case of Communication Symptom, so users have to take care while handling the device.

### 5.2.2. Contamination Symptom

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.2 proved the probability of failure of the system which is 0.208 due to the occurrence of Contamination Symptoms.

**Table 5.2: Probability due to which Contamination Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Dirty Instrument Cleaning Solvent | 0.12 |
| 2 | Error | 0.10 |
| 3 | Dirty Diffusion Pump Oil | 0.21 |
| 4 | Hydrocarbon Contamination of Carrier Gas | 0.15 |
| 5 | Series of Injection | 0.11 |
| 6 | Siloxane Peaks | 0.12 |
| 7 | Chemical Noise | 0.01 |
| 8 | High Sensitivity of the Ion Trap | 0.20 |

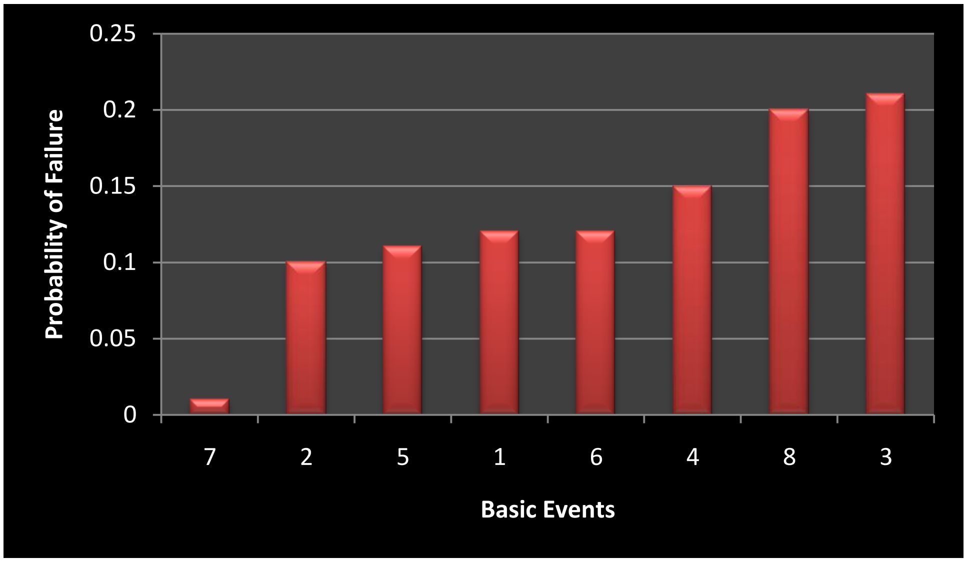

Figure 5.13: Graph between Probability of Failure and Basic Events of Contamination Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to dirty diffusion pump oil in case of Contamination Symptom, so users have to take care of the pump oil that is being used.

### 5.2.3 Filament Lens Control Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.3 proved the probability of failure of the system which is 0.31 due to the occurrence of Filament Lens Control Symptoms.

**Table 5.3: Probability due to which Filament Lens Control Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Loose Connection | 0.10 |
| 2 | Faulty Power Supply | 0.12 |
| 3 | Defective Connection Between Analog and Lens interface PCB | 0.21 |
| 4 | Problem with Aanalog PCB | 0.10 |
| 5 | Faulty Source Heater | 0.11 |
| 6 | Open Filament | 0.20 |
| 7 | Excess Oxygen Vapour | 0.29 |
| 8 | Solvent Vapours | 0.11 |

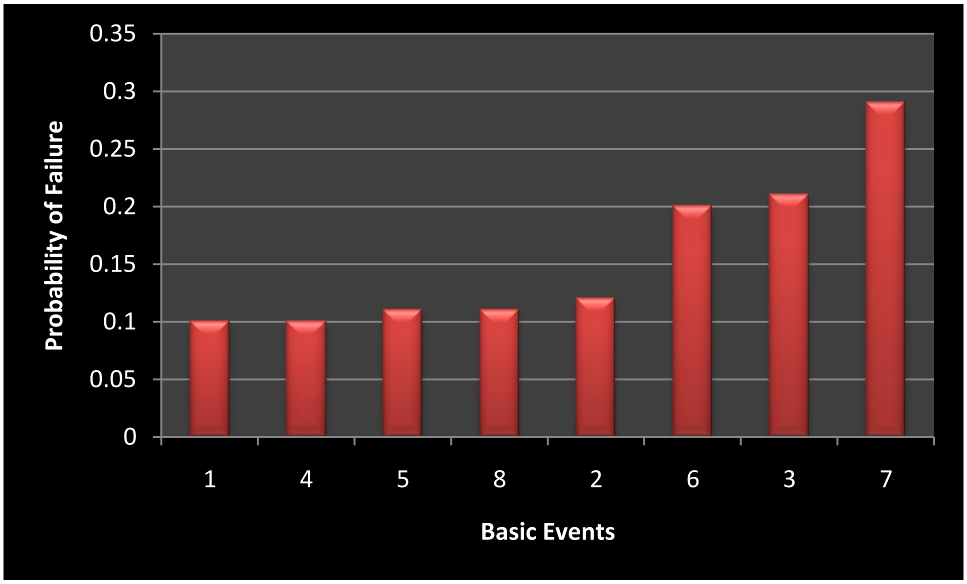

Figure 5.14: Graph between Probability of Failure and Basic Events of Filament Lens Control System

From the above graph, it is observed that the probability of failure of event is maximum due to applied excess of oxygen vapour in case of Filament Lens Control Symptom, so users have to take care of the oxygen vapour that is being used.

### 5.2.4 Heated Zone Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.4 proved the probability of failure of the system which is 0.08 due to the occurrence of Heated Zone Symptoms.

**Table 5.4: Probability due to which Heated Zone System failed**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Defective RTD | 0.05 |
| 2 | 24 V DC Power Supply Inoperable | 0.10 |
| 3 | Blown Ion Source Heater Fuse | 0.10 |
| 4 | Ion Source Cartridge Not Connected | 0.15 |
| 5 | Ion Source Not Hot Enough | 0.24 |
| 6 | Transfer Line Not Hot Enough | 0.09 |
| 7 | Ion Source Problem | 0.21 |
| 8 | Heated Zone Problem | 0.35 |

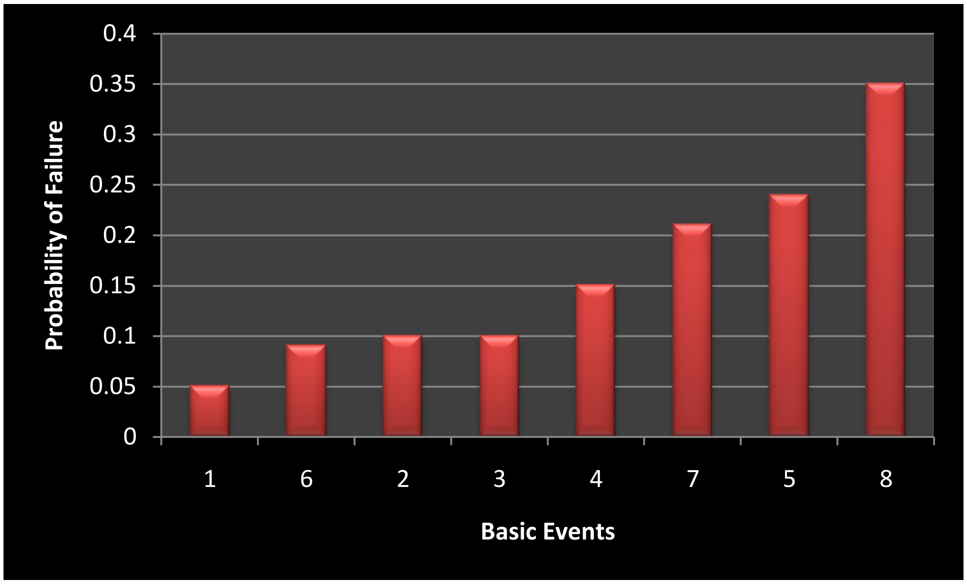

Figure 5.15: Graph between Probability of Failure and Basic Events of Heated Zone Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to heated zone in case of Heated Zone Symptom, so users have to take care of the heated zone that is being used.

### 5.2.5 High Vacuum Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.5 proved the probability of failure of the system which is 0.39 due to the occurrence of High Vacuum Symptoms.

**Table 5.5: Probability due to which High Vacuum Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Too High Foreline Pressure | 0.10 |
| 2 | Faulty Turbomolecular Pump Power Supply | 0.05 |
| 3 | Turbo Pump Shuts Off | 0.145 |
| 4 | Overheating of Diffusion Pump | 0.15 |
| 5 | Fore Pressure Not Low Enough | 0.27 |
| 6 | Faulty Cable Connection | 0.16 |
| 7 | Diffusion Pump not Turn On | 0.38 |
| 8 | Power Cable Not Connected | 0.05 |
| 9 | Pump Turn Off | 0.06 |
| 10 | Rotary Vane Pump Turn Off | 0.10 |

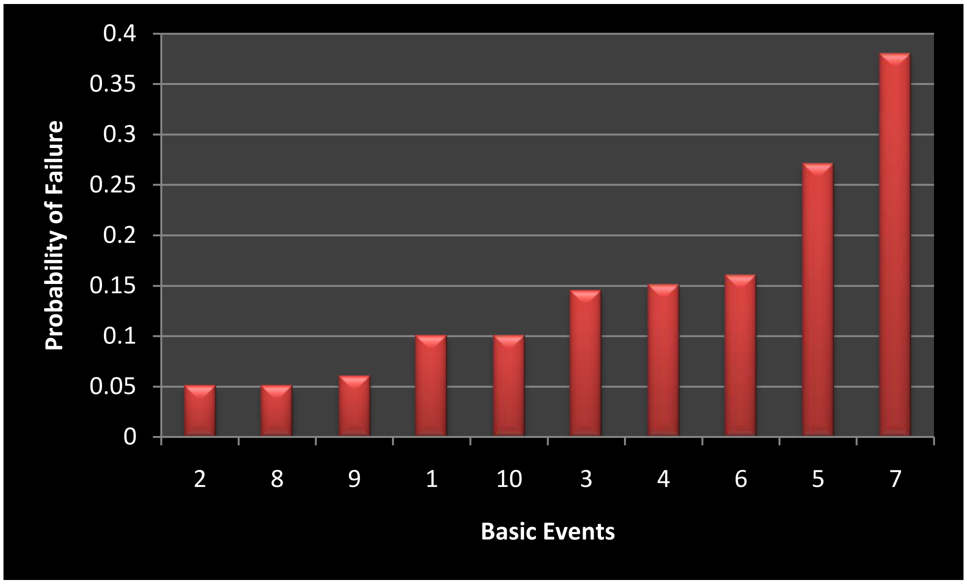

Figure 5.16: Graph between Probability of Failure and Basic Events of Filament Lens Control Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to turning off of the diffusion pump in case of High Vacuum Symptom, so users have to check whether the diffusion pump is on or off.

### 5.2.6 Linearity Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.6 proved the probability of failure of the system which is 0.12 due to the occurrence of Linearity Symptoms.

**Table 5.6: Probability due to which Linearity Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Bad Capillary Column | 0.08 |
| 2 | Too Thin High Concentration Samples | 0.10 |
| 3 | Incorrect Multiplier Settings | 0.14 |
| 4 | Dirty Ion Volume and Lenses | 0.17 |
| 5 | Poor Instrument Operating Condition | 0.05 |
| 6 | Non-Linear Response of GC activities | 0.11 |
| 7 | Variation Of Plot from Expected Peak | 0.15 |

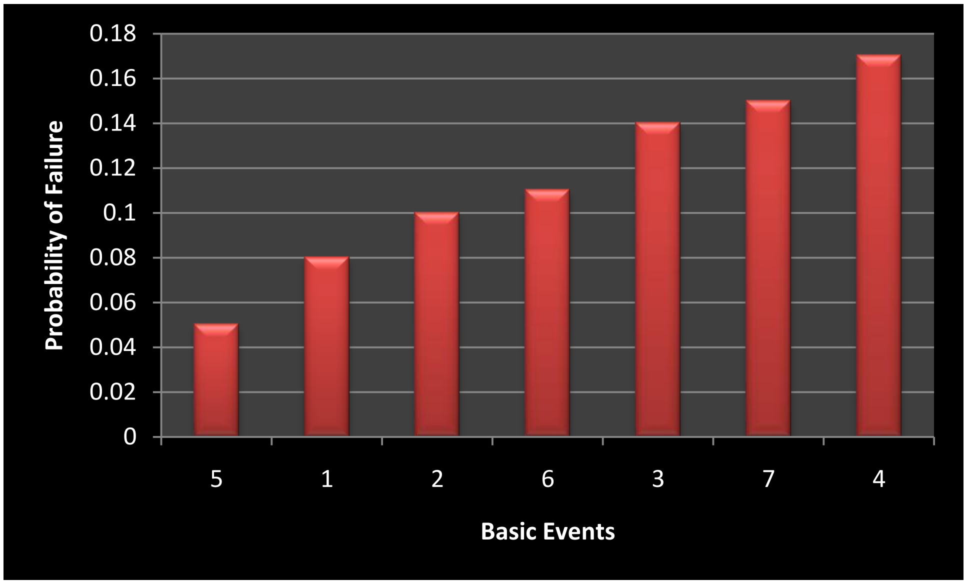

Figure 5.17: Graph between Probability of Failure and Basic Events of Linearity Control Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to dirty ion volume and lenses in case of Linearity Symptom, so users should use clean ion volume and lenses.

### 5.2.7 Power Supply Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.7 proved the probability of failure of the system which is 0.35 due to the occurrence of Power Supply Symptoms.

**Table 5.7: Probability due to which Power Supply Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | No Power Supply to Rotary Vane | 0.05 |
| 2 | Error from Other Supply | 0.10 |
| 3 | Rotary Vane Pump causes circuit breaker to trip | 0.14 |
| 4 | Faulty Power Module | 0.12 |
| 5 | Polaris Q turns on but circuit breaker trips | 0.24 |
| 6 | Disconnected Power Cord | 0.10 |
| 7 | Voltage Not Coming from the Electrical Outlet | 0.04 |
| 8 | Polaris Q Not Turn On | 0.136 |

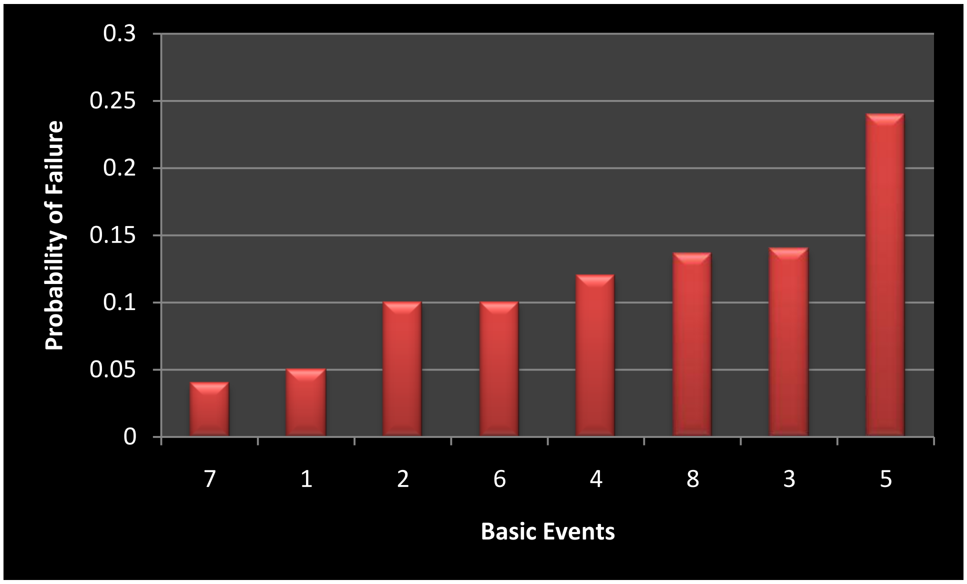

Figure 5.18: Graph between Probability of Failure and Basic Events of Power Supply Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to circuit breaker trips in case of Power Supply Symptom, so users have to be aware from any circuit tripping.

### 5.2.8. RF Control Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.8 proved the probability of failure of the system which is 0.33 due to the occurrence of RF Control Symptoms.

**Table 5.8: Probability due to which RF Control Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Fault with RF Generator Power Supply | 0.08 |
| 2 | RF feed through is arcing | 0.12 |
| 3 | Random Noise instead smooth RF Dip | 0.19 |
| 4 | Ring Electrode Not Contacting | 0.07 |
| 5 | Loose Cable | 0.12 |

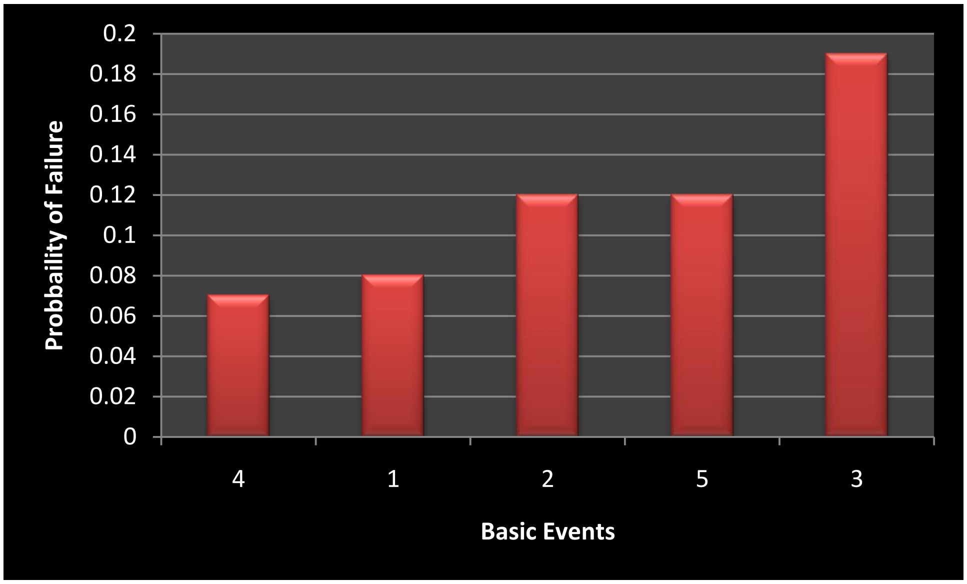

Figure 5.19: Graph between Probability of Failure and Basic Events of Power Supply Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to random noise in case of RF Control Symptom, so users have to control any random noise.

### 5.2.9 Sensitivity Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.9 proved the probability of failure of the system which is 0.34 due to the occurrence of Sensitivity Symptoms.

**Table 5.9: Probability due to which Sensitivity Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Leakage of Injector or Septum | 0.18 |
| 2 | Contamination of Injection Port | 0.17 |
| 3 | Insufficient Sample Delivery | 0.31 |
| 4 | Incorrect Match Syringe | 0.05 |

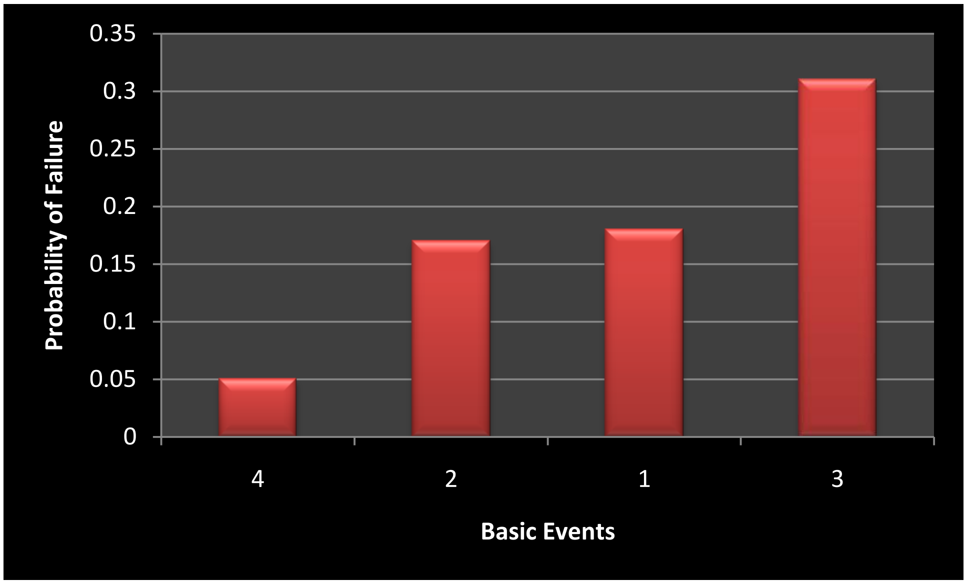

Figure 5.20: Graph between Probability of Failure and Basic Events of Sensitivity Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to insufficient sample delivery in case of Sensitivity Symptom, so users have to transfer sufficient sample delivery.

### 5.2.10 Stability Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.10 proved the probability of failure of the system which is 0.39 due to the occurrence of Stability Symptoms.

**Table 5.10: Probability due to which Stability Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Air Leak | 0.11 |
| 2 | High Vacuum Problem | 0.05 |
| 3 | Unstable Signal Response | 0.15 |
| 4 | Error | 0.10 |
| 5 | Ion Trap Control Problem | 0.12 |
| 6 | Unstable Mass Assign | 0.20 |
| 7 | Spiking Error | 0.06 |
| 8 | Sample Injection error | 0.12 |
| 9 | Reproducibility of Accurate Result | 0.17 |

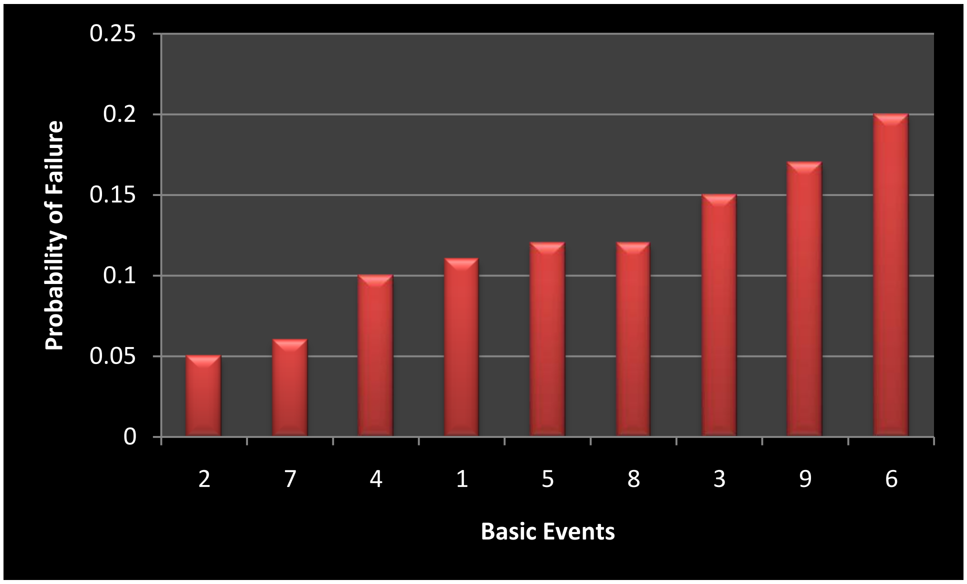

Figure 5.21: Graph between Probability of Failure and Basic Events of Stability Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to unstable mass assign in case of Stability Symptom, so users have to assign stable mass.

### 5.2.11 Tuning Symptoms

On the basis of data collected for various events, the results obtained using software as summed up in Table 5.11 proved the probability of failure of the system which is 0.395 due to the occurrence of Tuning Symptoms.

**Table 5.11: Probability due to which Tuning Symptoms occurred**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | GC column flow is too high | 0.10 |
| 2 | Dust on dynode or multiplier | 0.08 |
| 3 | Calibration gas vial open | 0.12 |
| 4 | Problem with ion trap | 0.05 |
| 5 | Ion trap misadjusted | 0.16 |
| 6 | Multiplier gain calibration fail | 0.17 |
| 7 | Lens misadjusted | 0.15 |
| 8 | Ion trap misadjusted | 0.30 |

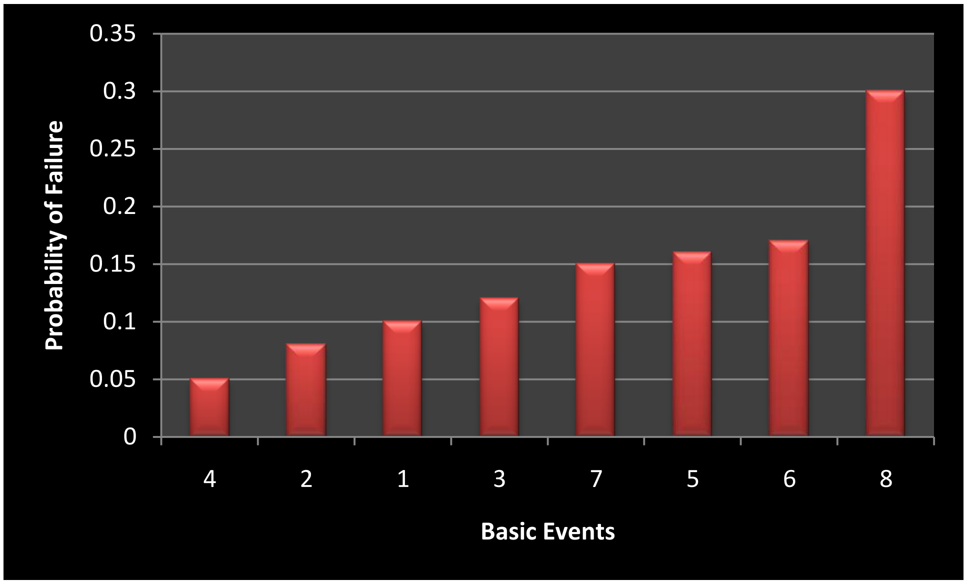

Figure 5.22: Graph between Probability of Failure and Basic Events of Tuning Symptoms

From the above graph, it is observed that the probability of failure of event is maximum due to misadjustment of ion trap in case of Tuning Symptom, so users must adjust the Ion Trap.

## 5.3 Polaris Q GC-MS Instrument

The probabilities of failure of all the subparts of Polaris Q have been calculated and it is shown in the above topics. The summation of all the results is implemented here. The chances of failure of Polaris Q depend upon all the subparts t hat is being calculated above. As Polaris Q have three parts namely:

1. Gas Chromatography
2. Mass Spectrometry
3. Autosampler

So, probability of failure of instrument depends on these three parts. Reliability of these instruments determine the reliability of Polaris Q. By using software, finally the probability of failure of GC-MS instrument is calculated.

The fault tree and the tabular formation of the same is shown below.

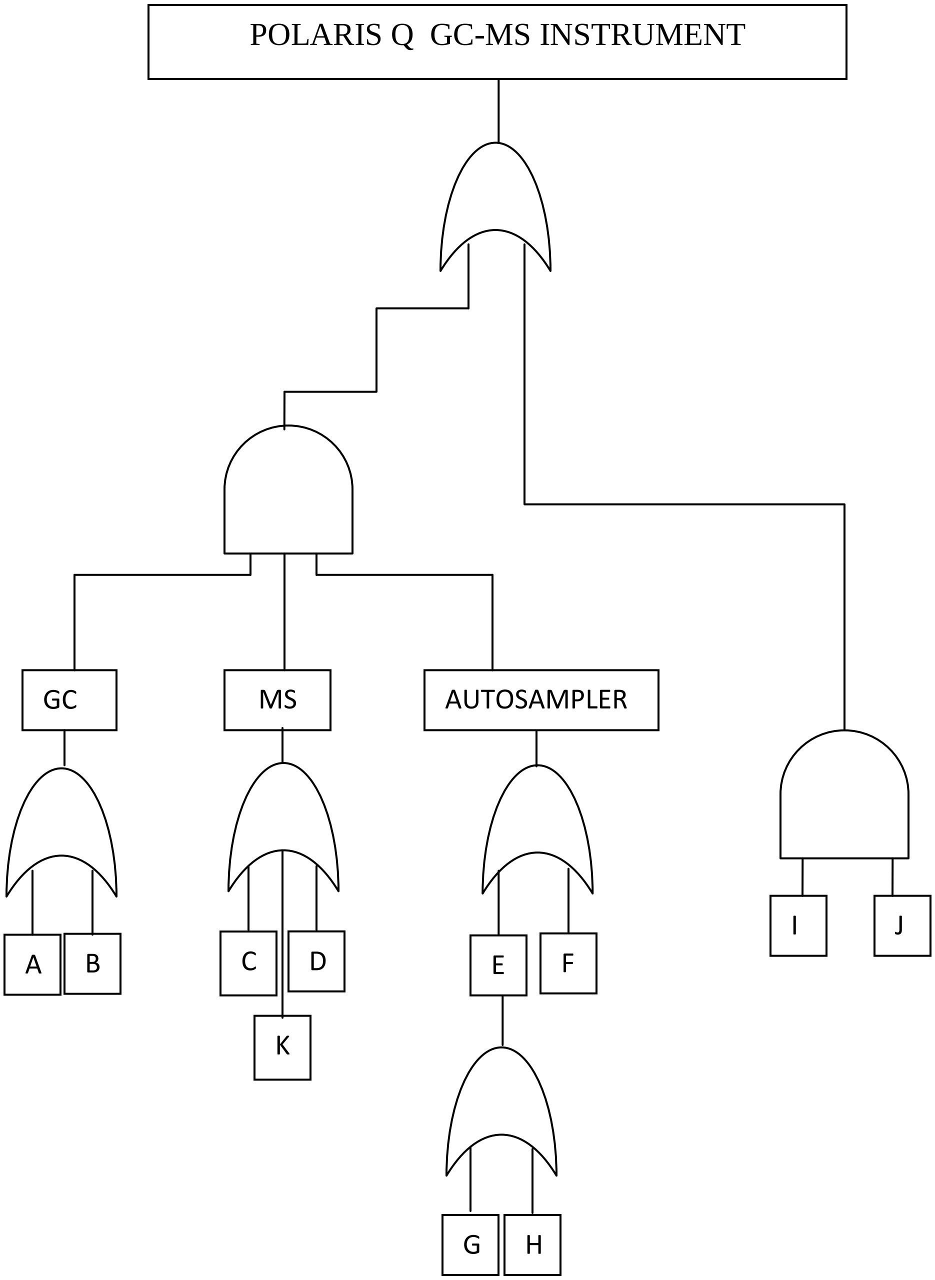

Figure 5.23 Polaris Q GC-MS Instrument

### 5.3.1 Tabular formation of the Polaris Q GC-MS

Below is the tabular representation of basic events and failure of probability of Polaris Q GC-MS instrument.

**Table 5.12: Probability due to which Polaris Q GC-MS failed**

| S.No. | Basic Events | Probability of Failure |
|---|---|---|
| 1 | Gas Chromatography | 0.45 |
| 2 | Mass Spectrometry | 0.49 |
| 3 | Autosampler | 0.46 |
| 4 | A | 0.39 |
| 5 | B | 0.12 |
| 6 | C | 0.16 |
| 7 | D | 0.21 |
| 8 | E | 0.31 |
| 9 | F | 0.33 |
| 10 | G | 0.34 |
| 11 | H | 0.16 |
| 12 | I | 0.35 |
| 13 | J | 0.08 |
| 14 | K | 0.39 |

Table 5.12 is the summation of all the above tables where all the events and its probabilities of failure are shown. On the basis of above table, finally the probability of failure of Polaris Q GC-MS is obtained which is calculated and the obtained value is 0.11. The chances of failure of Polaris Q are 11%.

From the graph shown below, it is observed that the failure of mass spectrometry, Gas Chromatography and Autosampler leads to the failure of Polaris Q but the major contribution of failure of this instrument is due to the failure of mass spectrometry. The failure of whole instrument depends upon all the three parts.

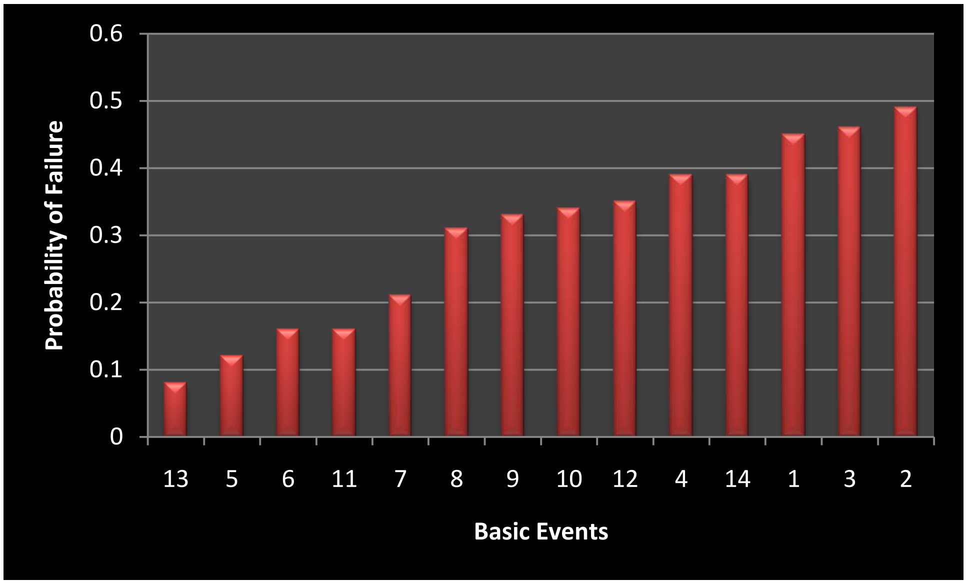

Figure 5.24: Graph between Probability of Failure and subparts of Symptoms Polaris QGc-MS Instrument

**Abbreviation:**

A: High Vacuum Symptoms

B: Linearity Symptoms

C: Communication Symptoms

D: Contamination Symptoms

E: Filament and Lens Control Symptoms

F: RF Control Symptoms

G: Sensitivity Symptoms

H: Tuning Symptoms

I: Power Supply Symptoms

J: Heated Zone Symptoms

K: Stability Symptoms

# CHAPTER 6

# CONCLUSION AND FUTURE SCOPE

## Conclusion

The reliability of the Polaris Q has been determined which is dependent upon three basic instruments, namely:

1. Mass Spectrometry
2. Gas Chromatography
3. Autosampler

The reliability of these instruments is calculated by finding the probability of success and failure of its subparts. After observing the calculated data of the subparts, finally it is concluded that although all these three instruments are responsible for the reliability of the Polaris Q but the major contribution of the reliable working of this instrument is dependent upon Mass Spectrometry. Moreover the 100% failure of Polaris Q occurs only if all the three instruments fail. Finally the probability of failure of Polaris Q GC-MS is obtained which is 0.11. The chance of failure of Polaris Q is 11%.

## Future Scope

In this thesis, the reliability of the Polaris Q has been calculated by determining the fault tree method. This can be extended further by means of another methods like Markov process, Monte carlo etc. The future work of this thesis can be employed with the help of another methods of calculating reliability to make a comparison study.

# REFERENCES

[1] William P.Karas "Reliability and Field Experience of Electronic Switching Systems" IEEE Transactions on Communication Technology, Vol. 15, No. 6, pp. 736-743, 1967.

[2] David J. Klinger, Charalampos I. Saraidaridis, Krisadee S. Vanderbei "Reliability Program Management: Today and Tomorrow" Reliability And Maintainability Symposium, Vol.11, pp. 85-92, 1992.

[3] Christopher A. Lane, Joseph D. Morrison "Achieving Reliability Growth On Real-Time Systems" Reliability And Maintainability Symposium, Vol. 16, pp.136-141, 1994.

[4] Saileshwar Krishnamurthy, Aditya P. Mathur "S. Krishnamurthy, A.P. Mathur, "On The Estimation of Reliability of A Software System Using Reliabilities of Its Components," , Eighth International Symposium On Software Reliability Engineering (ISSRE ), pp. 146-201, 1997.

[5] Jon G. Elerath , Alan P. Wood, Dave Christiansen, Michael Hurst-Hopf " Reliability Management And Engineering in A Commercial Computer Environment" IEEE Proceedings Annual Reliability And Maintainability Symposium. Vol.13, pp.124-127, 1999.

[6] Yusen Lin, Sourav Bhattcharya "System Engineering Encapsulation of Reliability Techniques" Object-Oriented Real-Time Dependable Systems, Proceedings. Fourth International Workshop on, Vol. 12, pp.138-146, 1999.

[7] David M. Nicol, Daniel L. Palumbo, Michael L. Ulrey "A Graphical Model-Based Reliability Estimation Tool And Failure Mode & Effects Simulator" IEEE Proceedings Annual Reliability and Maintainability Symposium pp. 74-81, 1999.

[8] Ronald E. Giuntini, Wyle Laboratories “Mathematical Characterization of Human Reliability For Multi-Tasksystem Operations” IEEE International Conference on Systems, Man, And Cybernetics, Vol. 2, pp. 1325-1329, 2000.

[9] Katerina GoˇSeva-Popstojanova “Failure Correlation In Software Reliability Models” IEEE Transactions On Reliability, Vol. 49, pp. 232-256, 2000 .

[10] D. David Dylis , Mary Gossin Priore “A Comprehensive Reliability Assessment Tool For Electronic Systems” Annual Proceedings On Reliability And Maintainability Symposium, pp: 308-313, 2001.

[11] A. O. Charles Elegbede, Chengbin Chu,” Reliability Allocation through Cost Minimization” IEEE Transactions on Reliability, Vol. 52, No. 1, 2003.

[12] Om P. Yadav, Nanua Singh, Parveen S. Goel ” A Practical Approach To System Reliability Growth Modeling and Improvement” Reliability and Maintainability Symposium, pp. 351- 359, 2003.

[13] Fashandi, A. Umberg, T. “Equipment Failure Definition: A Prerequisite for Reliability Test And Validation” Electronics Manufacturing Technology Symposium IEEE/CPMT/SEMI 28th International, pp. 357- 358, 2003.

[14] Manthos Economou “The Merits and Limitations Of Reliability Predictions” Reliability And Maintainability, 2004 Annual Symposium - RAMS, pp. 352- 357, 2004.

[15] Krasich, M.; Quigley, J.; Walls, L., "Modeling Reliability Growth In The Product Design Process," Reliability And Maintainability, 2004 Annual Symposium - RAMS , Vol.23, No.1, pp. 424-430, 26-29, 2004.

[16] Preston R. Macdiarmid, David J. Mahar, Jessica Glover, Wyatt E. Shankle, “PROTOCOL: An On-Line Environment for Reducing Product Reliability Risk” Reliability And Maintainability Symposium, On Page(S): 665-671, 2006.

[17] Ilse M. De Visser, Johannes A. Van Den Bogaard“The Risks Of Applying Qualitative Reliability Prediction Methods: A Case Study” The Risks Of Applying Qualitative Reliability Prediction Methods: A Case Study Reliability And Maintainability Symposium RAMS '06. Annual , pp. 532-538, 2006.

[18] John Nierwinski, Jr.”Reliability Sampling Methodology Using Simulation And Re-Sampling” IEEE Transactions On Reliability, Vol. 56, No. 1, pp. 24-38, 2007.

[19] Dr. Michel Houtermans, Mufeed Al-Ghumgham, Tino Vande Capelle, “Reliability Engineering & Data Collection To Improve Plant Safety & Availability” IEEE Second International Conference On Systems, pp. 42-42, 2007.

[20] Milena Krasich “Realistic Reliability Requirements for The Stresses In Use” Reliability And Maintainability Symposium, Vol. 29, Pp. 13-16, 2007

[21] Tanguy, C., "Exact Two-Terminal Reliability of Some Directed Networks," 6th International Workshop on Design and Reliable Communication Networks, Vol., No., pp.1-8, 7-10 Oct. 2007.

[22] Mihir R. Choudhury“Reliability Analysis of Logic Circuits” IEEE Transactions on Computer-Aided Design of Integrated Circuits and Systems, Vol. 28, No. 3, 2009