University of Tennessee, Knoxville

TRACE: Tennessee Research and Creative Exchange

Masters Theses

Graduate School

8-2004

Analysis and Simulation of a Batchwise Scotch Whisky Production process

Thomas Benton Rogers
University of Tennessee, Knoxville

Follow this and additional works at: https://trace.tennessee.edu/utk_gradthes

Part of the Chemical Engineering Commons

Recommended Citation

Rogers, Thomas Benton, "Analysis and Simulation of a Batchwise Scotch Whisky Production process. " Master's Thesis, University of Tennessee, 2004.
https://trace.tennessee.edu/utk_gradthes/4800

This Thesis is brought to you for free and open access by the Graduate School at TRACE: Tennessee Research and Creative Exchange. It has been accepted for inclusion in Masters Theses by an authorized administrator of TRACE: Tennessee Research and Creative Exchange. For more information, please contact trace@utk.edu.

To the Graduate Council:

I am submitting herewith a thesis written by Thomas Benton Rogers entitled "Analysis and Simulation of a Batchwise Scotch Whisky Production process." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Charlie Moore, Major Professor

We have read this thesis and recommend its acceptance:

John Collier, Robert Counce

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by Thomas Benton Rogers entitled "Analysis and Simulation of a Batchwise Scotch Whisky Production Process." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Masters of Science, with a major in Chemical Engineering.

Charlie Moore, Major Professor

We have read this thesis
and recommend its acceptance:

John Collier

Robert Counce

Acceptance for the Council:

Vice Chancellor and Dean of
Graduate Studies

Thesis
2004
.R65

Analysis and Simulation of a Batchwise Scotch Whisky Production Process

A Thesis
Presented for the
Masters of Science Degree
The University of Tennessee, Knoxville

Thomas Benton Rogers

August 2004

DEDICATION

This thesis is dedicated to my loving and supportive family and friends without whom I would have been lost.

ACKNOWLEDGEMENTS

This project was made possible by the effort and support of many people. I would like to thank the wonderful people at the Bruichladdich Distillery in Islay Scotland for their contributions, particularly the contributions of Jim McEwan, Master Distiller at Bruichladdich. Their knowledge and help has been invaluable to this work. I would also like to thank Phil Perkins and Paul Angelino of Bush Brothers and Company. Their help was instrumental in conducting the research presented here. Special thanks must be extended to my major professor Dr. Charlie Moore whose guidance and advice have been invaluable to me both in this work and in my life outside this work. Special thanks must also be extended to Dr. John Collier whose encouragement and interest first sparked my own interest and passion for the subject of this research. Many thanks to Dr. Pete Counce who has been most helpful in helping me see beyond the everyday tasks of this work to consider its greater usefulness. I must also thank my friend and co-researcher Samuel Morton for his time, effort, and enthusiasm which has more often than not spurred me to greater achievement. I need to thank my parents Jim and Teresa Rogers, my sister Meegan, my brother Adam, Allison and my many friends who have helped me through the tough times during the course of this work. I also give thanks to God for the strength and comfort whose enduring love and grace have seen me through my times of tribulation and given me a joy beyond measure.

ABSTRACT

Scotch whisky is produced in a two step distillation process that has remained relatively unchanged for decades, even centuries. The chemical composition of the whisky is vital to its flavor and character. Much work has been done to analyze and study the final composition of different whiskies. However, to date little work has been published that studies the composition of the distillate with respect to distillation time. The goal of this work is to develop an experimental basis for study of the scotch whisky production process. Experimental data would allow us to gain a better understanding of the effects of distillation and aging. Samples collected during the distillation process were analyzed using gas-chromatography mass spectrometry. This analysis allowed the development of composition curves for several components found in whisky to help understand process decisions made during distillation. The experimental data developed during the chemical analysis provided a physical basis for development of a process simulation. The simulation was done using the HYSYS® Simulation software. The batch distillation process was modeled using a tray distillation column with a large reboiler and low reflux. These conditions closely mimic the operation of the actual process. The simulation successfully modeled the experimental data for both the major and minor components. Simulation studies have also been able to produce suggestions for process improvements that could increase the economic yield of the distillery.

TABLE OF CONTENTS

PART I - INTRODUCTION 1

1. OVERVIEW AND RATIONALE 2
    1.1 Rationale for the Research 2
    1.2 Research Problem 3
    1.3 Research Objectives 3
    1.4 Summary of Deliverables 3
2. INTRODUCTION 5
3. BACKGROUND 9
    3.1 Chemical Analysis 9
    3.2 Simulation and Modeling 11
4. LITERATURE CITED 13

PART II - GC/MS ANALYSIS OF SCOTCH WHISKY DISTILLATE SAMPLES 15

ABSTRACT 16
INTRODUCTION 17
MATERIALS AND METHODS 23
    Gas Chromatographic Analysis 23
    Quantitation 24
RESULTS AND DISCUSSION 28
    Identified Compounds 28
    Wash Still Data 29
    Spirit Still Data 37
CONCLUSIONS 46
LITERATURE CITED 57
APPENDIX 59

PART III - SCOTCH WHISKY DISTILLATION MODELING AND SIMULATION 104

ABSTRACT 105
INTRODUCTION 106
MATERIALS AND METHODS 114
RESULTS AND DISCUSSION 117
    Wash Still Feed Conditions 117
    Wash Still Model Ethanol Tuning 118
    Wash Still Model Minor Component Tuning 122
    Final Wash Still Model 125
    Spirit Still Simulation 125

Spirit Still Feed Conditions 131
Spirit Still Ethanol Tuning 132
Spirit Still Minor Component Profiles 133
Process Improvements 139
Future Work 142
LITERATURE CITED 144
APPENDIX 146

PART IV - CONCLUSIONS AND FUTURE WORK 149

1. SUMMARY 150
2. PROPOSED IMPROVEMENTS 152
3. FUTURE WORK 154

VITA 155

LIST OF TABLES

PART II
1. Standard solution composition in volume percent Ethanol 27
2. Identified Compounds from GC/MS Analysis 28

PART III

1. Wash Still Feed Composition 118
2. Spirit Still Feed Composition 132
3. Heat Flux to Reboiler Wash Still 147
4. Heat Flux to Reboiler Spirit Still 148

LIST OF FIGURES

PART II

1. Production Process Diagram 19
2. Ethanol Calibration Curve 25
3. Water Calibration Curve 26
4. Wash Still Sample Taken at 0:00 Minutes of Distillation 30
5. Wash Still Sample Taken at 10:00 Minutes of Distillation 31
6. Wash Still Sample Taken at 50:00 Minutes of Distillation 32
7. Wash Still Sample Taken at 90:00 Minutes of Distillation 33
8. Wash Still Sample Taken at 140:00 Minutes of Distillation 34
9. Wash Still Sample Taken at 200:00 Minutes of Distillation 35
10. Wash Still Sample Taken at 270:00 Minutes of Distillation 36
11. Low Wines and Feints Receiver Sample 38
12. Foreshots Sample Taken at 15:00 Minutes of Distillation 39
13. Foreshots Sample Taken at 60:00 Minutes of Distillation 40
14. Spirit Sample Taken at 65:00 Minutes of Distillation 41
15. Spirit Sample Taken at 135:00 Minutes of Distillation 42
16. Spirit Sample Taken at 195:00 Minutes of Distillation 43
17. Spirit Sample Taken at 245:00 Minutes of Distillation 44
18. Feints Sample Taken at 260:00 Minutes of Distillation 45
19. Ethanol Concentration vs. Distillation Time in Wash Still 47
20. Minor Component Concentrations vs. Distillation Time in Wash Still 48
21. Ethanol Concentration vs Distillation Time in Spirit Still 49
22. Minor Component Concentrations vs Distillation Time in Spirit Still 50
23. Spirit Still Phases 54
24. Peak Area Calculation Program 60
25. Wash Still Sample Taken at 20:00 Minutes of Distillation 62
26. Wash Still Sample Taken at 30:00 Minutes of Distillation 63
27. Wash Still Sample Taken at 40:00 Minutes of Distillation 64
28. Wash Still Sample Taken at 60:00 Minutes of Distillation 65
29. Wash Still Sample Taken at 70:00 Minutes of Distillation 66
30. Wash Still Sample Taken at 80:00 Minutes of Distillation 67
31. Wash Still Sample Taken at 100:00 Minutes of Distillation 68
32. Wash Still Sample Taken at 110:00 Minutes of Distillation 69
33. Wash Still Sample Taken at 120:00 Minutes of Distillation 70
34. Wash Still Sample Taken at 130:00 Minutes of Distillation 71
35. Wash Still Sample Taken at 150:00 Minutes of Distillation 72
36. Wash Still Sample Taken at 160:00 Minutes of Distillation 73
37. Wash Still Sample Taken at 170:00 Minutes of Distillation 74
38. Wash Still Sample Taken at 180:00 Minutes of Distillation 75

39. Wash Still Sample Taken at 190:00 Minutes of Distillation 76
40. Wash Still Sample Taken at 210:00 Minutes of Distillation 77
41. Wash Still Sample Taken at 220:00 Minutes of Distillation 78
42. Wash Still Sample Taken at 230:00 Minutes of Distillation 79
43. Wash Still Sample Taken at 240:00 Minutes of Distillation 80
44. Wash Still Sample Taken at 250:00 Minutes of Distillation 81
45. Wash Still Sample Taken at 260:00 Minutes of Distillation 82
46. Foreshots Sample Taken at 0:00 Minutes of Distillation 83
47. Foreshots Sample Taken at 30:00 Minutes of Distillation 84
48. Foreshots Sample Taken at 45:00 Minutes of Distillation 85
49. Spirit Sample Taken at 75:00 Minutes of Distillation 86
50. Spirit Sample Taken at 85:00 Minutes of Distillation 87
51. Spirit Sample Taken at 95:00 Minutes of Distillation 88
52. Spirit Sample Taken at 105:00 Minutes of Distillation 89
53. Spirit Sample Taken at 115:00 Minutes of Distillation 90
54. Spirit Sample Taken at 125:00 Minutes of Distillation 91
55. Spirit Sample Taken at 145:00 Minutes of Distillation 92
56. Spirit Sample Taken at 155:00 Minutes of Distillation 93
57. Spirit Sample Taken at 165:00 Minutes of Distillation 94
58. Spirit Sample Taken at 175:00 Minutes of Distillation 95
59. Spirit Sample Taken at 185:00 Minutes of Distillation 96
60. Spirit Sample Taken at 205:00 Minutes of Distillation 97
61. Spirit Sample Taken at 215:00 Minutes of Distillation 98
62. Spirit Sample Taken at 225:00 Minutes of Distillation 99
63. Spirit Sample Taken at 235:00 Minutes of Distillation 100
64. Feints Sample Taken at 270:00 Minutes of Distillation 101
65. Feints Sample Taken at 280:00 Minutes of Distillation 102
66. Feints Sample Taken at 290:00 Minutes of Distillation 103

PART III

1. Production Process Diagram 107
2. Wash Still Simulation Schematic 119
3. Constant Heat Flux Simulations of Wash Still 121
4. Experimental Data with Variable Heat Flux Simulation 123
5. Interaction Parameter Adjustments for Ethyl Acetate 126
6. Interaction Parameter Adjustments for 1-Propanol 127
7. Interaction Parameter Adjustments for 2-M-1-Butanol 128
8. Interaction Parameter Adjustments for Isoamyl Alcohol 129
9. Spirit Still Simulation Schematic 130
10. Spirit Still Simulation Results 134
11. Spirit Still Ethyl Acetate Simulation with Reflux Ratio 135
12. Spirit Still 1-Propanol Simulation with Reflux Ratio 136

13. Spirit Still 2-M-1-Butanol Simulation with Reflux Ratio 137
14. Spirit Still Isoamyl Alcohol Simulation with Reflux Ratio 138

Part 1
Introduction

1. OVERVIEW AND RATIONALE

The purpose of this thesis is to serve as a partial fulfillment of the requirements to obtain a Masters of Science in Chemical Engineering. This thesis is composed of four Parts. Part I presents an introduction to the topic of research and a rationale for the research. It also includes the research problem and the research objectives and deliverables. In addition to this a review of the literature is included in Part I. Part II presents the experimental results of a distillate sample analysis using Gas Chromatography Mass Spectrometry as a stand alone peer review journal article. Part III discusses a model for the distillation process under study and proposes possible improvements based on simulation. Part IV is a summary of the work with a discussion of conclusions and future work.

1.1 Rationale for the Research

This research involves a study of Scotch whisky production at a small scale traditional distillery. The traditional operation of the distillation process uses a minimum of computer hardware and does not require extensive data logging. The research aim was to develop a set of data sufficient to characterize the time dependent nature of a batch distillation of whisky spirit. With this basis of knowledge it would then be possible to develop a computer simulation of the distillation process.

The simulation could then be used to better understand the mechanics of the distillation and provide a basis for proposing improvements.

1.2 Research Problem

The distillery does not utilize data logging as part of the normal operation. To address the scarcity of data in the process distillate samples were collected during a normal operation cycle. The distillate samples were collected from both stages of the distillation to develop a time dependent profile of composition. The samples were analyzed for chemical composition and used as the basis for model development.

1.3 Research Objectives

The objective of this research is to develop an experimental basis for a time dependent study of the whisky batch distillation. A working model of the distillation process was also to be developed subsequent to developing the experimental basis for such a model. An important feature of this work will be the use of the model to propose improvements that could be made to the process. The improvements will be based on simulations of different process conditions.

1.4 Summary of Deliverables

The deliverables from this work are a chemical analysis of distillate samples collected on site at the distillery, a working model of the distillation process, and two peer review journal articles. In support of

the model will be a discussion of diverse simulations which serve as the basis for possible process improvements. The final deliverables are two peer review journal articles detailing the work completed.

2. INTRODUCTION

Scotch whisky is produced in many areas of Scotland under a variety of conditions. Large distillers often produce millions of liters of whisky in a year. A majority of whiskies are then blended to produce the bottled product. The blending process consists of taking Scotch malt and mixing it with several other malts until the desired flavor is reached. Often coloring agents are added into the whisky to match the desired color in the final bottling. Single malt Scotch is produced from only a single type of whisky from a single distillery and requires the aged malt to already contain the proper flavor compounds to produce the desired result. Single malts are typically more valuable than blended whiskies and therefore consistent production results are highly desirable. The nature of the production process makes it more difficult to maintain the desired quality and composition of the malt. This is especially true for traditional distilleries that have very little or no computer interaction during the production of the whisky.

There are typically two methods for whisky manufacture, continuous distillation and batch wise distillation. Continuous distillation is normally used for American whiskey or bourbon and therefore plays little role in the manufacturing of Scotch whisky. Batchwise distillation is the normal means of producing Scotch and follows a simple pattern. Grain is allowed to sachrify and is ground into

a powdery substance called grist. The grist is then leached of sugar and the resulting sugar-water mixture is fermented with yeast. The fermentation product is sent into large pot stills of distinctive design and distilled. The distillate product from the first pot still is sent to a second pot still and distilled again to produce the desired alcohol mixture for barreling. Once the distillate is barreled it is allowed to age until it is deemed to be ready for bottling, usually a minimum of 8 years. [1]

Scotch whisky is a complex mixture which contains many flavor compounds that contribute to the overall taste of the whisky. Many of the flavor compounds are found only in very small concentrations in the final product, yet they are major components of the taste and character of any particular whisky. [1] Several types of substances contribute to the flavor, alcohols, esters, organic acids, aldehydes, ketones, and others. [2-4] The flavor of any whisky is vital to its ability to sell and consumers expect the whisky to have a consistent flavor from one production to the next. The ability to control the composition of these minor components is important to the overall profitability of the production process.

In the case of Scotch whisky, the government imposed duties and taxes are collected on the total amount of alcohol barreled. As the whisky ages it loses some of it alcohol content, therefore the distillery is paying taxes on alcohol they cannot sell. This puts even greater pressure

on the distiller to maximize the alcohol recovered from the fermentation process while maintaining consistent product. This leads traditional distilleries to stay with a particular production process that works with little consideration given to process improvement for fear of changing the overall product.

The object of this work is to create a model of the Bruichladdich Distillery distillation process. Bruichladdich Distillery is located on the island of Islay, Scotland. It operates as a traditional distillery with no computerized controls. The distillation proceeds as two distinct batch distillations. The first step concentrates the alcohol from the beer, or fermentation product, to a much higher alcohol content while leaving behind a large portion of the water and almost all solids such as dead yeast cells. The second distillation further concentrates the alcohol and is split into three distillate segments. The first segment, or cut, which includes approximately one third of the distillate product is called the foreshots and is high in alcohol concentration. The second segment is the product or spirit cut which is collected for barreling. This cut is also approximately one third of the distillate product. The third and final cut is the feints and is lower in alcohol content then either of the first two cuts. The foreshots and feints are collected in a large holding tank and recycled in subsequent distillations to maximize alcohol recovery. Throughout this process, which takes roughly 8 hours to complete, the

operators monitor the alcohol content of the distillate using hydrometer measurements taken during the distillation. Based on these measurements and established practice at the distillery the operators adjust the steam flow into the distillation vessel.

To carry out the modeling of this process it was necessary to collect liquid samples throughout the distillation process. Samples of the distillate and feed liquids were collected during both the first and second distillation steps. The samples were analyzed to determine the composition of the distillate and feed liquids to help identify the chemicals present during the distillation. The analysis also provides a basis for comparing the predicted results from the model to the actual process conditions. Therefore, the sample analysis is used to determine the success and accuracy of the process model.

3. BACKGROUND

This chapter gives a brief overview of the decisions and rationales that constitute the basis of this work. Included in this discussion is a review of the literature applicable to this work. The first section provides information relevant to material dealing with the analysis and classification of chemicals by GC-MS. The second section addresses the simulation model and the literature on process modeling, batch process modeling, and modeling using HYSYS™.

3.1 Chemical Analysis

There are many ways to identify an unknown substance. Analysis methods include gas chromatography (GC), mass spectrometry (MS), nuclear magnetic resonance (NMR), infrared spectroscopy (IR) and combinations of these and many other methods. [5-7] GC and gas chromatography-mass spectrometry (GC/MS) are popular methods of analysis for many types of unknown compounds. GC/MS has a wide range of application and extensive literature is available on its uses. As discussed in [5] the basis of GC analysis is the separation of chemicals by affinity with the chosen column stationary phase. The affinity of each compound effects the elution time of the compound through the column which is the main factor in determining the identity of the compound when using GC alone. However the elution time will be influenced by several other factors mainly the columns stationary phase but also

column length and carrier gas flow rate which can vary widely from one machine to the next.

Mass spectrometry is often used in conjunction with gas chromatography because mass spectroscopy has the ability to identify individual compounds based on their mass spectral signals. GC-MS as it is commonly referred to, first separates the individual components in an unknown sample and then using a mass spectral detector records the unknown's mass signal. The mass spectral data is then compared to mass spectral data libraries to identify the compound from the library that most closely matches the observed spectra. The elution time from the GC column can also be used for verification of chemical identity by comparison to standards of known compounds that have been run under the same conditions.

There are some limitations on GC-MS analysis. Unknowns that have very low concentrations can be difficult to isolate and it is often necessary to use a solvent for analysis. Large solvent peaks can mask or distort other peaks that elute at nearly the same time. Large solvent peaks can also make it difficult to obtain accurate integration results from the signal because of the significant fraction of the area made up by the single peak. The best solvents elute before any of the other compounds so that a solvent delay can be used and allow the detector to ignore the solvent peak in the analysis of the signal. It can also be

difficult to isolate minor components from a solution without pre-concentration steps. [8]

3.2 Simulation and Modeling

Process simulation and modeling has been a part of chemical engineering for many years. One of the many uses of a process model is to allow an engineer to modify an existing process and evaluate its performance without actually disturbing the process. This ability has been invaluable to the chemical engineering profession. As computers have gotten faster and more powerful it has become possible to model more and more complex systems accurately and quickly. However, it is important to establish the validity of the process model before any work is done that relies on the model.

The basis for any process simulator is the fundamental mass and energy equations that govern the mass and energy balances of the system. Another fundamental part of the model is the method for including the interactions of the components of the system with each other and the unit operations that are being simulated. With so many methods available to the engineer to account for the interactions of the molecules it is vital that good judgment be used in selecting a thermodynamic framework for the chosen simulation environment. [9-10]

The system under consideration for this work is a mixture of mainly ethanol and water. There are several minor components that

include longer chain alcohols, fusel oils, and other fermentation products. The overwhelming amount of ethanol and water in the system make it imperative to select a thermodynamic system that can accurately account for the non idealities present in the system. There is a wealth of information on ethanol-water VLE data and model parameters to fit the data. [11-12] Upon inspection of this data it seems that with proper tuning many equations of state and activity models can accurately model the ethanol-water vapor liquid equilibrium. Based solely on this data it was impossible to implicitly select one preferred thermodynamic system. As the HYSYS™ simulation program is the modeling system used for this work the literature provided with the program was examined. The manuals and help documentation with the software included an example simulation of an ethanol production plant. The plant simulated was a continuous production simulation but the essential elements of the simulation were similar enough to the work presented here that some guidance could be gleaned from the work. [13] The authors of the manuals selected the NRTL or Non Random Two Liquid thermodynamic package. The available literature suggests that NRTL thermodynamic package is an appropriate simulation package for this work.

4. LITERATURE CITED

1. The Alcohol Textbook, 3rd edition.; Jacques, K.; Lyons, T.P.; Kelsall, D.R.; Nottingham University Press: Nottingham, United Kingdom, 1999

2. Guichard, H.; Lemesle, S.; Ledauphin, J.; Barillier, D.; Picoche, B.; Chemical and Sensorial Aroma Characherization of Freshly Distilled Calvados 1. Evaluation of Quality and Defects on the Basis of Key Odorants by Olfactometry and Sensory Analysis. *J. Agric. Food Chem.* **2003**, 51, 424-432

3. Ledauphin, J.; Guichard, H.; Saint-Clair, J.F.; Picoche, B.; Barillier, D.; Chemical and Sensorial Aroma Characterization of Freshly Distilled Calvados 2. Identification of Volatile Compounds and Key Odorants. *J. Agric. Food Chem.* **2003**, 51, 433-442

4. Aroma of Beer, Wine and Distilled Alcoholic Beverages, Nykanen, L.; Suomalainen, H.; D. Reidel Publishing Company, 1983, Boston USA

5. Handbook of Instrumental Techniques for Analytical Chemistry, Settle F.; Prentice Hall, 1997

6. Goodner, K.L.; Jella, P.; Rouseff, R.L.; Determination of Vanillin in Orange, Grapefruit, Tangerine, Lemon, and Lime Juices Using GC-Olfactometry and GC-MS/MS, *J. Agric. Food Chem.* **2000**, 48, 2882-2886

7. Walker, T.; Morris, J.; Therlfall, R.; Main, G.; Analysis of Wine Components in Chythiana and Syrah Wines, *J. Agric. Food Chem.* **2003**, 51, 1543-1547

8. Fitzgerald, G.; James, K.J.; MacNamara, K.; Stack, M.A.; Characterisation of whiskies using solid-phase microextraction with gas chromatography-mass spectrometry. *J. Chorma. A.* **2000**, 896 351-359

9. Agarwal,R.; Li,Y.K.; Santollani, O.; Satyro, M.A.; Vieler, A.; Uncovering the Realities of Simulation. *Chem. Engr. Prog.* **2001**, 97, 5, 42-52

10. Agarwal,R.; Li,Y.K.; Santollani, O.; Satyro, M.A.; Vieler, A.; Uncovering the Realities of Simulation. *Chem. Engr. Prog.* **2001**, 97, 6, 64-72

11. Vapor-Liquid Equilibrium Data Collection Aqueous-Organic Systems Vol I, Part 1, J Gmehling, U Onken, DECHEMA Chemistry Data Series Vol.1 Part 1, 150-196

12. Vapor-Liquid Equilibrium Data Collection Aqueous-Organic Systems Vol I, Part 1 (Supplement 1), J Gmehling, U Onken, W Arlt, DECHEMA Chemistry Data Series Vol.1 Part 1a, 116-157

13. HYSYS Help Documentation C1 Ethanol Plant, pg. C1-1 - C1-16

Part II

GC/MS Analysis of Scotch Whisky Distillate Samples

This is a copy of a paper to be submitted for publication in the Journal of Agricultural and Food Chemistry by Ben Rogers, Samuel Morton, and John Collier. Ben Rogers was the primary author of this work with advice and support from Samuel Morton and John Collier.

ABSTRACT

Scotch whisky is produced in a two step distillation process that has remained relatively unchanged for decades, even centuries. The chemical composition of the whisky is vital to its flavor and character. Much work has been done to analyze and study the final composition of different whiskies. However, to date no work has been published that studies the composition of the distillate with respect to distillation time. The goal of this work is to develop an experimental basis for study of the scotch whisky production process to gain a better understanding of the effects of distillation and aging. Samples collected during the distillation process were analyzed using gas-chromatography mass spectrometry. This analysis allowed the development of composition curves for several components found in whisky to help understand process decisions made during distillation.

INTRODUCTION

Scotch whisky is a complex mixture which contains many flavor compounds that contribute to the overall taste of the whisky. Many of the flavor compounds are found only in very small concentrations in the final product, yet they are major components of the taste and character of any particular whisky. [1] Several types of substances contribute to the flavor, alcohols, esters, organic acids, aldehydes, ketones, and others. [2-4] The flavor of any whisky is vital to its ability to sell and consumers expect the whisky to have a consistent flavor from one production to the next. The ability to control the composition of these minor components is important to the overall profitability of the production process. In order to control the composition of the whisky you must first know specifically which compounds are present.

The composition of bottled Scotch has been studied by several different groups [5-9] but to date there has not been a published analysis of the distilled spirit prior to aging, mixing, and bottling. Aging of the whisky has a dramatic effect on its flavor [10] and is therefore very important, but it is difficult to assess how important without knowing the effect of distillation on final quality. This study will analyze a series of samples taken during the distillation process at a traditional distillery in Scotland. The goal of this work is to determine the composition of a scotch whisky distillate as distillation proceeds. Time dependent

distillate composition information will help explain some of the process decisions that have been handed down through traditional practice and whisky lore. It is commonly held that spirit cut of a scotch manufacturing process is chosen as the optimal combination of ethanol and flavor compounds. By choosing only the middle band of the distillate many minor components are being excluded either because they distilled before or after the bounds of the spirit cut. This work should begin to establish the experimental proof of this long held belief by identifying those compounds excluded by the spirit cut.

The distillation processes has two steps. The first step is distillation in the wash still. The second step is distillation in the spirit still. Samples were collected from both distillation steps. Figure 1 shows a diagram of the Scotch production process from malting to distillation. Each stage (malting, milling, fermentation, distillation, and barreling) of the production will be discussed briefly here.

The first stage, malting, is the process that converts grain starches found in the barley into fermentable sugars. It also is the point in the process where peating occurs. Peating is done by heating wet barley over a peat fire and allowing the barley to absorb the flavor of the peat smoke. After malting the grain is sent to the second processing stage, milling, and is milled into grist which is rough flour. The flour is filtered to remove any small stones and other impurities. The filtered grist is

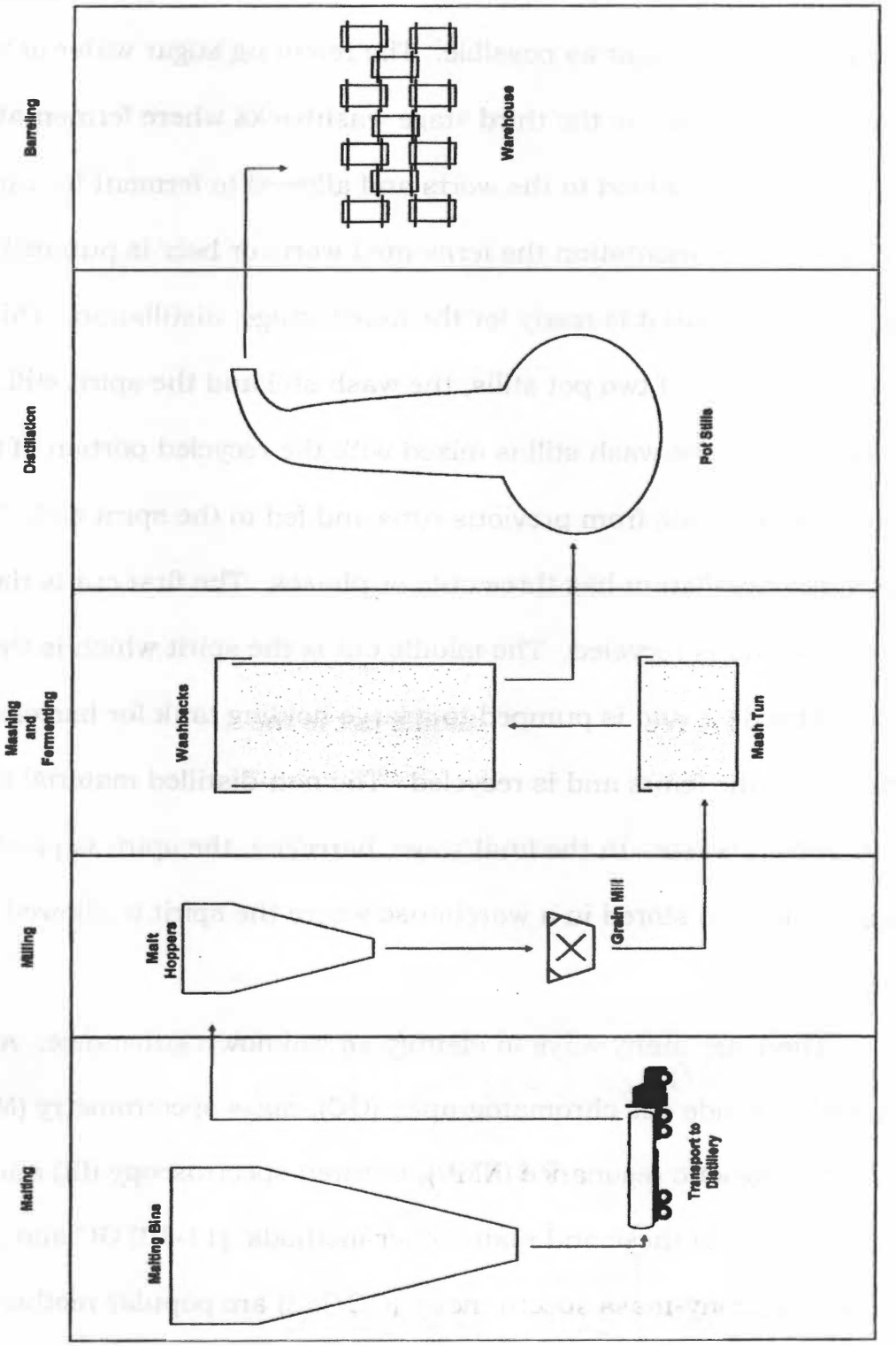

Figure 1: Production Process Diagram

pumped into the mash tun where the sugars in the grist are extracted by leaching. The grist is washed three or four times with hot water to extract as much sugar as possible. The resulting sugar water or worts is cooled and pumped to the third stage washbacks where fermentation occurs. Yeast is added to the worts and allowed to ferment for up to 72 hours. After fermentation the fermented worts or beer is pumped into a holding tank until it is ready for the fourth stage, distillation. This takes place in a series of two pot stills, the wash still and the spirit still. The distillate from the wash still is mixed with the recycled portion of the spirit still distillate from previous runs and fed to the spirit still. The spirit still distillation has three cuts or phases. The first cut is the foreshots and is recycled. The middle cut is the spirit which is the desired product and is pumped to a large holding tank for barreling. The final cut is the feints and is recycled. The non-distilled material from both stills is waste. In the final stage, barreling, the spirit is placed into large casks and stored in a warehouse where the spirit is allowed to age and mature.

There are many ways to identify an unknown substance. Analysis methods include gas chromatography (GC), mass spectrometry (MS), nuclear magnetic resonance (NMR), infrared spectroscopy (IR) and combinations of these and many other methods. [11-13] GC and gas chromatography-mass spectrometry (GC/MS) are popular methods of

analysis for many types of unknown compounds. GC/MS has a wide range of application and extensive literature is available on its uses. As discussed in [11] the basis of GC analysis is the separation of chemicals by affinity with the chosen column stationary phase. The affinity of each compound effects the elution time of the compound through the column which is the main factor in determining the identity of the compound when using GC alone. However the elution time will be influenced by several other factors mainly the columns stationary phase but also column length and carrier gas flow rate which can vary widely from one machine to the next.

Mass spectrometry is often used in conjunction with gas chromatography because mass spectroscopy has the ability to identify individual compounds based on their mass spectral signals. GC-MS as it is commonly referred to, first separates the individual components in an unknown sample and then using a mass spectral detector records the unknown's mass signal. The mass spectral data is then compared to mass spectral data libraries to identify the compound from the library that most closely matches the observed spectra. The elution time from the GC column can also be used for verification of chemical identity by comparison to standards of known compounds that have been run under the same conditions.

There are some limitations on GC-MS analysis. Unknowns that have very low concentrations can be difficult to isolate and it is often necessary to use a solvent for analysis. Large solvent peaks can mask or distort other peaks that elute at nearly the same time. Large solvent peaks can also make it difficult to obtain accurate integration results from the signal because of the significant fraction of the area made up by the single peak. The best solvents elute before any of the other compounds so that a solvent delay can be used and allow the detector to ignore the solvent peak in the analysis of the signal. It can also be difficult to isolate minor components from a solution without pre-concentration steps. [9]

MATERIALS AND METHODS

Scotch whisky distillate samples were obtained during a single series of batch still operations. The distillate samples came from a single fermented charge that was distilled first in the wash still and then in the spirit still. The samples were collected during June 2003 at the Bruichladdich Distillery on the island of Islay, Scotland. The samples were collected throughout the wash still distillation at intervals of 10 minutes. Spirit still samples were collected roughly every 10 minutes from the beginning of the distillation until approximately 50 minutes into the feints cut. No further samples were collected after this point due to limitations on available sample vials. The samples were collected in glass sample vials, labeled, sealed with shipping tape, and shipped from Scotland to the University of Tennessee for analysis. The glass vials were left sealed until just before analysis to prevent evaporation or contamination. The analysis was performed in Knoxville, Tennessee in the analytical laboratory of Bush Brothers and Company.

Gas Chromatographic Analysis. The individual component separation was performed using a HP 6890 gas chromatogram (Palo Alto, CA) with a 5973 Mass Selective Detector. The MSD was held at 280°C and scanned from 10 amu to 550 amu with a frequency of 2.74 scans/sec. The column used in this analysis was a DB-WAX column 30m x .25 mm x .25 µm (J&W Scientific, Folsom, CA) The oven

temperature profile was 35°C for 10 min, 5°C/min to 180°C held for 5 min, 20°C/min to 200°C held for 5 min. The column pressure profile was .25 psi for 10 min then 2 psi/min to 5 psi. The carrier gas was hydrogen produced by a hydrogen generator and the flow rate was variable with pressure. Injector temperature was a constant 250°C, .25 psi, and 33.2 mL/min flow. The column was run with a 25:1 split ratio for each injection. Component peaks from chromatographic data were identified using mass spectral data and retention time comparisons. The GC/MS database used for comparison was the Wiley7N library. The samples were run a total of three times under the same conditions. The chromatographic data was integrated using a self developed analysis routine for calculating peak area that is included in the appendix. The peak area calculation makes a correction for the average baseline of the signal and then performs peak analysis by identifying peaks of interest and integrating under the curve using a trapezoidal approximation.

Quantitation. A calibration curve was produced using 11 standard solutions of ethanol and water at the concentrations shown in Table 1. Each standard was run 5 times to determine the calibration curve for ethanol and water concentrations. The calibration curves are shown in Figures 2 and 3. The ethanol calibration curve was used to estimate the concentration of the minor components.

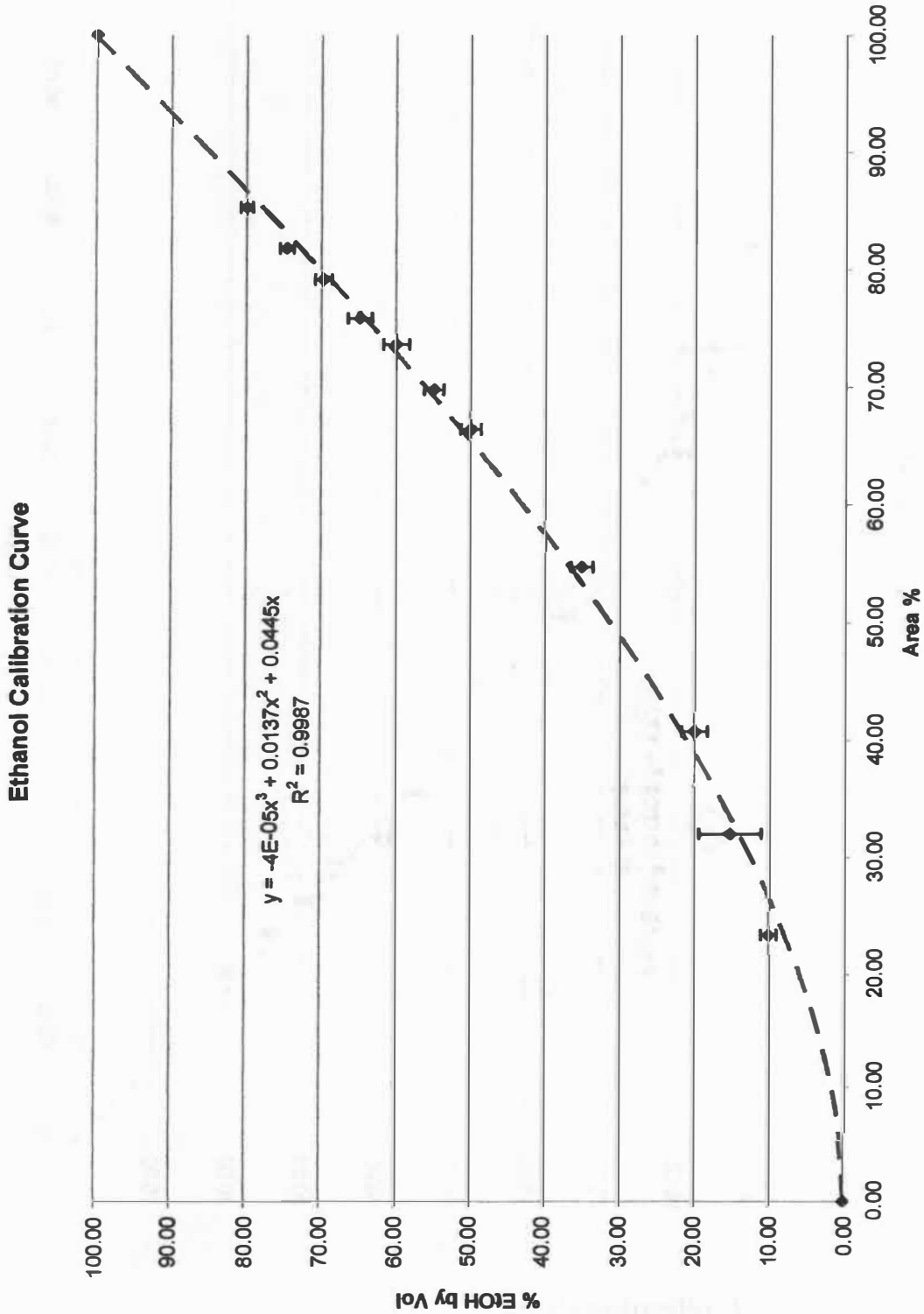

Figure 2: Ethanol Calibration Curve

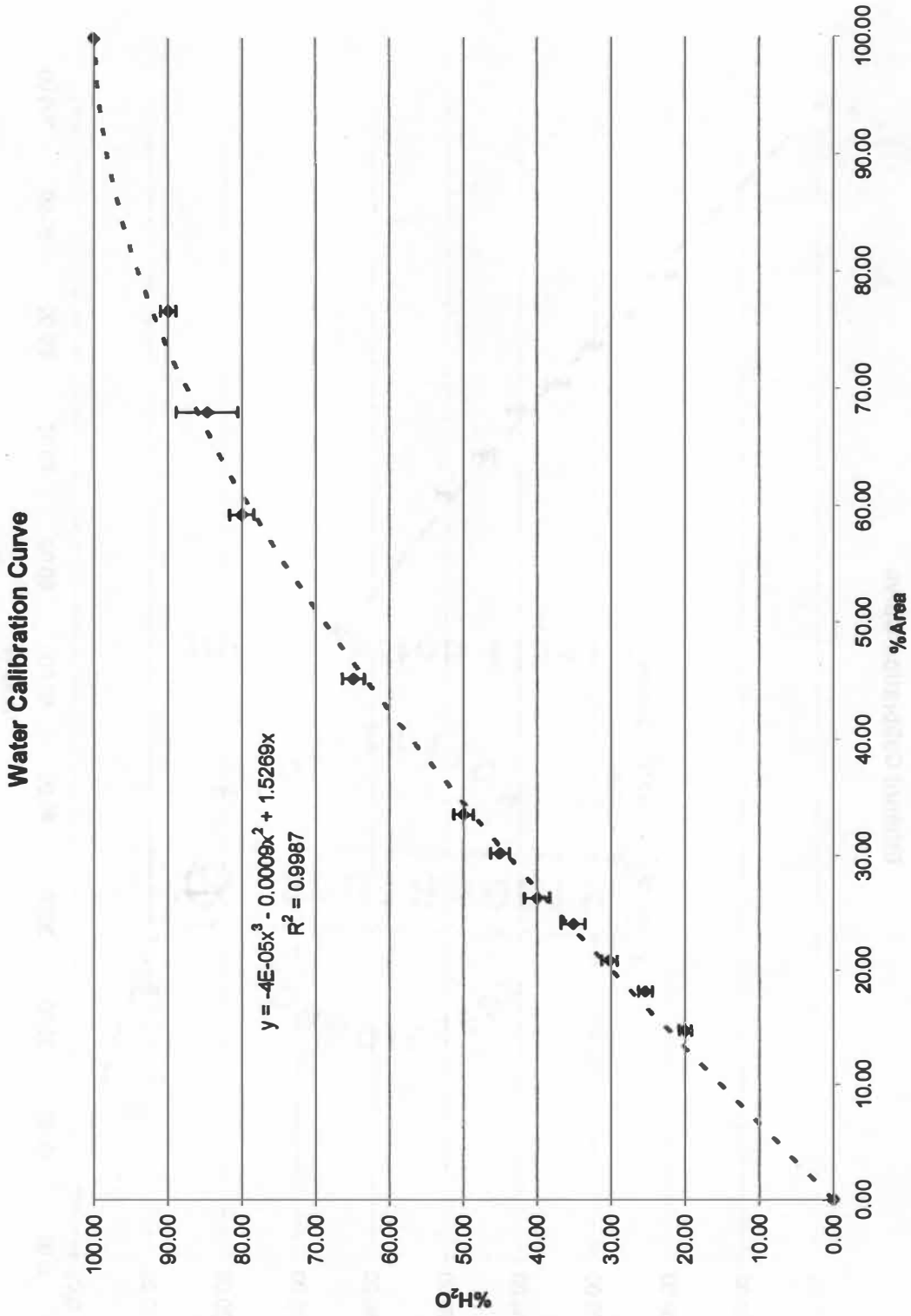

Figure 3: Water Calibration Curve

Table 1 – Standard solution composition in volume percent ethanol

Standard	%EtOH	%H2O
1	10.07	89.93
2	15.23	84.77
3	20.00	80.00
4	35.10	64.90
5	50.00	50.00
6	54.97	45.03
7	60.00	40.00
8	64.90	35.10
9	69.80	30.20
10	74.67	25.33
11	80.00	20.00

The ethanol calibration curve was constrained by two conditions, first that it must have a zero intercept, and second that it must also pass through the point (100, 100). These conditions correspond to zero percent by volume ethanol and 100 percent by volume ethanol. The same conditions applied to the water calibration curve. As seen in Figures 2 and 3 the data appears to have an inflection point due to the non ideal nature of the ethanol water mixture. Therefore a third order polynomial was used for the calibration curve.

RESULTS AND DISCUSSION

Identified Compounds. The GC/MS analysis has shown the presence of several minor components in the distillate samples taken from the Bruichladdich distillation process. Table 1 is a list of the components reliably identified in the distillate samples. Of these compounds only ethyl acetate, ethanol, 1-propanol, water, 2-M-1 butanol, and isoamyl alcohol are present in significant amounts during the course of the distillation.

The components listed in Table 2 are each present in an identifiable amount at some point during the distillation.

Table 2 - Identified Compounds from GC/MS Analysis

Identified Compounds	
Wash Still	**Spirit Still**
2. Ethyl Acetate	2. Ethyl Acetate
3. Acetal	3. Acetal
4. Ethanol	4. Ethanol
8. 1-Propanol	8. 1-Propanol
9. Water	9. Water
10. 2-M-1 Butanol	10. 2-M-1 Butanol
11. Isoamyl Acetate	11. Isoamyl Acetate
13. Isoamyl Alcohol	13. Isoamyl Alcohol
15. Ethyl Caprylate	14. Ethyl n-Caproate
16. Ethyl Caprate	15. Ethyl Caprylate
17. Ethyl Laurate	16. Ethyl Caprate
18. Phenethyl Alcohol	17. Ethyl Laurate
21. Capric Acid	18. Phenethyl Alcohol
23. Lauric Acid	20. Ethyl Palmitate
	21. Capric Acid

Some of the compounds are identifiable in only a few samples, in some cases only in one sample. This is almost certainly a result of the extremely low concentration of most of the minor identifiable components. There are more components whose identity could not be reasonably determined whose concentrations are even smaller. This discrepancy exists because the analysis method scanned a range of masses that include water and ethanol. Inclusion of the two major components of the mixture makes it much harder to determine the existence of other minor components because of interference from water and ethanol.

Wash Still Data. Figures 4-10 are examples of typical GC chromatograms from the wash still analysis with identified compounds labeled. The numbers on each chart correspond to the compound listed in Table 2. Wash still samples are labeled with the wash still numbers and spirit still samples with the spirit still numbers. The low wines and feints receiver is also labeled with the spirit still numbers.

Figure 4 shows the analysis of the first distillate sample from the wash still. Each of the peaks observed in this chromatogram has been reliably identified by mass spectral analysis. Figure 5 shows the second sample taken during the wash still distillation which has the largest number of observable peaks. It is evident that there are significantly more peaks in this chromatogram than in Figure 4. This is evidence of

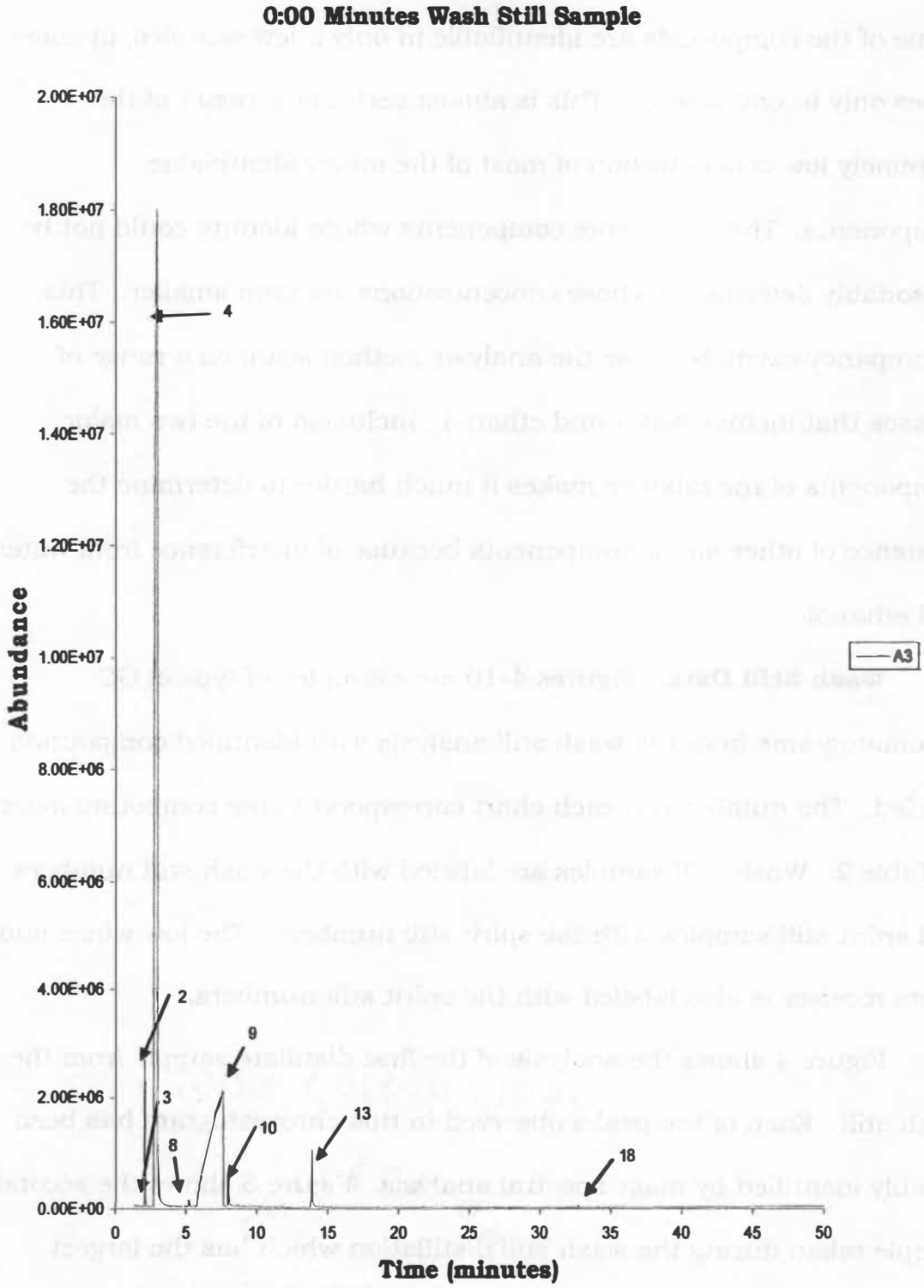

Figure 4: Wash Still Sample Taken at 0:00 Minutes of Distillation

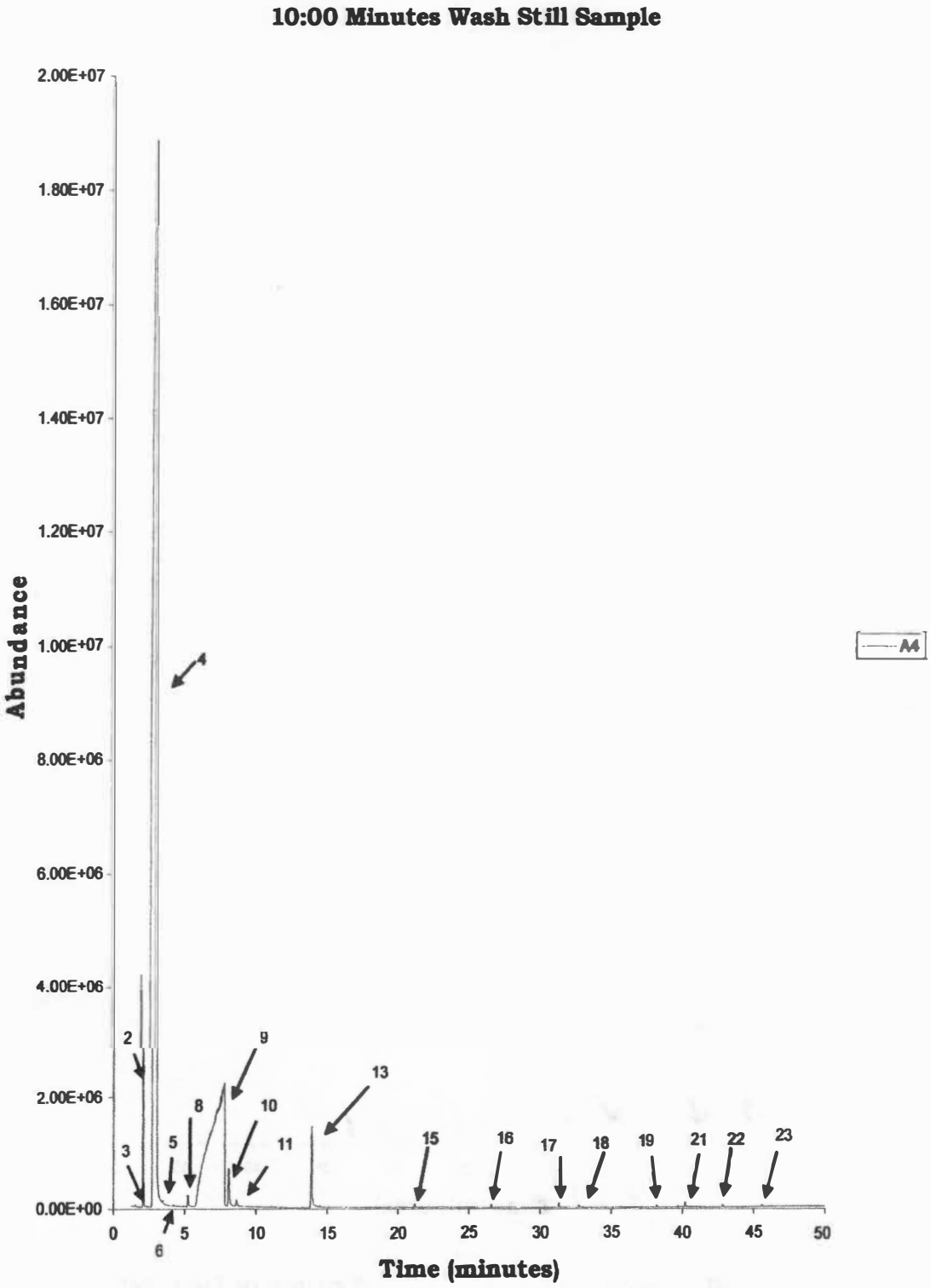

Figure 5: Wash Still Sample Taken at 10:00 Minutes of Distillation

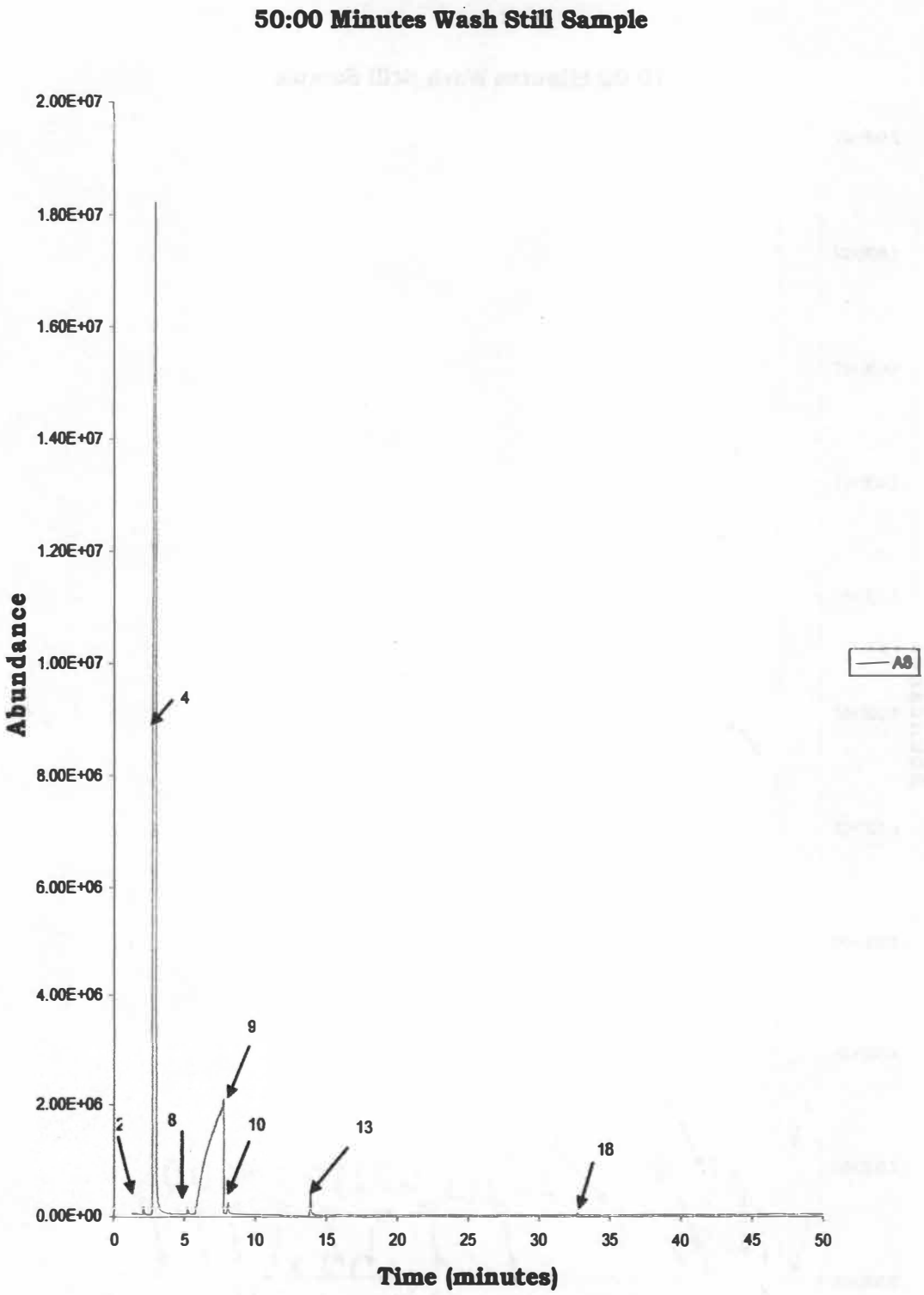

Figure 6: Wash Still Sample Taken at 50:00 Minutes of Distillation

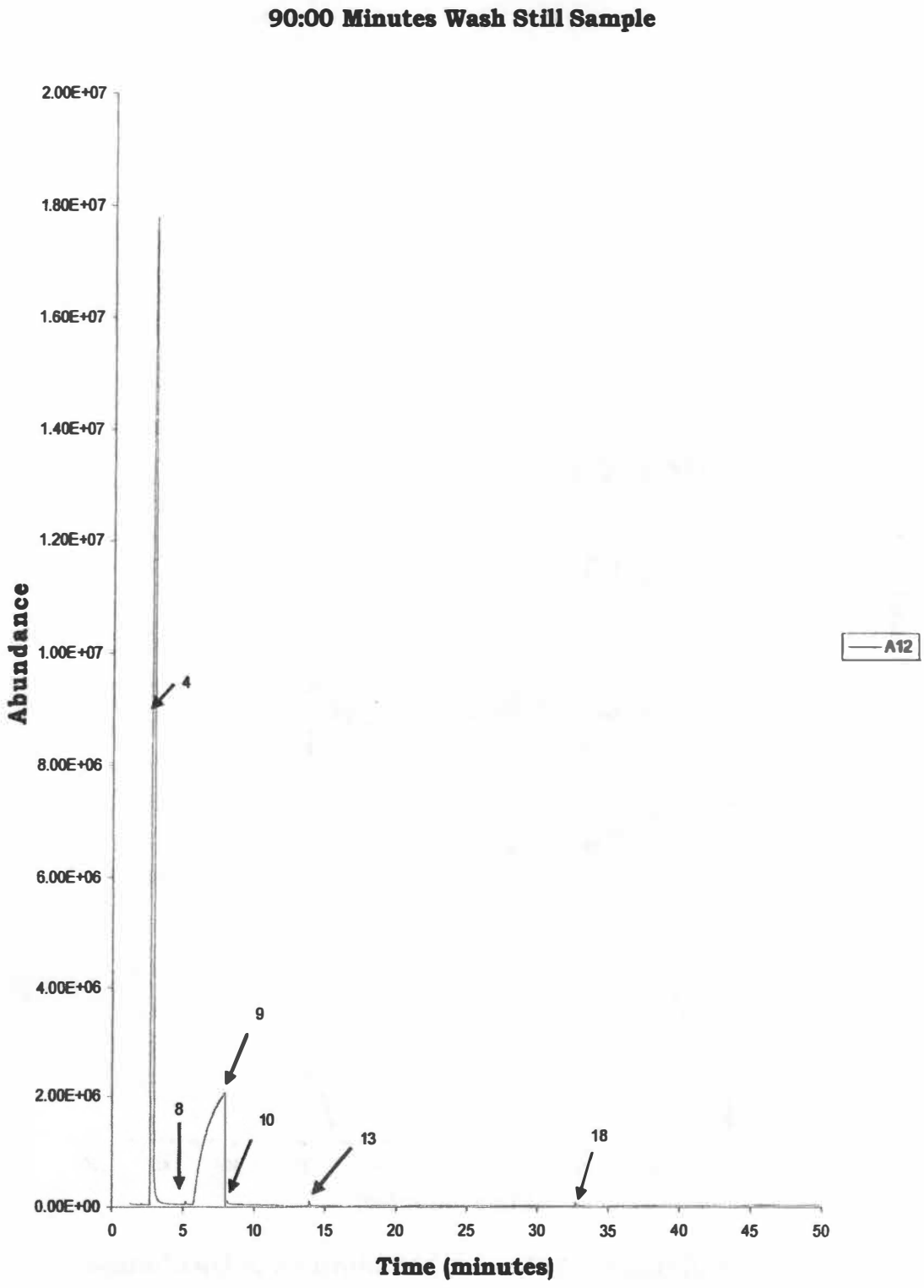

Figure 7: Wash Still Sample Taken at 90:00 Minutes of Distillation

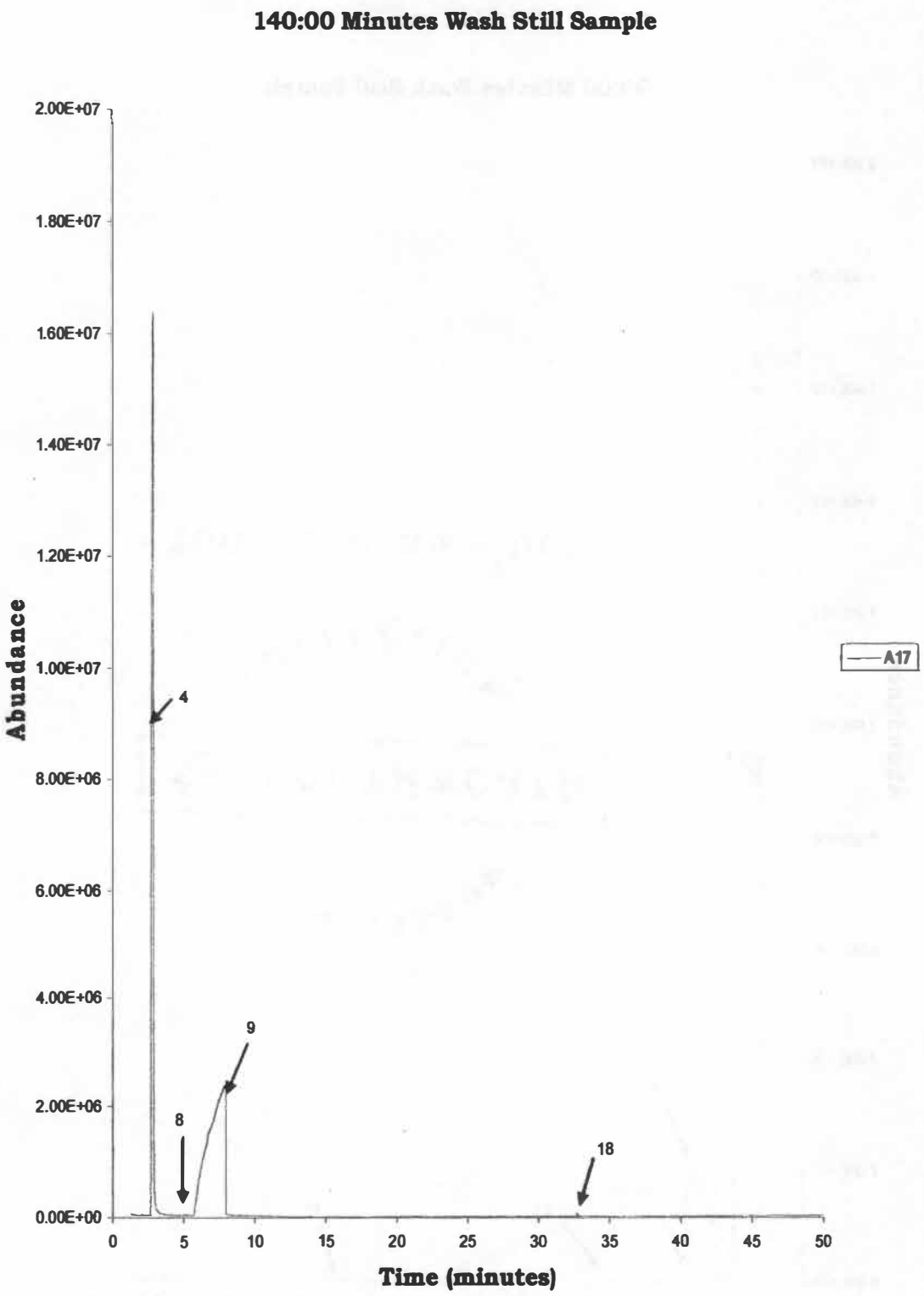

Figure 8: Wash Still Sample Taken at 140 Minutes of Distillation

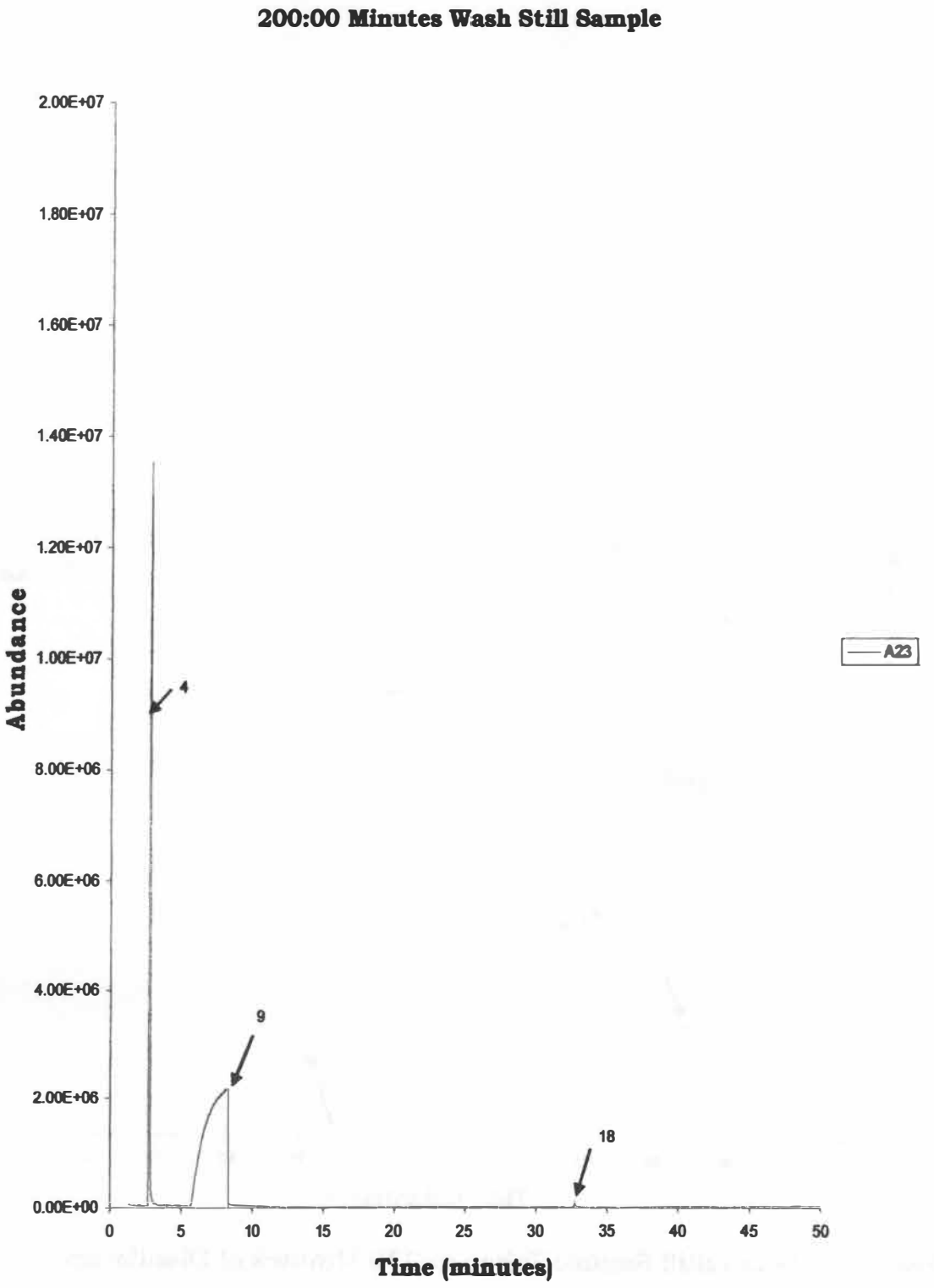

Figure 9: Wash Still Sample Taken at 200 Minutes of Distillation

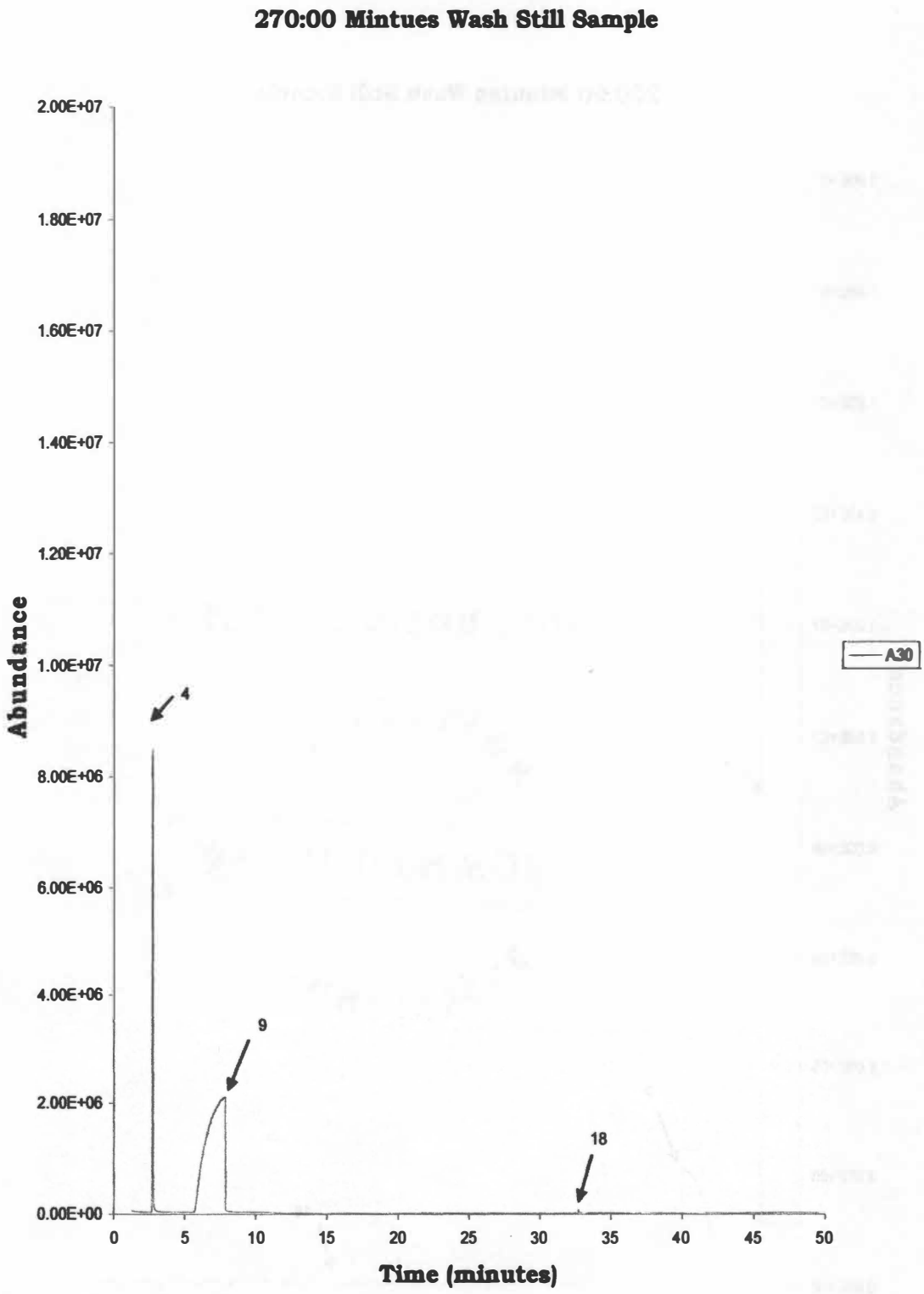

Figure 10: Wash Still Sample Taken at 270 Minutes of Distillation

the presence of several other unidentifiable compounds. Figures 6-10 are spaced over the rest of the distillation run and have peaks consistent with those found in the first two chromatograms.

Spirit Still Data. Figures 11-18 are examples of typical GC chromatograms from the spirit still analysis with identified compounds labeled. Figure 11 shows the chromatogram for the low wines and feints charger that supplies the feed to the spirit still. Figure 12 shows the second sample collected from the spirit still which is recycled as foreshots. This sample had the largest number of visible peaks of any spirit still sample. Figure 13 shows the last sample taken during the foreshots cut of the spirit still. Figure 14 shows the first sample taken during the spirit cut of the spirit still distillation. Figures 15 and 16 are chromatograms of samples taken during the spirit cut. Figure 17 is the last sample taken during the spirit cut. Figure 18 is the first sample taken during the feints cut of the spirit still distillation.

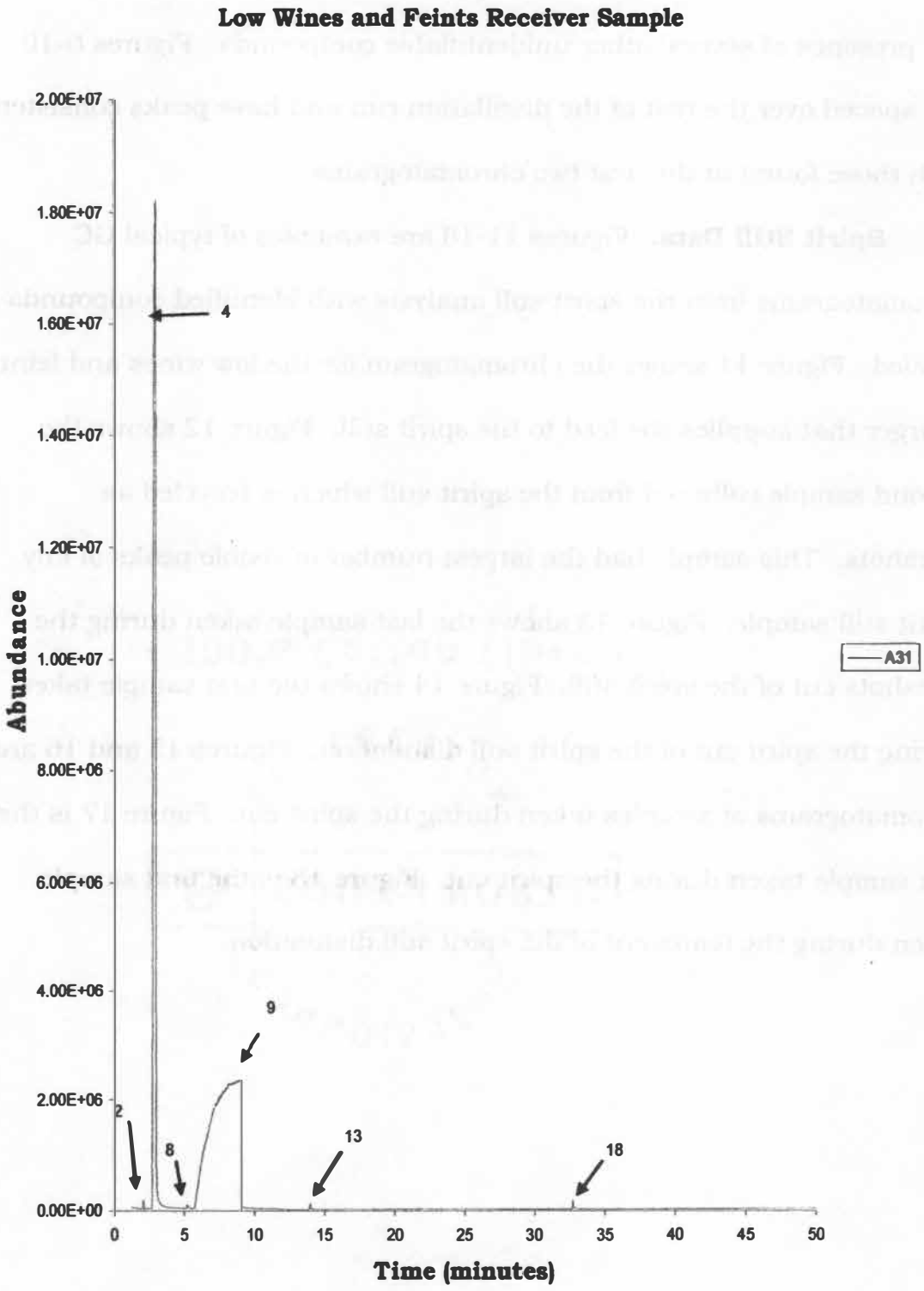

Figure 11: Low Wines and Feints Receiver Sample

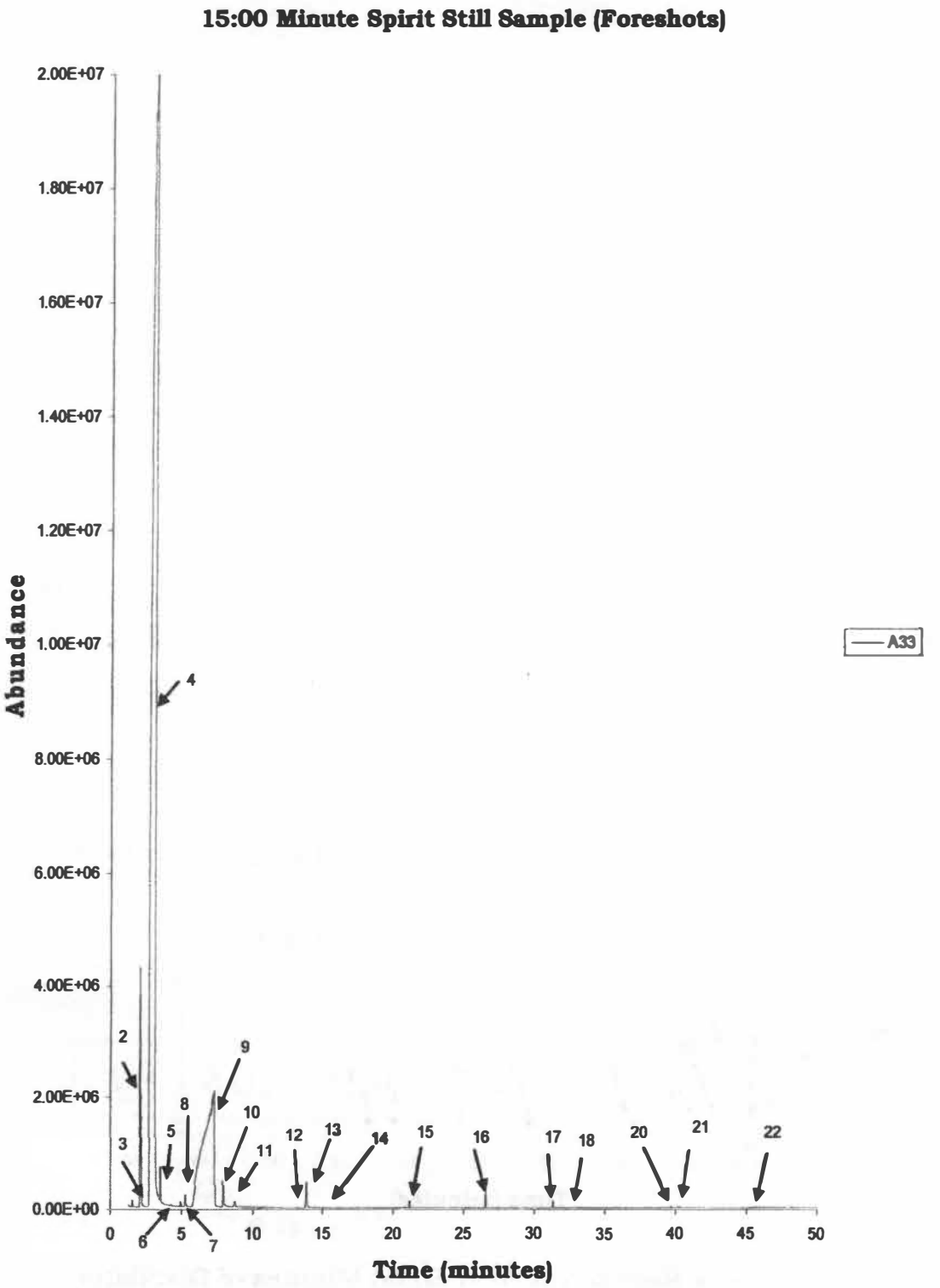

Figure 12: Foreshots Sample Taken at 15:00 Minutes of Distillation

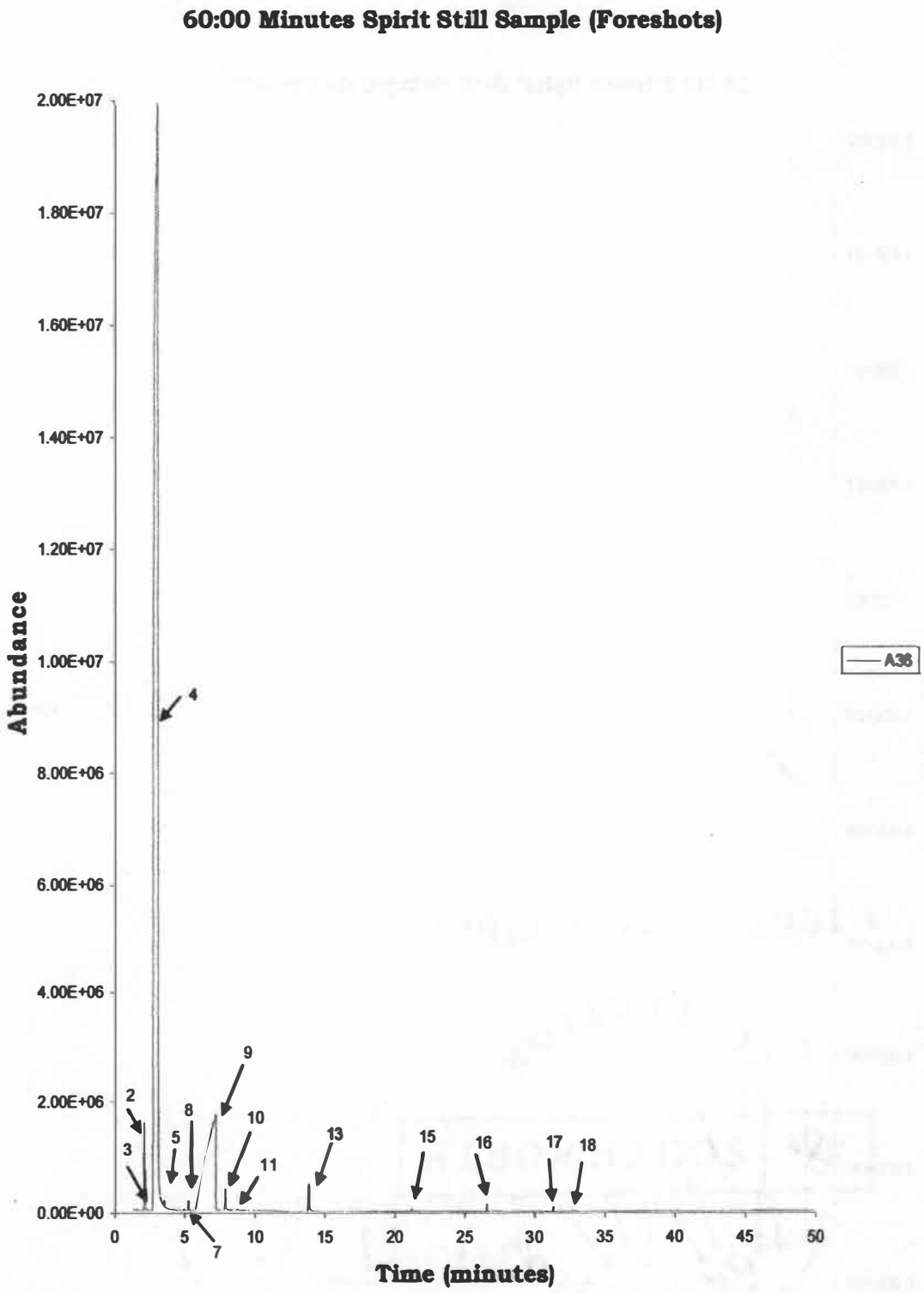

Figure 13: Foreshots Sample Taken at 60:00 Minutes of Distillation

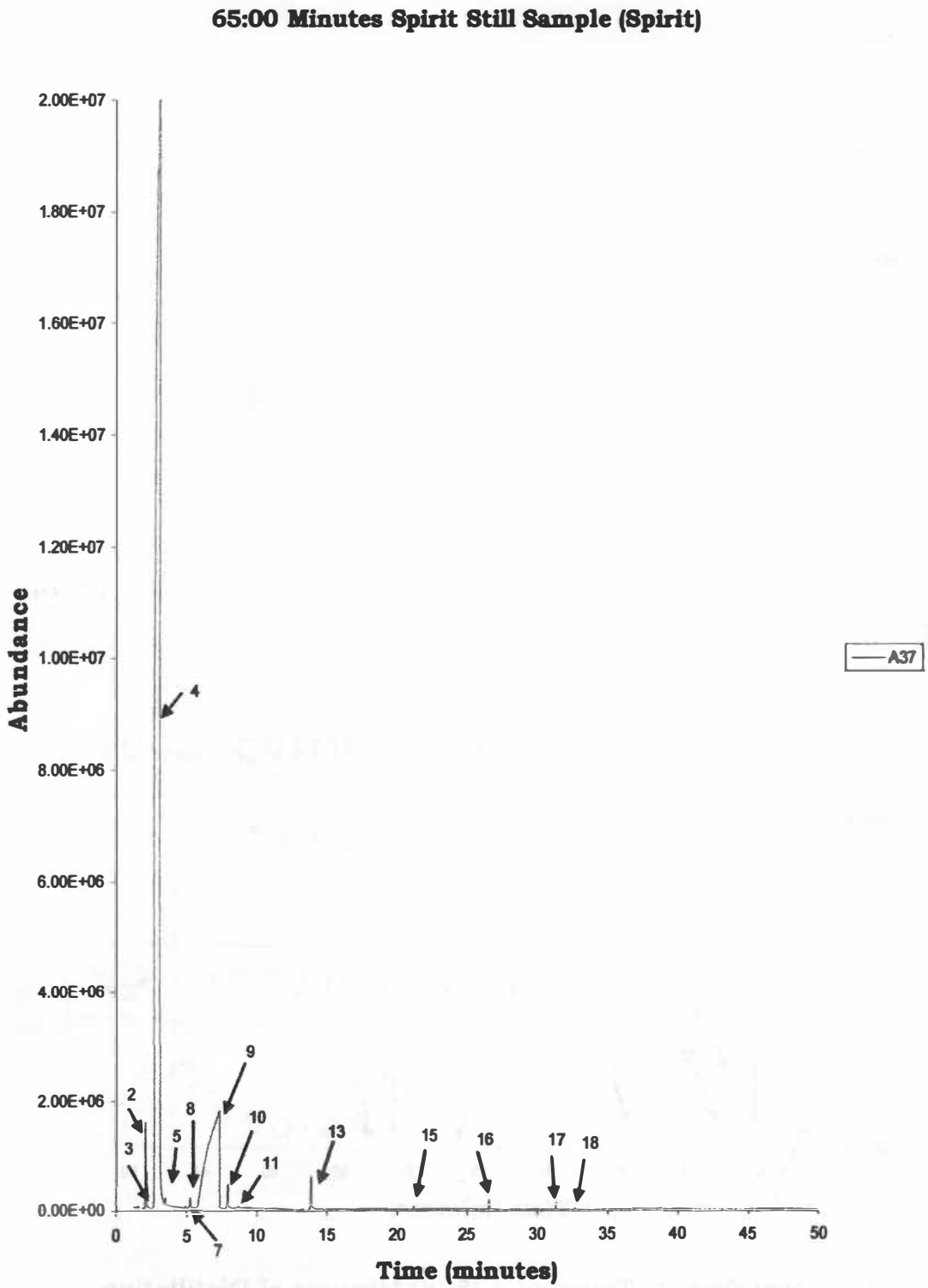

Figure 14: Spirit Sample Taken at 65:00 Minutes of Distillation

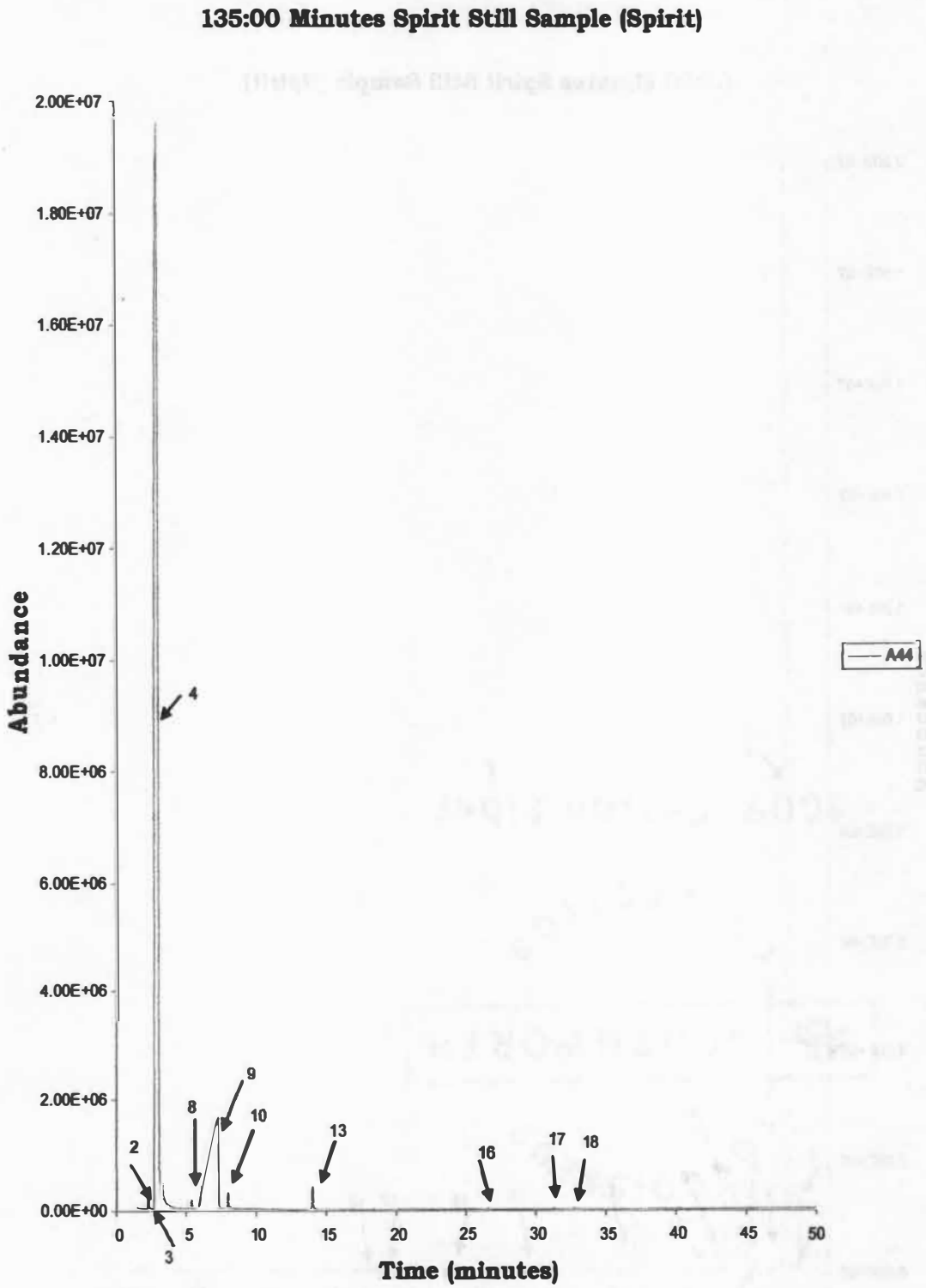

Figure 15: Spirit Sample Taken at 135:00 Minutes of Distillation

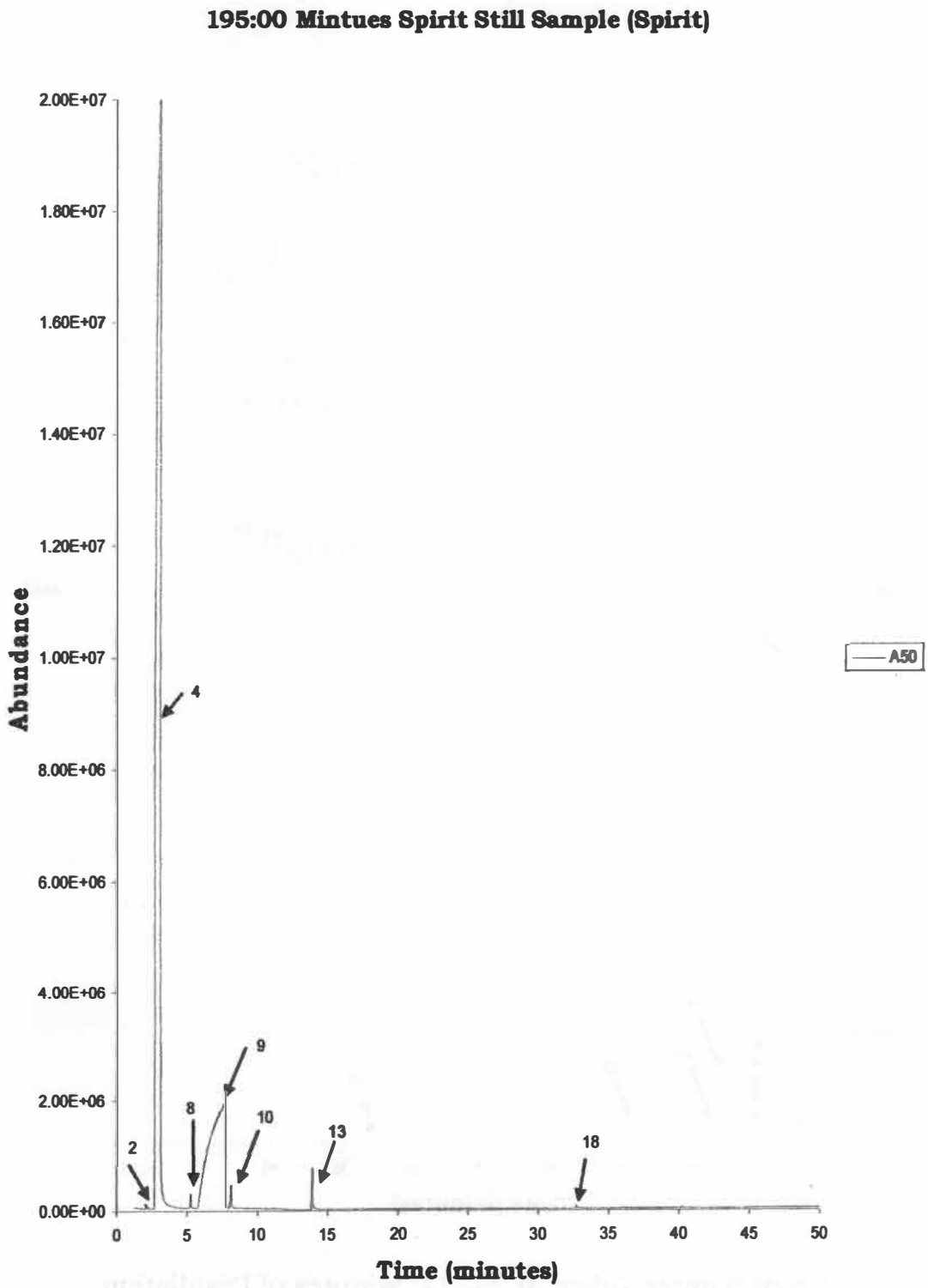

Figure 16: Spirit Sample Taken at 195:00 Minutes of Distillation

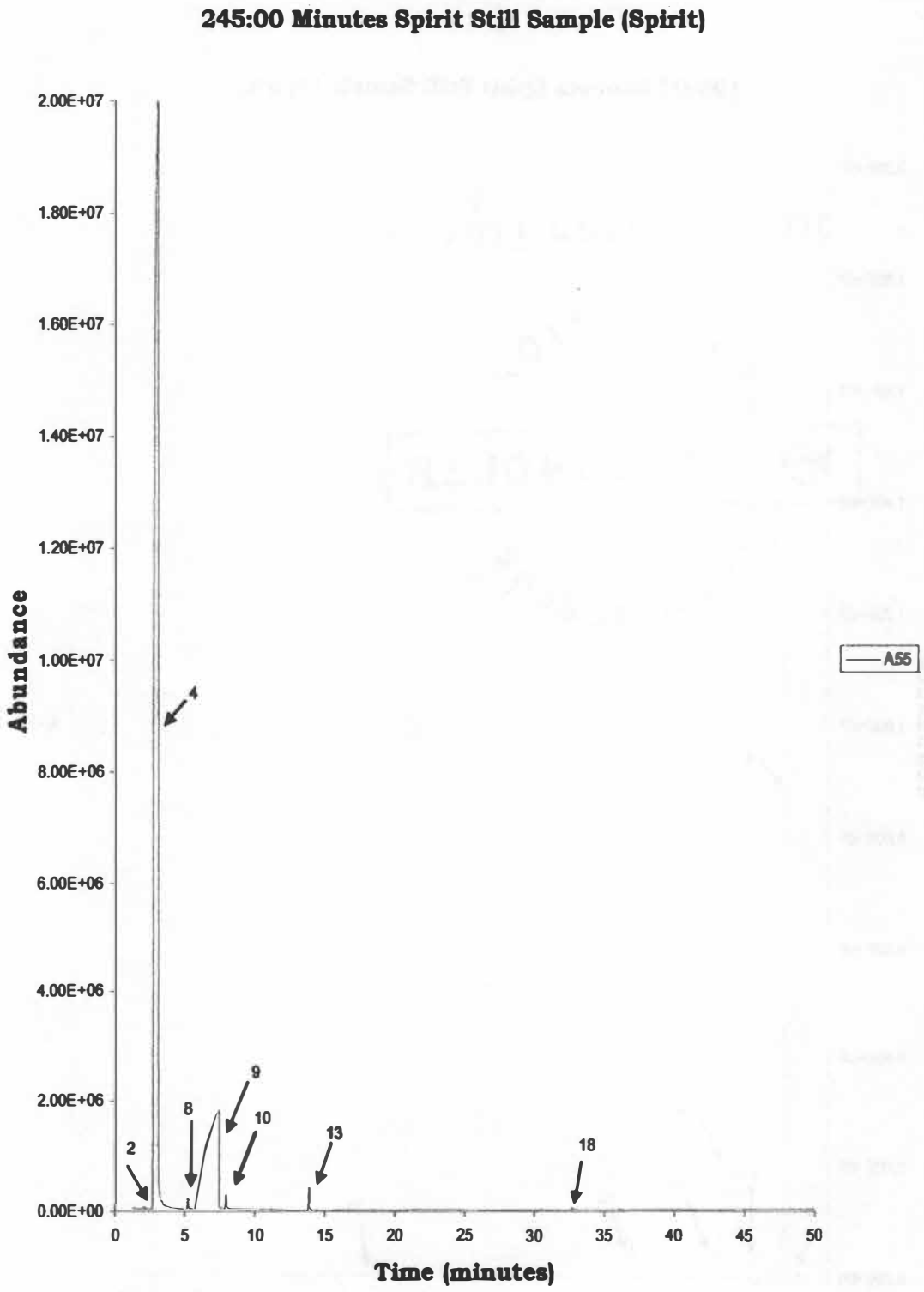

Figure 17: Spirit Sample Taken at 245:00 Minutes of Distillation

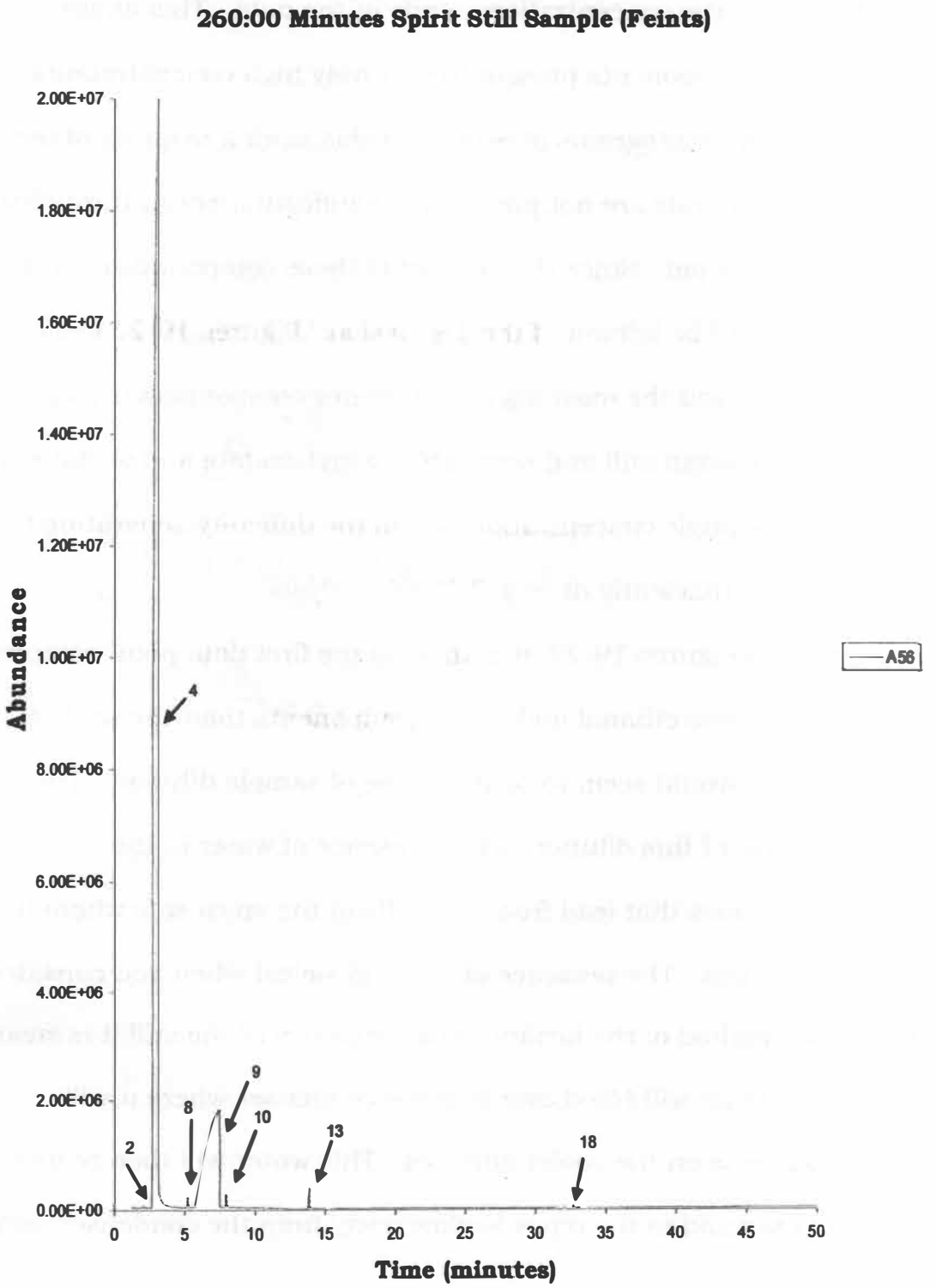

Figure 18: Feints Sample Taken at 260:00 Minutes of Distillation

CONCLUSIONS

With such a wealth of experimental data it is possible to develop curves describing the concentration trends in the data. This ability is limited to those components present in relatively high concentrations. As seen in the chromatograms presented in this work a majority of the identifiable compounds are not present in significant amount throughout most of the distillation. Since the amount of these compounds cannot be quantified they will be left out of the discussion. Figures 19-22 show the trends of ethanol and the most significant minor components through time for both the wash still and spirit still. Ethyl acetate and acetal were combined into a single concentration due to the difficulty separating the two compounds sufficiently during GC/MS analysis.

As seen in Figures 19-22 in both stills the first data point sampled has significantly less ethanol and minor components than the second data point. This would seem to be indicative of sample dilution. The most likely cause of this dilution is the presence of water in the condenser and pipes that lead from the stills to the spirit safe where the samples were taken. The presence of water is logical when you consider the operation method of the facility. After each run of the still it is steam cleaned. The steam will bleed over into the condenser where it will naturally condense on the cooler surfaces. This water will then remain in the condenser and in the pipes leading away from the condenser until

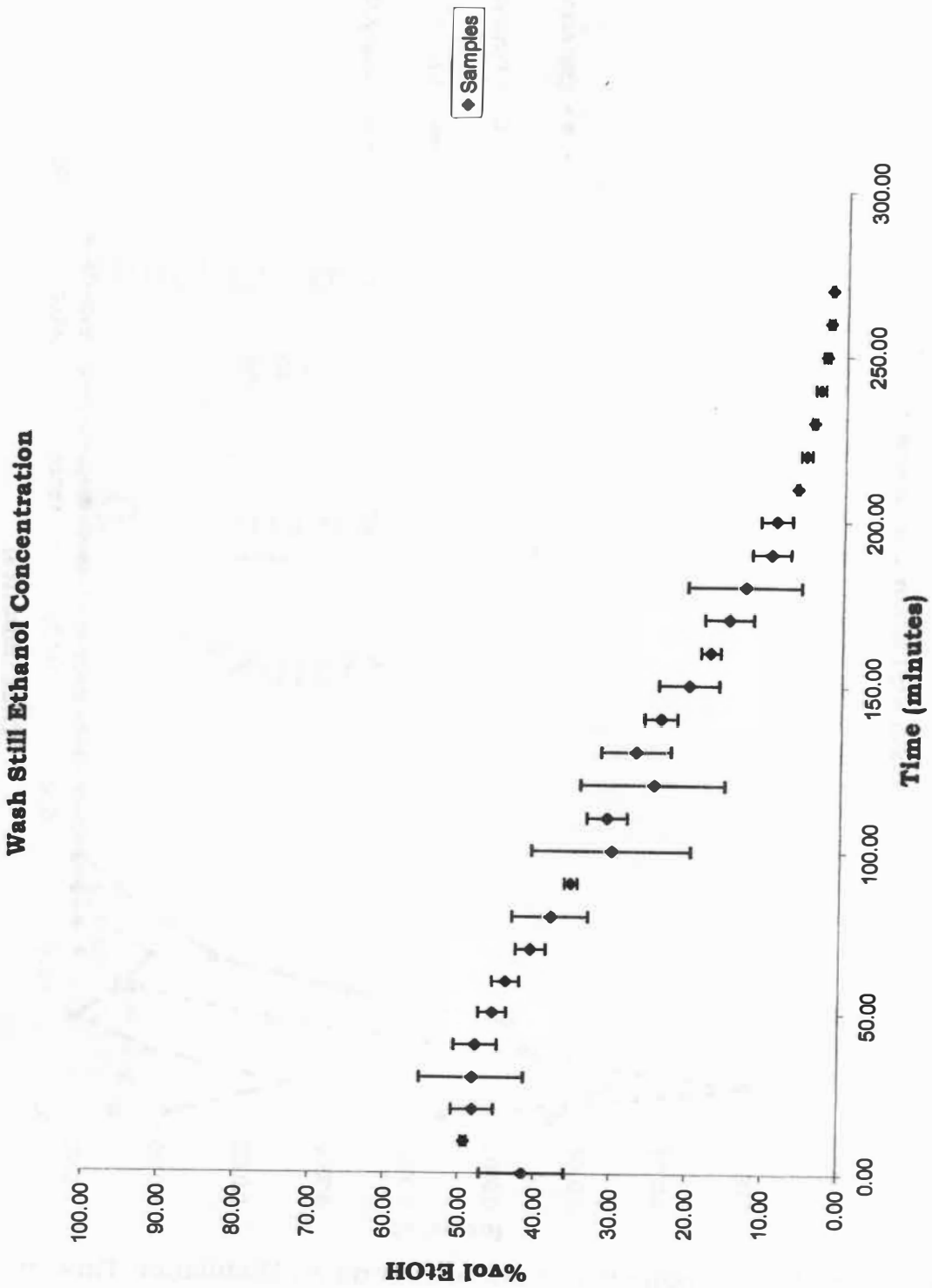

Figure 19: Ethanol Concentration vs. Distillation Time in Wash Still

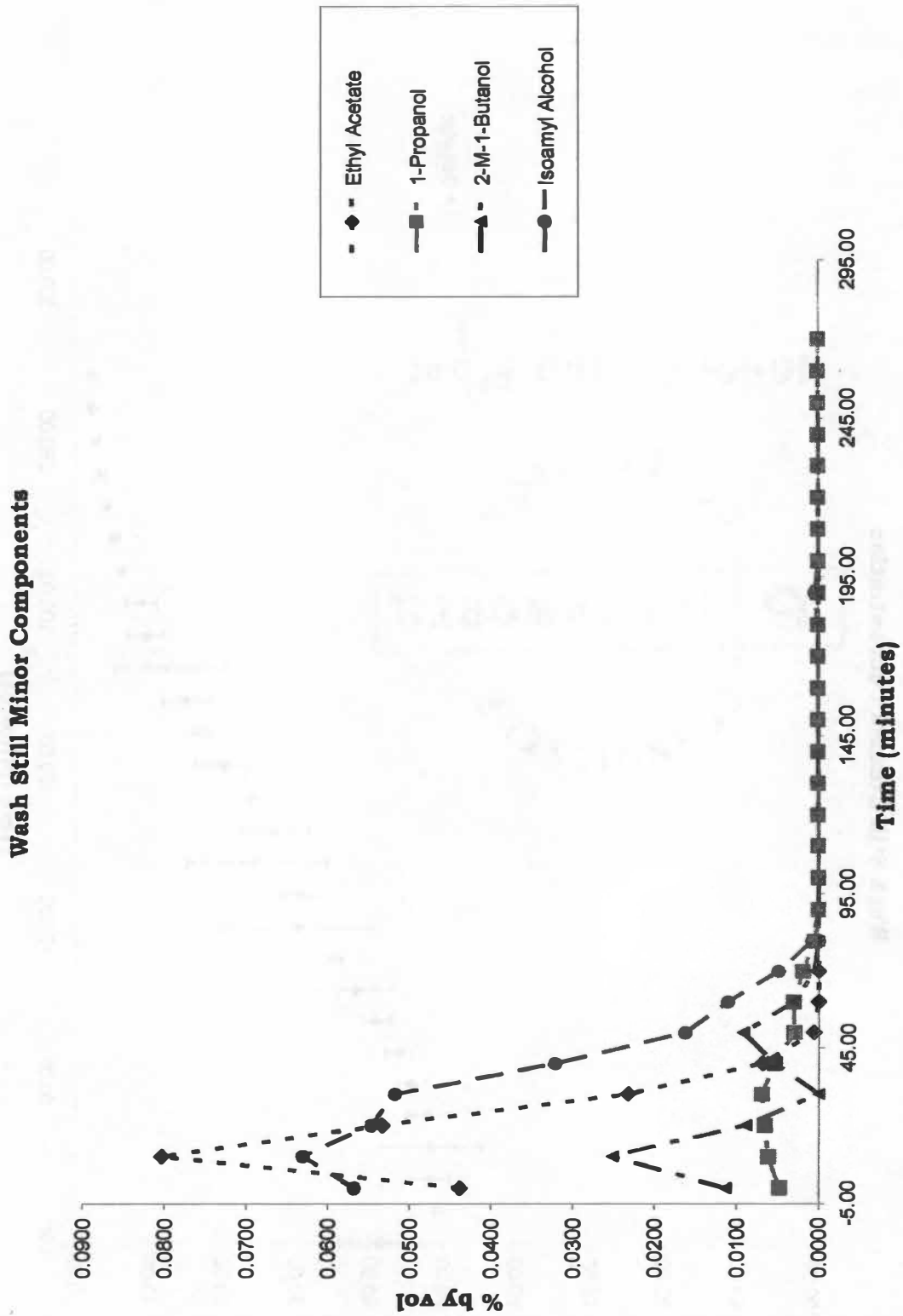

Figure 20: Minor Component Concentrations vs. Distillation Time in Wash Still

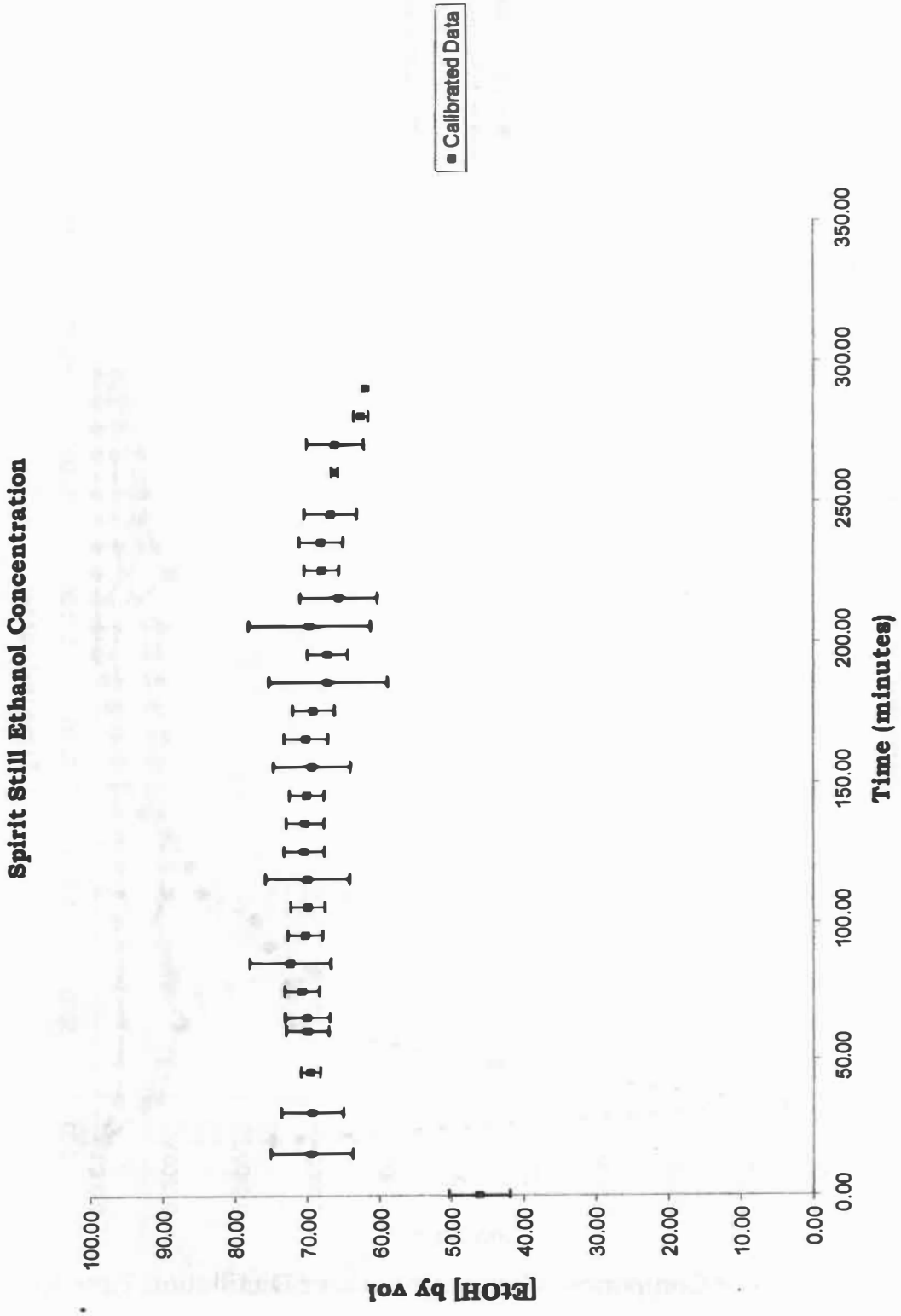

Figure 21: Ethanol Concentration vs Distillation Time in Spirit Still

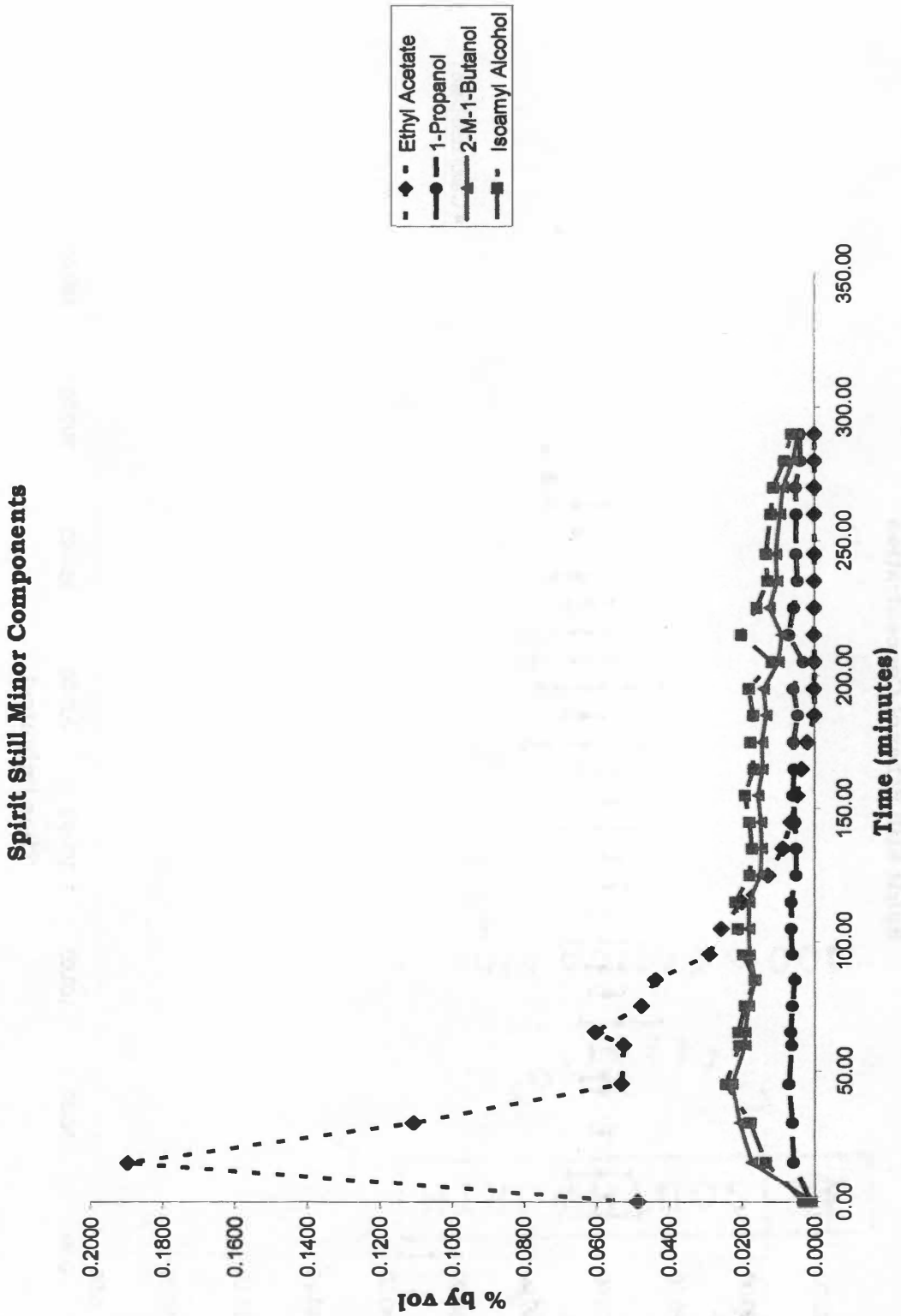

Figure 22: Minor Component Concentrations vs Distillation Time in Spirit Still

something pushes it through the system. The first sample collected at the distillery for each still is part of the very first liquid coming out of the condenser. The fluid is therefore a mixture of the first distillate product which should be highest in alcohol content and the water present in the condenser and pipes. Therefore the first data point will be skewed toward lower ethanol and minor component concentrations. This makes the first data point of each trend unreliable.

The wash still sample analysis produced the results shown in Figures 19 and 20. As can be seen in Figure 19 the ethanol concentration trends significantly downward throughout the distillation slowing only when the concentration of ethanol becomes very low. This is the behavior one would expect of the low boiling key component of a batch distillation.

The minor component concentration profiles shown in Figure 18 follow a similar pattern. The operational nature of the wash still is such that all distillate is pumped into the low wines and feints receiver. This means that nothing that is boiled over in the wash still is excluded from the next distillation step. Therefore the trends in minor component concentration do not reflect significant processing decisions. They only establish the compounds present in the feed to the spirit still. Other components present in the feed to the wash still remain in the wash still after distillation is complete. This liquid is called the pot ale and is

stored in a sealed tank until a truck comes to carry it to the disposal site in the channel between Islay and Jura. No sample of this liquid was obtained so there is no way to be sure of the composition of this stream. Operational knowledge suggests that there should be large amounts of yeast, bacteria, and water present in this liquid.

The low wines and feints receiver is the source of the feed to the spirit still. It is a holding tank for the output from the wash still and the recycle streams from the spirit still. A sample of this liquid was taken and analyzed. The analysis of this sample indicated that only four minor component compounds were present in any significant amount, ethyl acetate, 1-propanol, isoamyl alcohol, and phenethyl alcohol. This analysis seems to contradict the evidence of the spirit still distillate analysis. It would seem that several compounds present in the spirit distillate are missing. Since the spirit still feed comes from the low wines and feints receiver it would be unlikely for those compounds to be present in the distillate and not be present in the feed. To explain this discrepancy it is postulated that the sample taken from the low wines and feints receiver was not well mixed. The ethanol concentration determined by analysis of this sample seems reasonable. This could be a result of the large amount of ethanol in the holding tank or it could be a result of the analysis method being too coarse to isolate the other minor flavor components in the sample.

The spirit still samples are the source of the most useful information. The major and minor component concentration profiles can give hints about the reasons behind process decisions that have been implemented through multiple generations of distillery operation. As explained by the operators and managers of the distillery the method of distillation has remained largely unchanged in decades of production. The operators make process adjustments based more on tradition and experience than on a specific understanding of the underlying chemistry of the distillation. Currently there is no process analysis other than a hygrometer measurement for alcohol content used to determine where the phase breakpoints should be. This does not mean that the decisions are incorrect or inadequate, but a fuller understanding of the underlying phenomena can help to optimize the production.

The process phases are labeled on Figure 23. As can be seen from the figure the first phase consists of the first five samples. The second phase or spirit cut begins with the sixth sample. Comparison of the fifth and sixth samples indicates that the ethanol concentration is nearly identical. The concentration of the minor components also has little difference between the two samples. This would seem to indicate that there is very little practical difference between the distillate samples 5 and 6 and thus the distinction in the process seems artificial. However, there is a distinct decline in ethyl acetate and acetal through the early

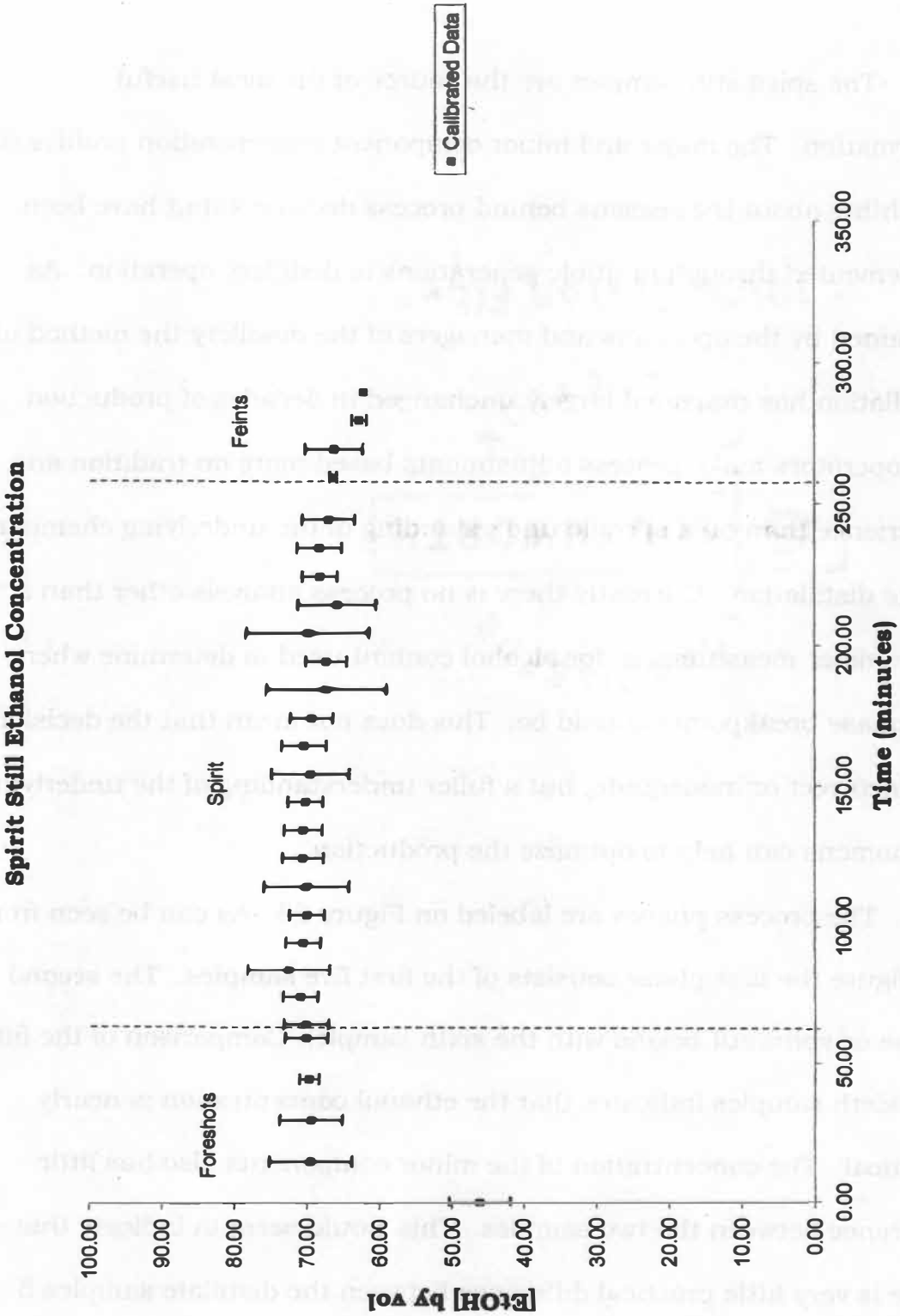

Figure 23: Spirit Still Phases

part of the distillation as shown in Figure 22. This decline could be the reason for the process decision.

The boundary between the second and third phase is similarly constructed. The second phase ends with sample 24 and the third phase begins with sample 25. Again the ethanol concentrations are nearly the same, both approximately 66% ethanol. The minor components again show no practical difference from one sample to the next. This also suggests that the distinction is largely superficial.

However it would be improper to state these conclusions as fact. Without a detailed analysis of all the components present in the distillate it is possible that the process breakpoints are related to another substance that is present in too low a concentration to have been included in this work.

The body of experimental work that has been performed up to this point is significant. However, due to current equipment limitations it is impractical to perform further analysis of the samples for the trace components. A different method of analysis is needed to establish a reliable method for the determination and quantization of the remaining flavor components. Research has suggested that solid-phase microextraction (SPME) analysis could provide the kind of results that would allow for further study of this topic. [9, 14-17]

In addition to conducting SPME analysis on the samples to quantify the minor components more samples are needed. As has been discussed the first samples taken were likely diluted by the presence of water in the condenser and pipes at the beginning of distillation. Also the low wines and feints receiver sample seems to have been poorly mixed. Taking more samples both to replace suspect samples already collected and to acquire more data points during the analysis could prove critical to the development of a dependable experimental basis for analysis of scotch whisky.

The experimental basis is important for computer modeling work currently being undertaken as well as for studies designed to analyze the effect of aging on the whisky. Combined with the work already in the literature on the analysis of the final whisky product after aging, this work and the studies of the effects of barreling should provide a solid foundation for better understanding of the scotch whisky production process. Better understanding can and should lead to production improvements that benefit not only the producers but the consumers as well.

LITERATURE CITED

1. Lyons, T.P.; Production of Scotch and Irish whiskies: their history and evolution. In The Alcohol Textbook, 3rd edition.; Jacques, K.; Lyons, T.P.; Kelsall, D.R.; Nottingham University Press: Nottingham, United Kingdom, 1999

2. Guichard, H.; Lemesle, S.; Ledauphin, J.; Barillier, D.; Picoche, B.; Chemical and Sensorial Aroma Characherization of Freshly Distilled Calvados 1. Evaluation of Quality and Defects on the Basis of Key Odorants by Olfactometry and Sensory Analysis. *J. Agric. Food Chem.* **2003**, 51, 424-432

3. Ledauphin, J.; Guichard, H.; Saint-Clair, J.F.; Picoche, B.; Barillier, D.; Chemical and Sensorial Aroma Characterization of Freshly Distilled Calvados 2. Identification of Volatile Compounds and Key Odorants. *J. Agric. Food Chem.* **2003**, 51, 433-442

4. Aroma of Beer, Wine and Distilled Alcoholic Beverages, Nykanen, L.; Suomalainen, H.; D. Reidel Publishing Company, 1983, Boston USA

5. Gonzalez-Arjona, D.; Gonzalez-Gallero, V.; Pablos, F.; Gonzalez, A.G.; Authentication and differentiation of irish whiskeys by higher alcohol congener analysis. *Anal. Chimica Acta.* **1999**, 381, 257-264

6. Demyttenaere, J.C.R.; Martinez, J.I.S.; Verhe, R.; Sandra, P.; DeKimpe, N.; Analysis of volatiles of malt whisky by solid-phase microextraction and stir bar sorptive extraction. *J. Chroma. A.* **2003**, 985, 221-232

7. Sharpe, F.R.; Chappell, C.G.; An Introduction to Mass Spectrometry and its Application in the Analysis of Beer, Wine, Whisky and Food. *J. Inst. Brew.* **1990**, 96, 381-393

8. Adam, T.; Duthie, E.; Feldmann, J.; Investigations into the Use of Copper and Other Metals as Indicators for the Authenticity of Scotch Whiskies. *J. Inst. Brew.* **2002**, 108(4), 459-464

9. Fitzgerald, G.; James, K.J.; MacNamara, K.; Stack, M.A.; Characterisation of whiskies using solid-phase microextraction with gas chromatography-mass spectrometry. *J. Chorma. A.* **2000**, 896 351-359

10. Mosedale, J.R.; Puech, J.L.; Wood maturation of distilled beverages. *Trends in Food Sci. & Tech.* **1998**, 9, 95-101

11. Handbook of Instrumental Techniques for Analytical Chemistry, Settle Frank, Prentice Hall, 1997

12. Goodner, K.L.; Jella, P.; Rouseff, R.L.; Determination of Vanillin in Orange, Grapefruit, Tangerine, Lemon, and Lime Juices Using GC-Olfactometry and GC-MS/MS, *J. Agric. Food Chem.* **2000**, 48, 2882-2886

13. Walker, T.; Morris, J.; Therlfall, R.; Main, G.; Analysis of Wine Components in Chythiana and Syrah Wines, *J. Agric. Food Chem.* **2003**, 51, 1543-1547

14. Zhang, Z.; Pawliszyn, J.; Headspace Solid-Phase Microextraction. *Anal. Chem.* **1993**, 65, 1843-1852

15. Zhang. Z.; Pwliszyn, J.; Quantitative Extraction Using an Internally Cooled Solid Phase Microextraction Device. *Anal. Chem.* **1995**, 67, 34-43

16. Demyttenaere, J.C.R.; Dagher, C.; Sandra, P.; Kallithraka, S.; Verhe, R.; DeKimpe, N.; Flavour analysis of Greek white wine by solid-phase microextraction-capillary gas chromatography-mass spectrometry. *J. Chroma. A.* **2003**, 985 233-246

17. Vaz Freire, L.M.T.; Freitas, A.M.C.; Relva, A.M.; Optimization of Solid Phase Microextraction Analysis of Aroma Compounds in a Portuguese Muscatel Wine Must. *J. Microcolumn Sep.* **2001**,13(6), 236-242

APPENDIX

```
% Ben Rogers
% Matlab Program
% Integration Routine
clear all
close all
clc

data=dlmread('C:\Mass Spec Data\Sample Analysis 3\A3_59.txt','\t',3,0);

fid = fopen('C:\Mass Spec Data\Sample Analysis 3\components.csv','a');
sampleid = input('What is the sample id? [1...59]\n');
success = input('Run good? yes - 1 no - 0 \n');
if success == 0
   fprintf(fid,'\n');
end
fprintf(fid,'%i, ',sampleid);
data=[data(:,1),data(:,2)];

%Baseline correction

for ii = 1:1:length(data)
if data(ii,2) > 5E5
   avgdata(ii) = 20000;
else
   avgdata(ii) = data(ii,2);
end
end
average = avg(avgdata);
cordata = data(:,2)-average;
for ii = 1:1:length(data)
   if cordata(ii) < 0
      cordata(ii) = 0;
   end
end

%Find the indices of peaks
qq = 1;
for ii = 1:1:length(data)
   if cordata(ii) > 100000 & cordata(ii-1) < 100000
      index(qq) = ii;
      qq = qq + 1;
   elseif cordata(ii) > 100000 & cordata(ii+1) < 100000
      index(qq) = ii;
      qq = qq +1;
   end
```

Figure 24: Peak Area Calculation Program

```
end
index=index';

%Choose integration range
rr=1;
for ss = 1:2:length(index)
peakarea = 0;
for jj = index(ss):1:index(ss+1)-1
   area = .5*(cordata(jj)+cordata(jj+1))*(data(jj+1,1)-data(jj,1));
   peakarea = peakarea + area;
end
peaks(rr)=peakarea;
rr=rr+1;
totarea = 0;
for jj = 1:1:length(data)-1
   area = .5*(cordata(jj)+cordata(jj+1))*(data(jj+1,1)-data(jj,1));
   totarea = totarea + area;
end
end
for tt=1:1:length(peaks)
   areapercent(tt) = (peaks(tt)/sum(peaks))*100;
end
ppercent = (sum(peaks)/totarea)*100;
aa = 1;
for ii = 1:1:length(peaks)
fprintf('%3.0g Peak Area is %10.4g and Percent of Total Area is
%10.4g\n',ii,peaks(ii),areapercent(ii))
fprintf('Peak Occurs at time %10.2g\n\n',data(index(aa),1))
aa = aa + 2;
end
fprintf('Peaks acount for %10.4g percent of total area\n',ppercent)

% Plug it in a datafile
aa=1;
for jj = 1:1:length(peaks)
   fprintf(fid,'%f, %f, ',data(index(aa,1)),areapercent(jj));
   aa = aa + 2;
end

fprintf(fid,'\n');
fclose(fid);
```

Figure 24: Continued

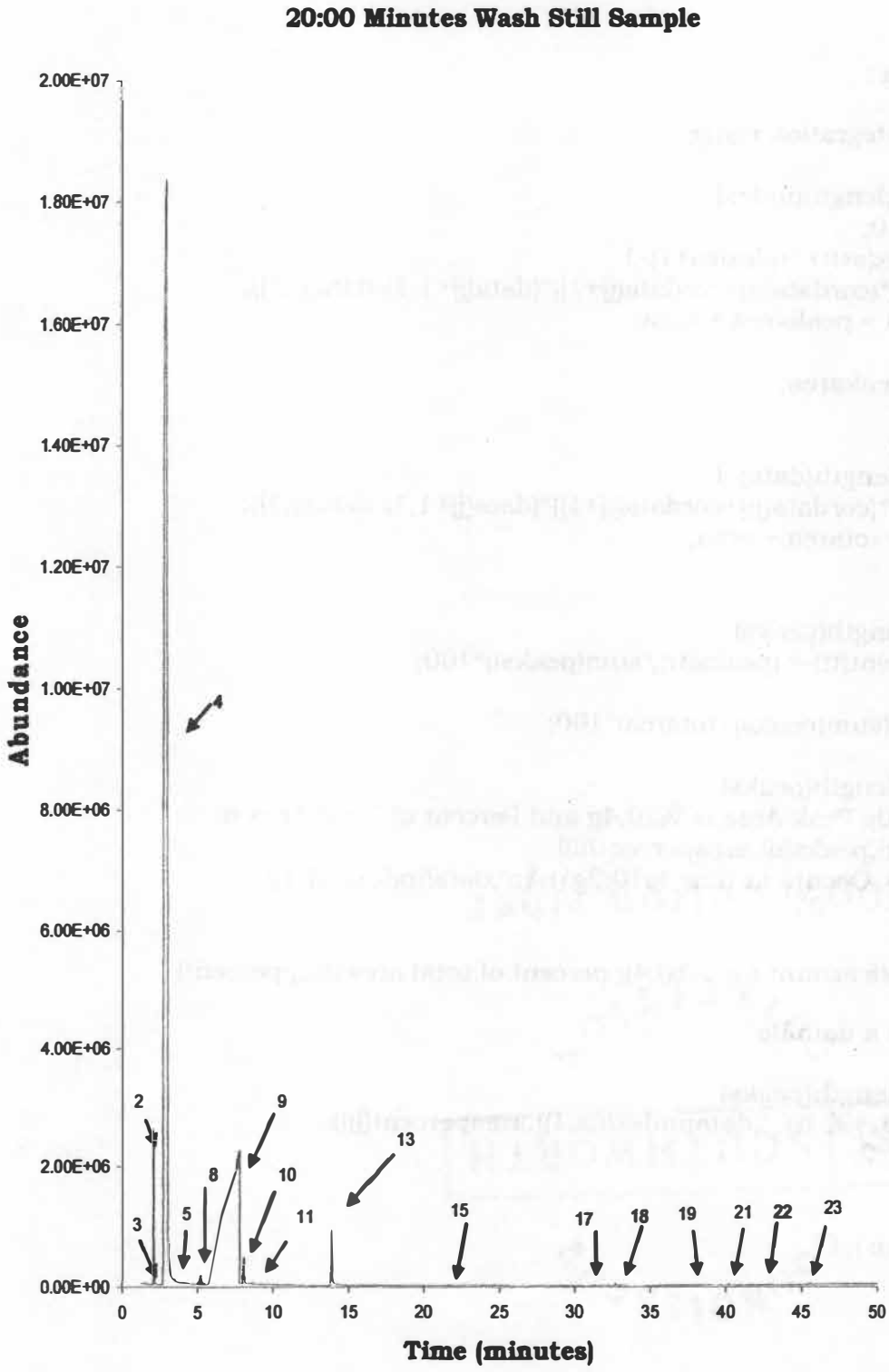

Figure 25: Wash Sample Taken at 20:00 Minutes of Distillation

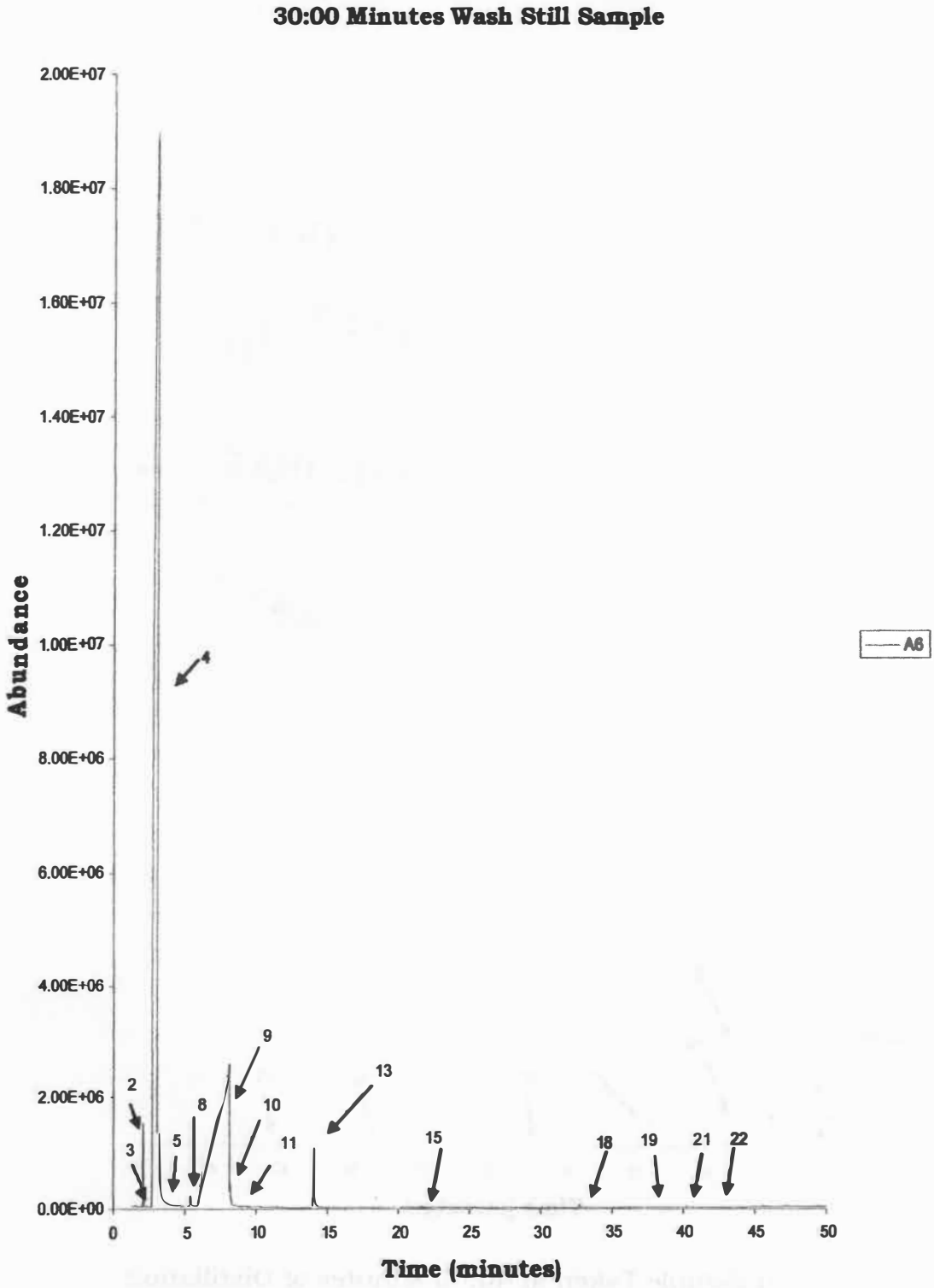

Figure 26: Wash Sample Taken at 30:00 Minutes of Distillation

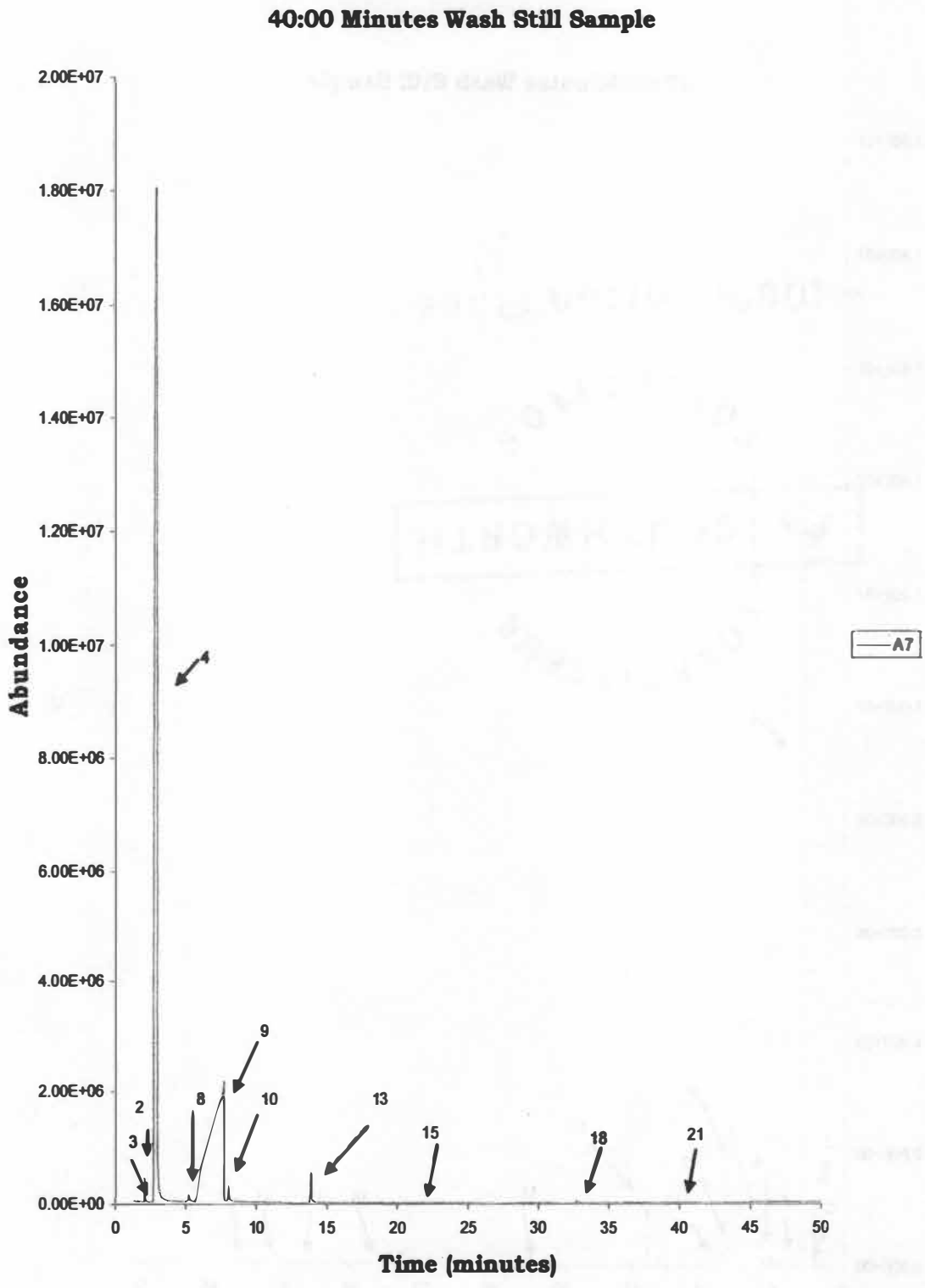

Figure 27: Wash Sample Taken at 40:00 Minutes of Distillation

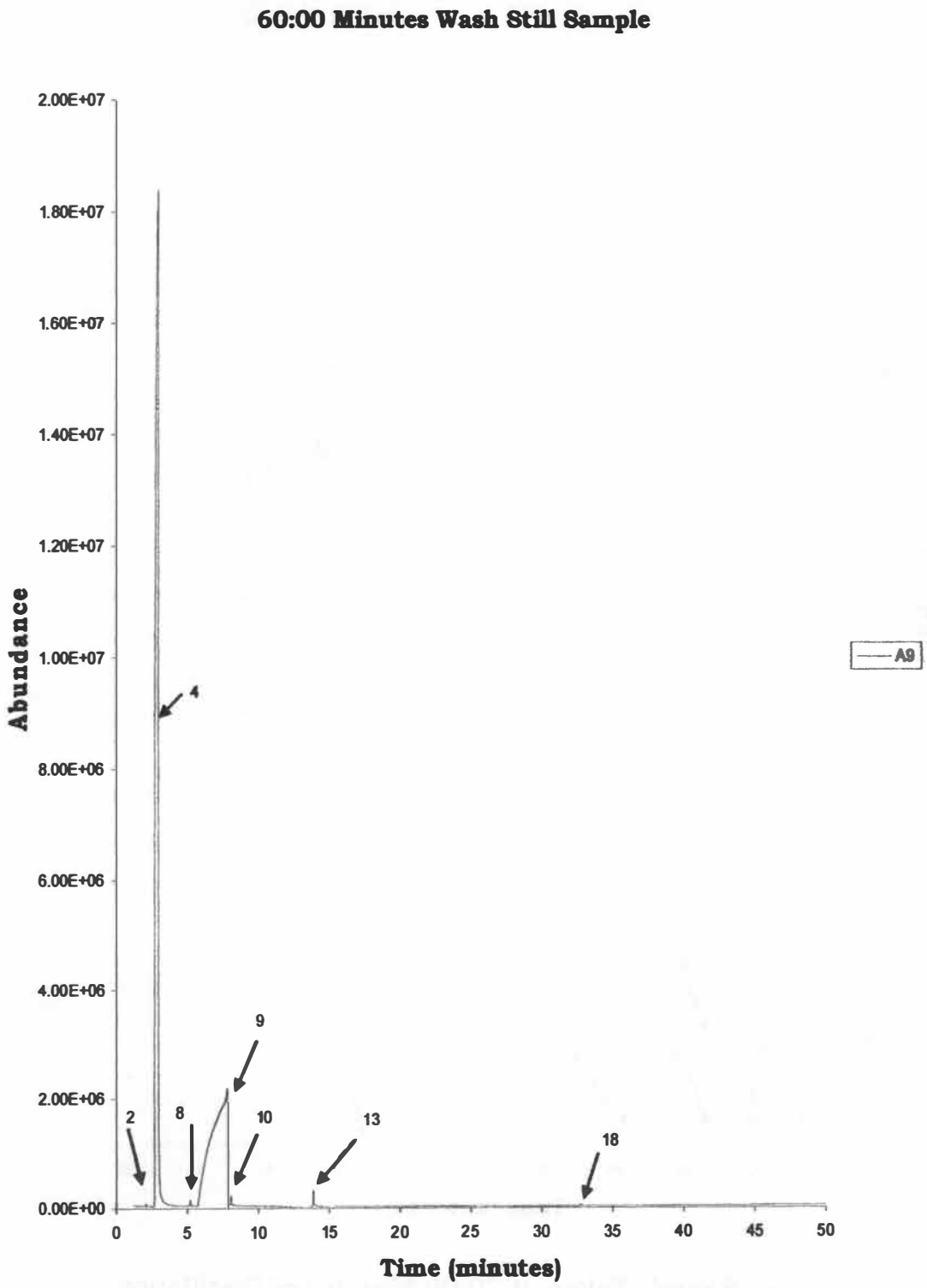

Figure 28: Wash Sample Taken at 60:00 Minutes of Distillation

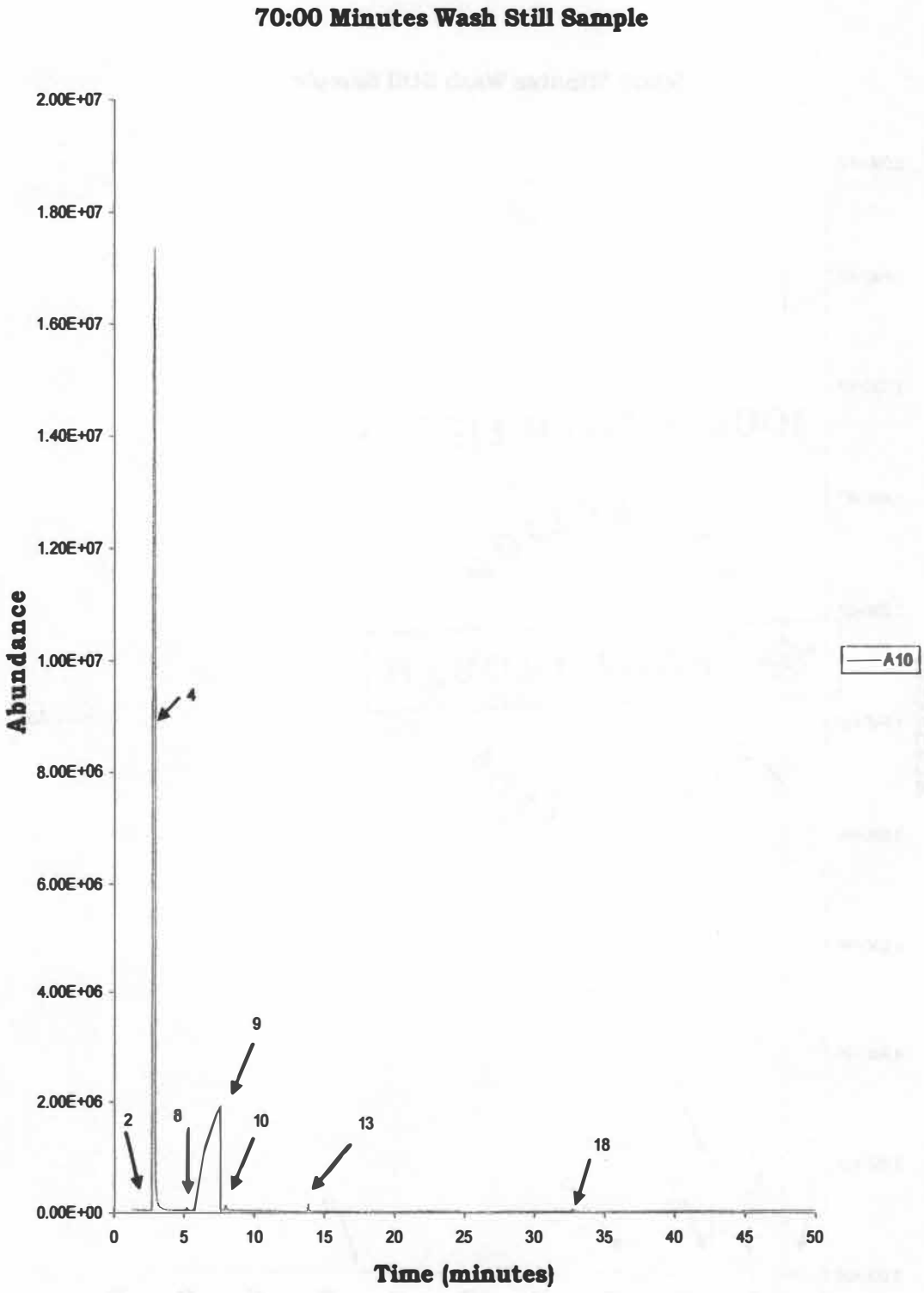

Figure 29: Wash Sample Taken at 70:00 Minutes of Distillation

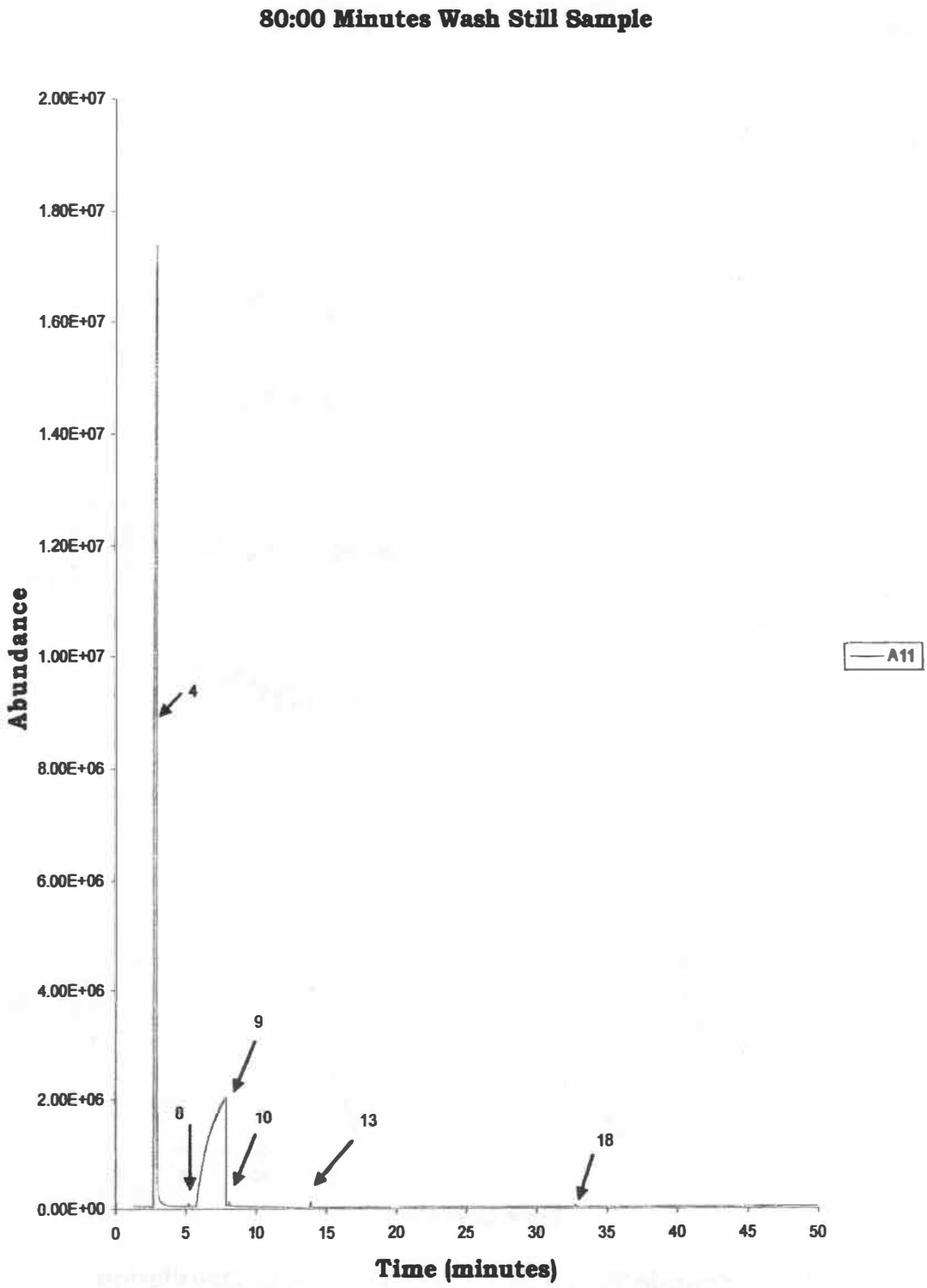

Figure 30: Wash Sample Taken at 80:00 Minutes of Distillation

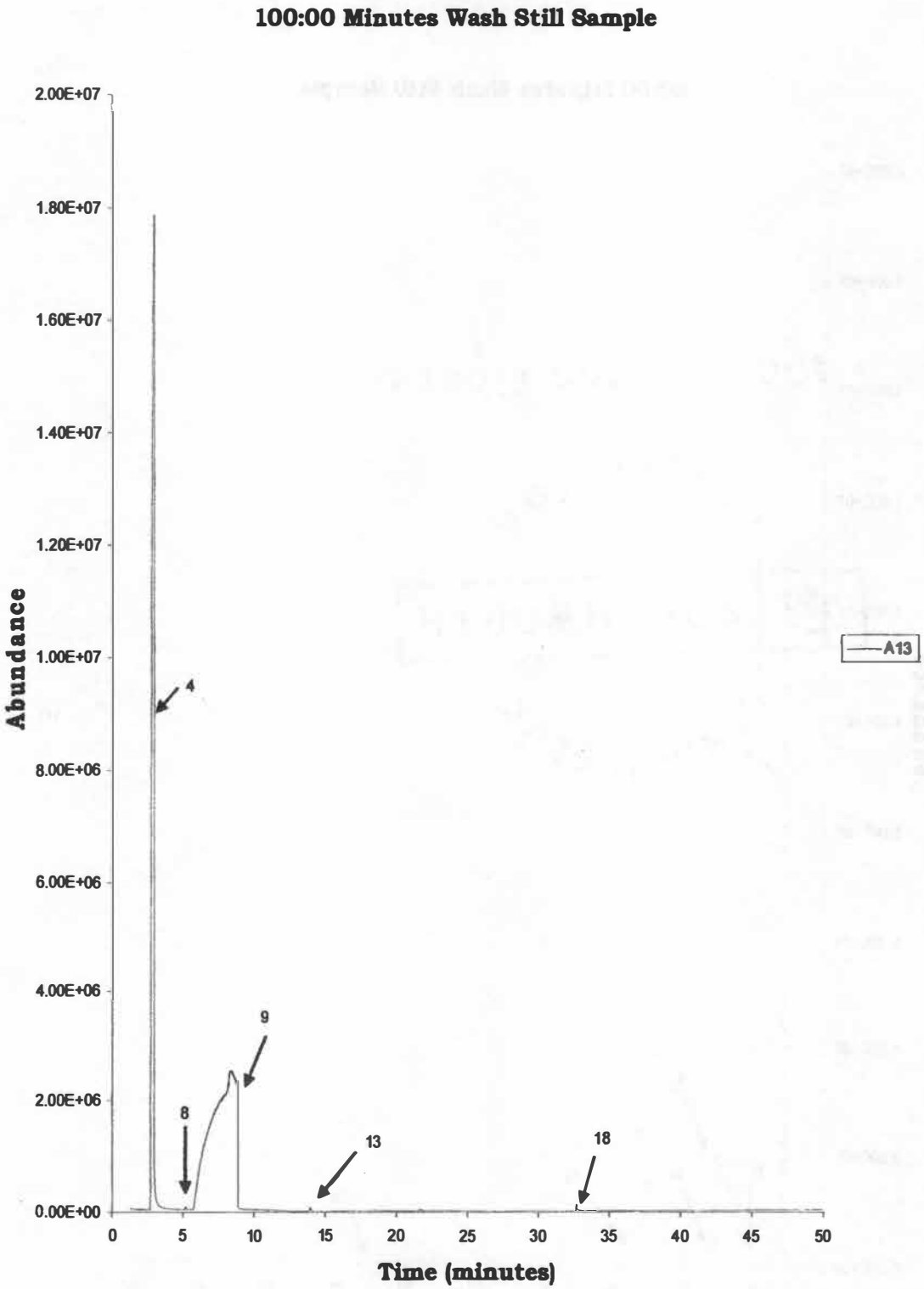

Figure 31: Wash Sample Taken at 100:00 Minutes of Distillation

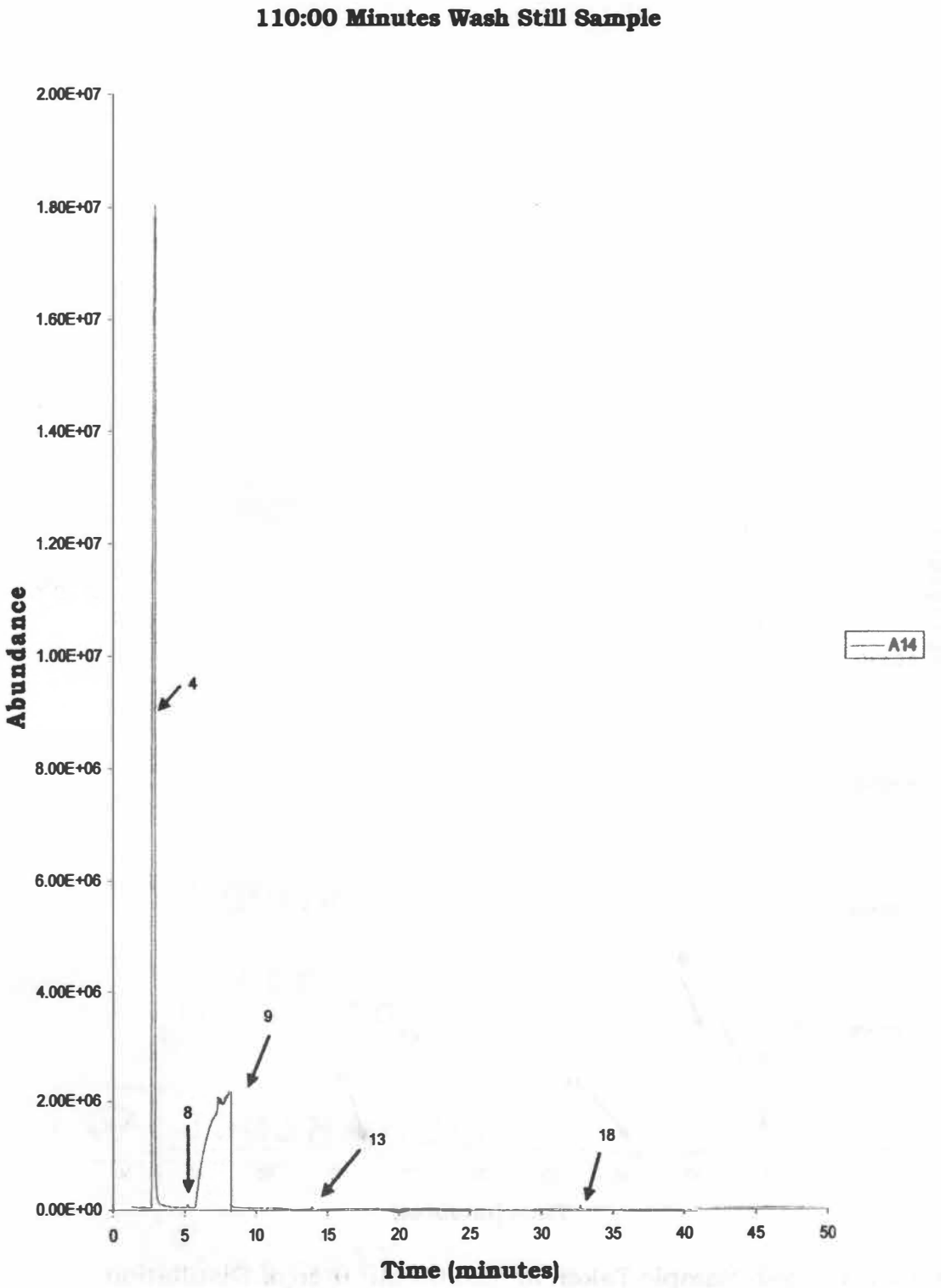

Figure 32: Wash Sample Taken at 110:00 Minutes of Distillation

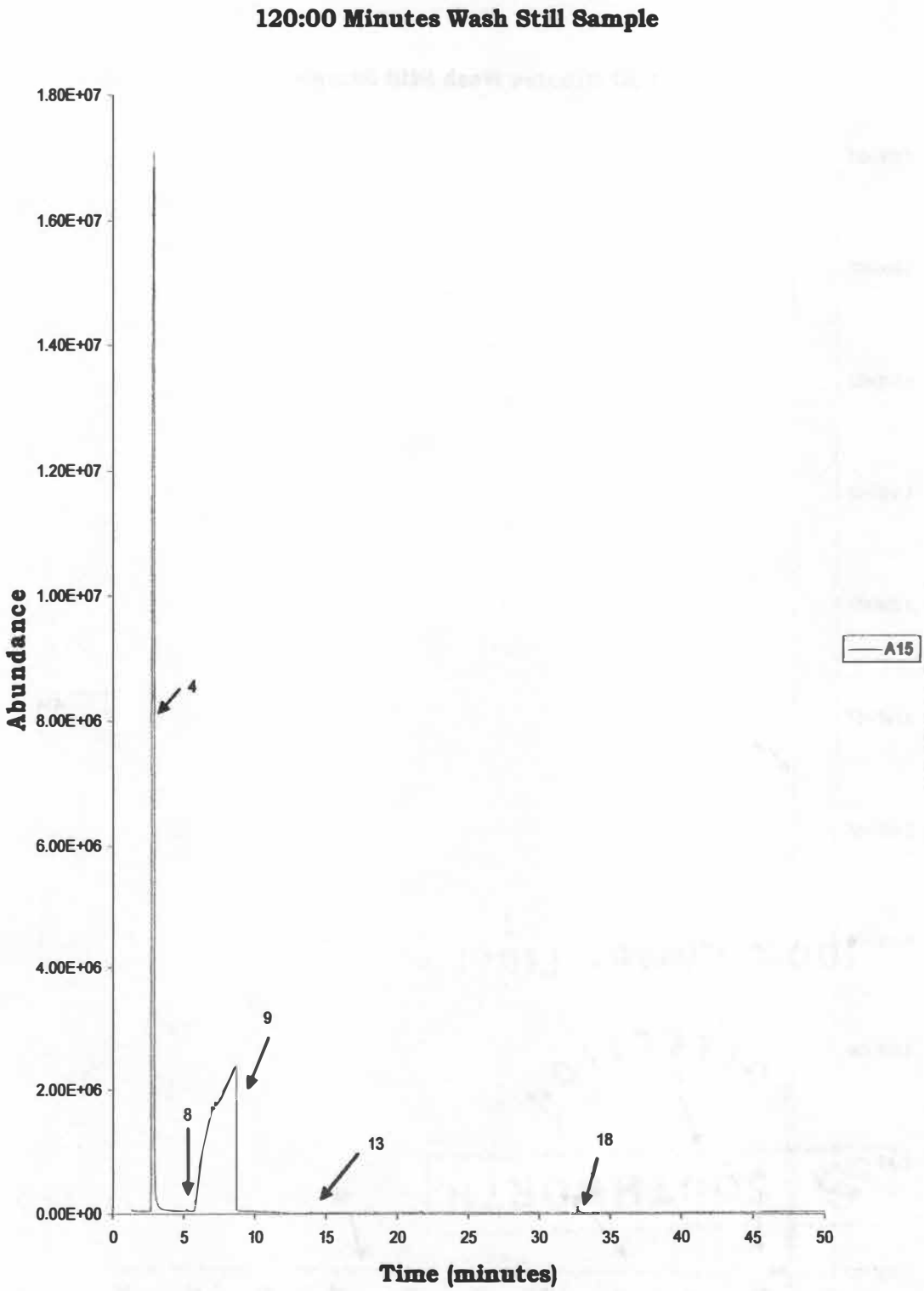

Figure 33: Wash Sample Taken at 120:00 Minutes of Distillation

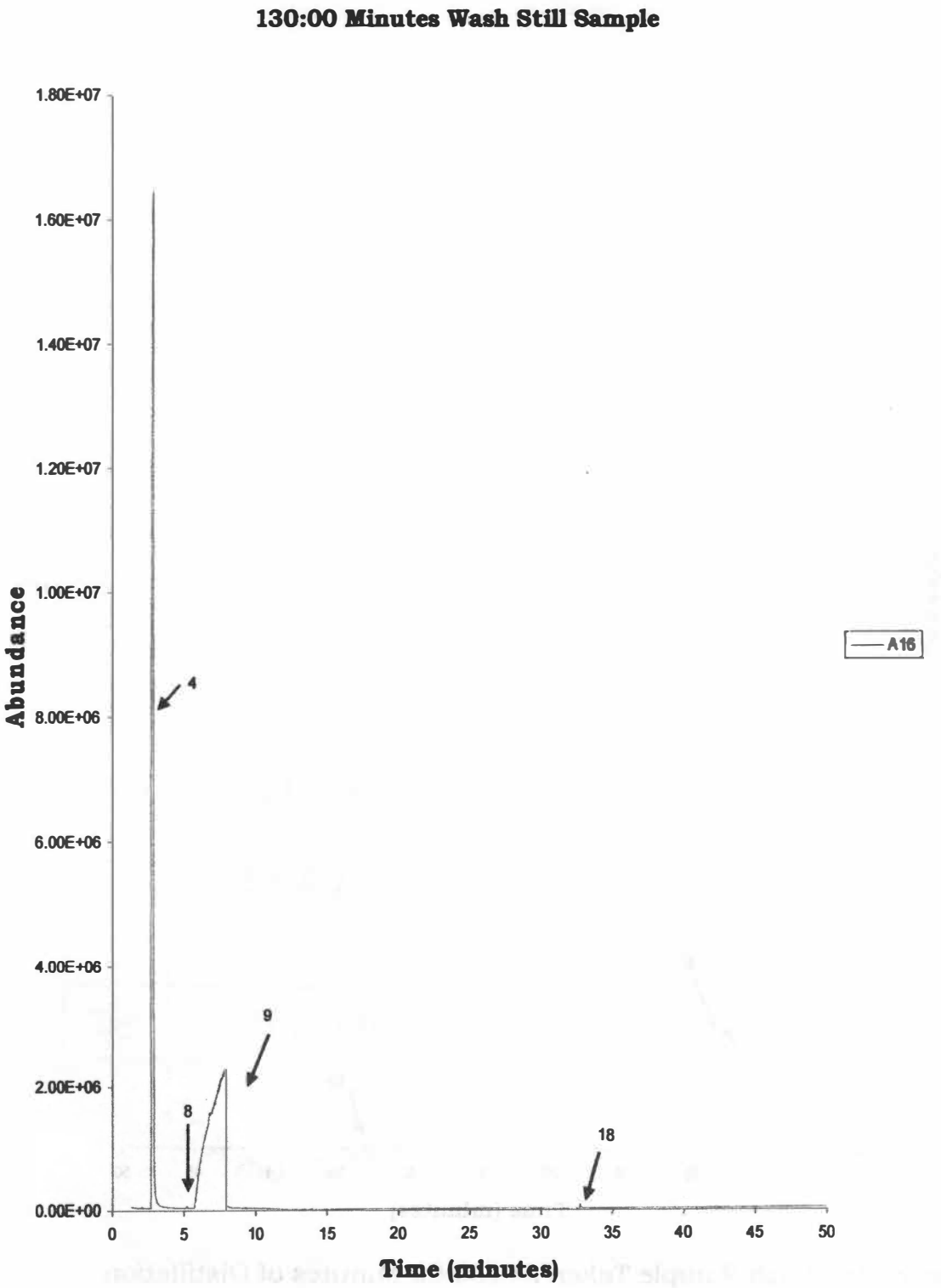

Figure 34: Wash Sample Taken at 130:00 Minutes of Distillation

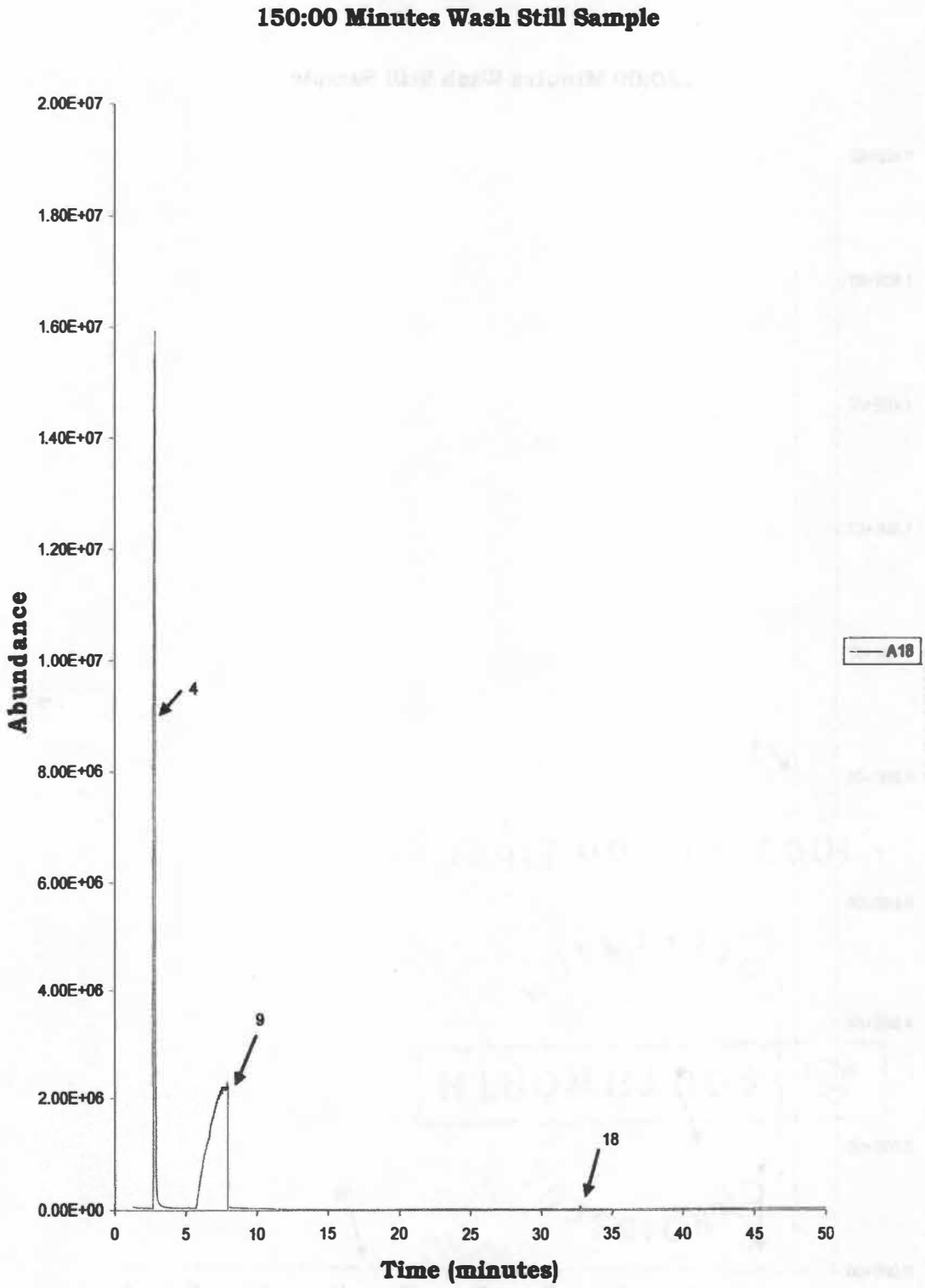

Figure 35: Wash Sample Taken at 150:00 Minutes of Distillation

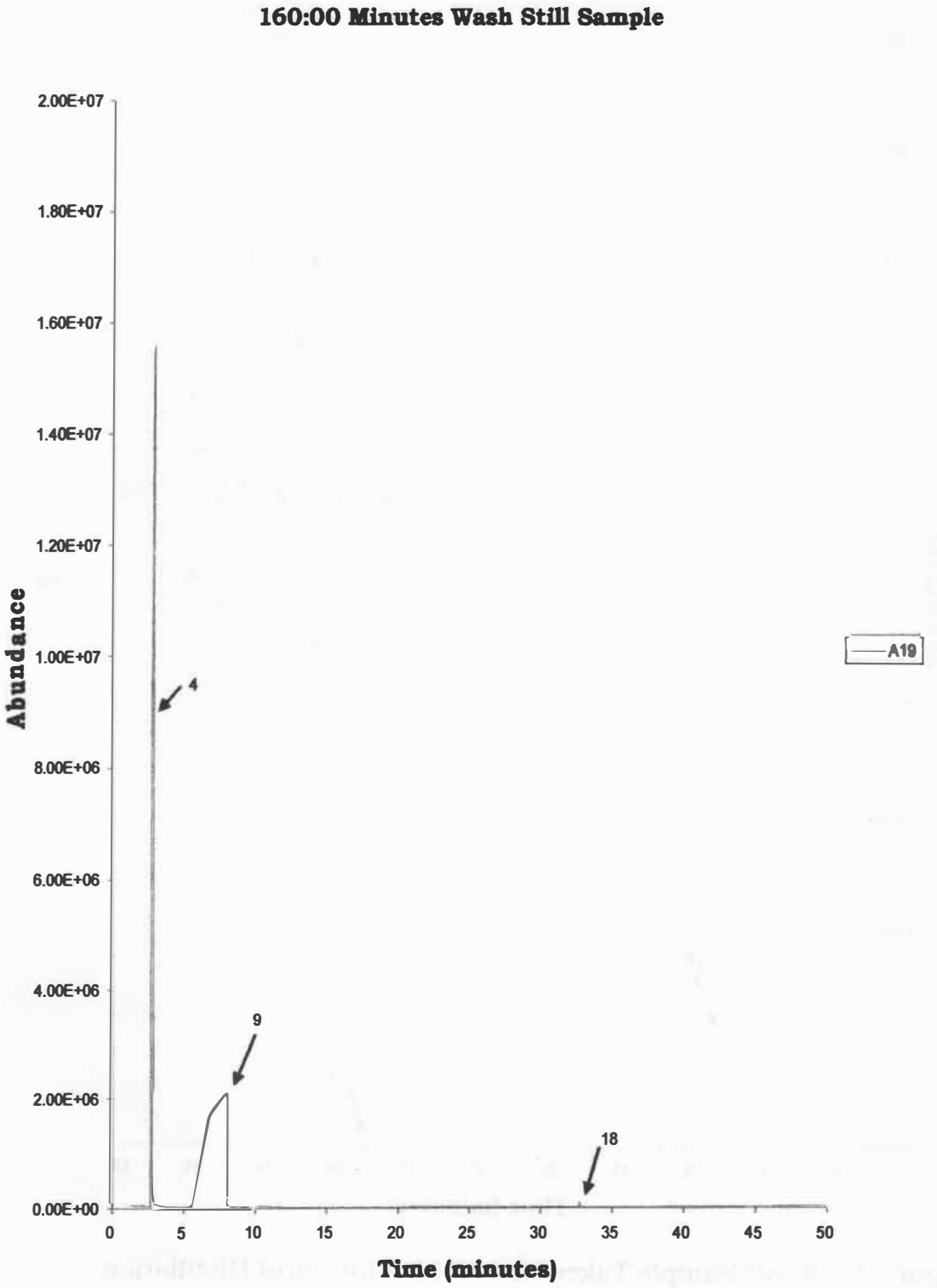

Figure 36: Wash Sample Taken at 160:00 Minutes of Distillation

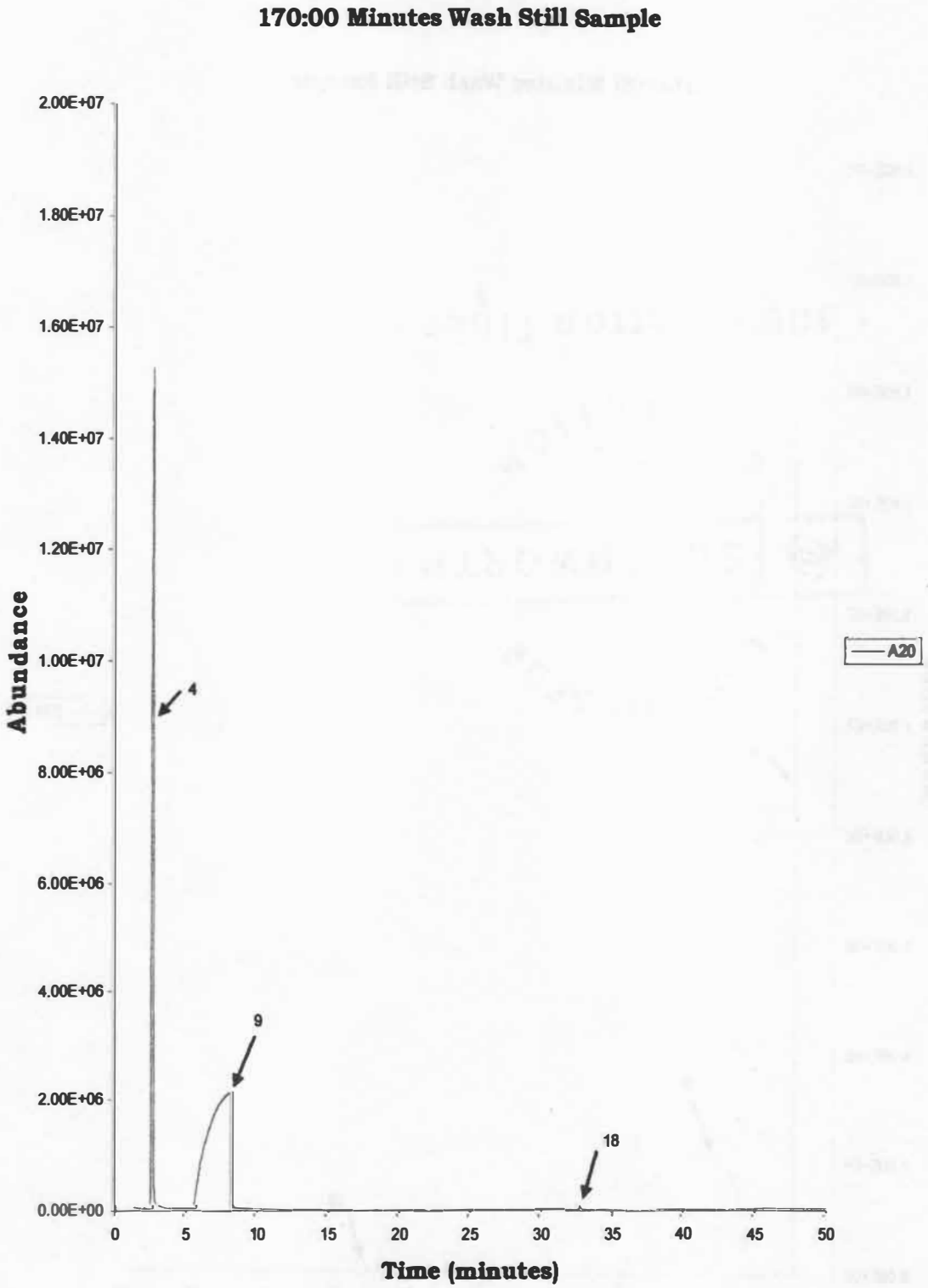

Figure 37: Wash Sample Taken at 170:00 Minutes of Distillation

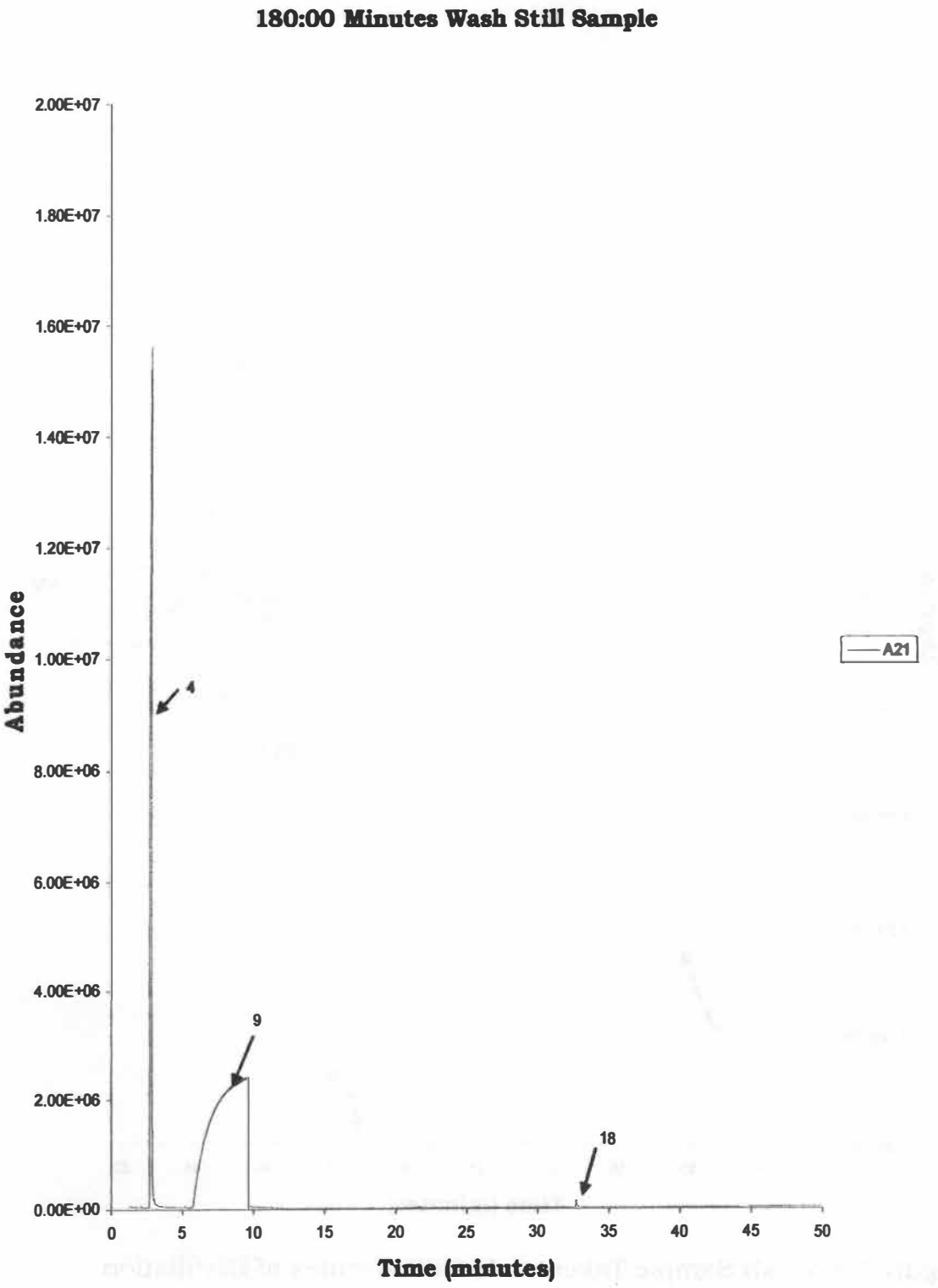

Figure 38: Wash Sample Taken at 180:00 Minutes of Distillation

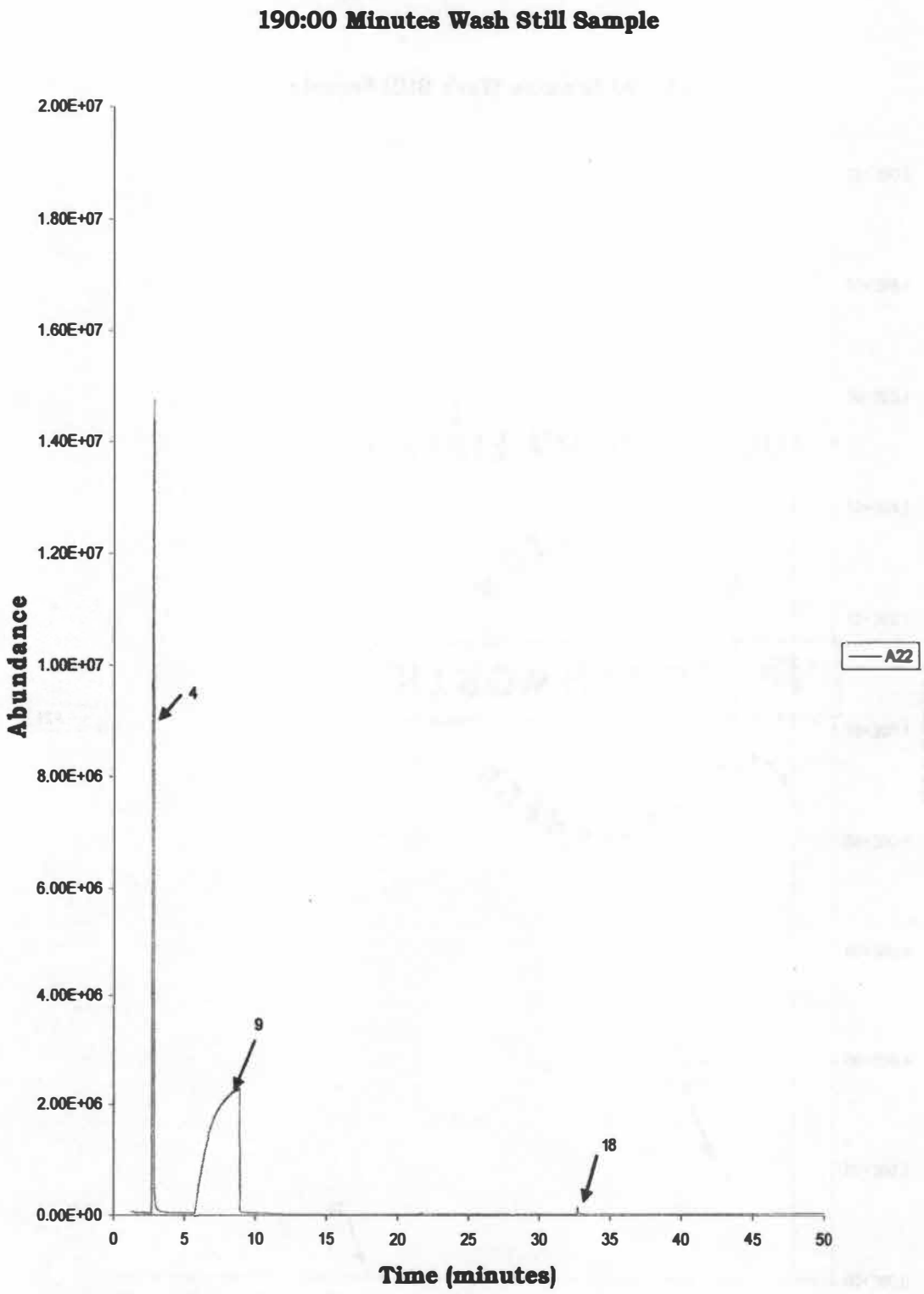

Figure 39: Wash Sample Taken at 190:00 Minutes of Distillation

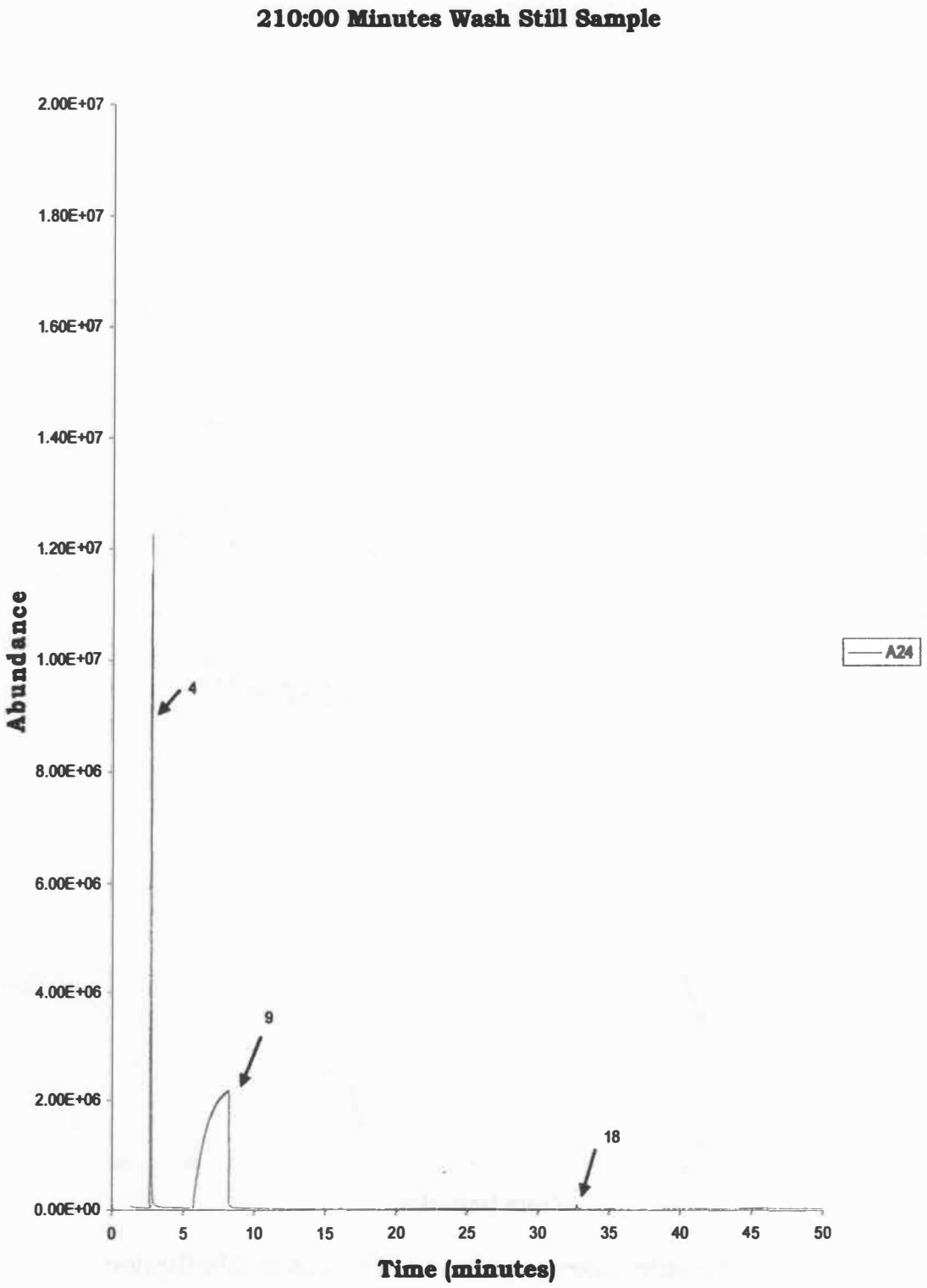

Figure 40: Wash Sample Taken at 210:00 Minutes of Distillation

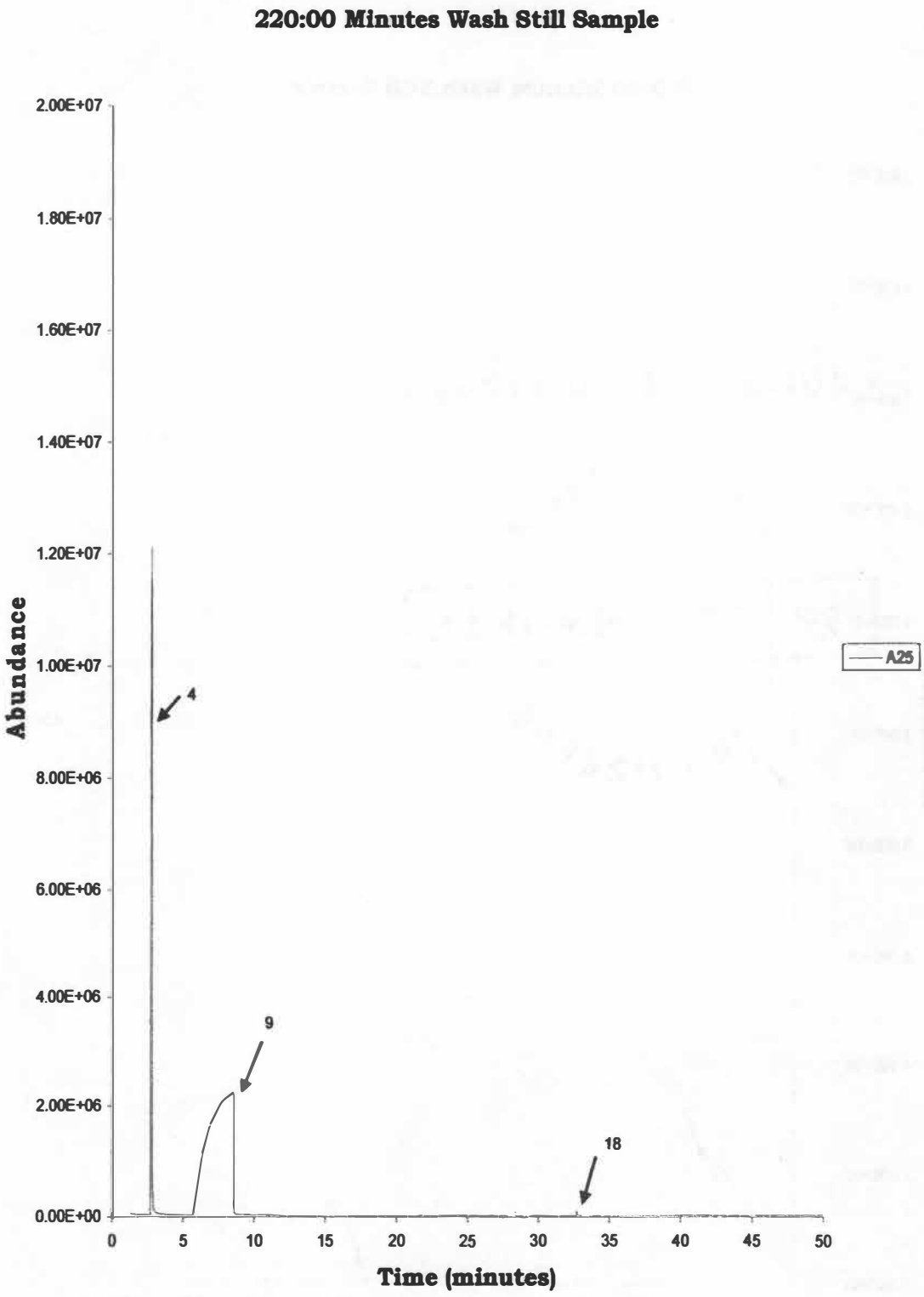

Figure 41: Wash Sample Taken at 220:00 Minutes of Distillation

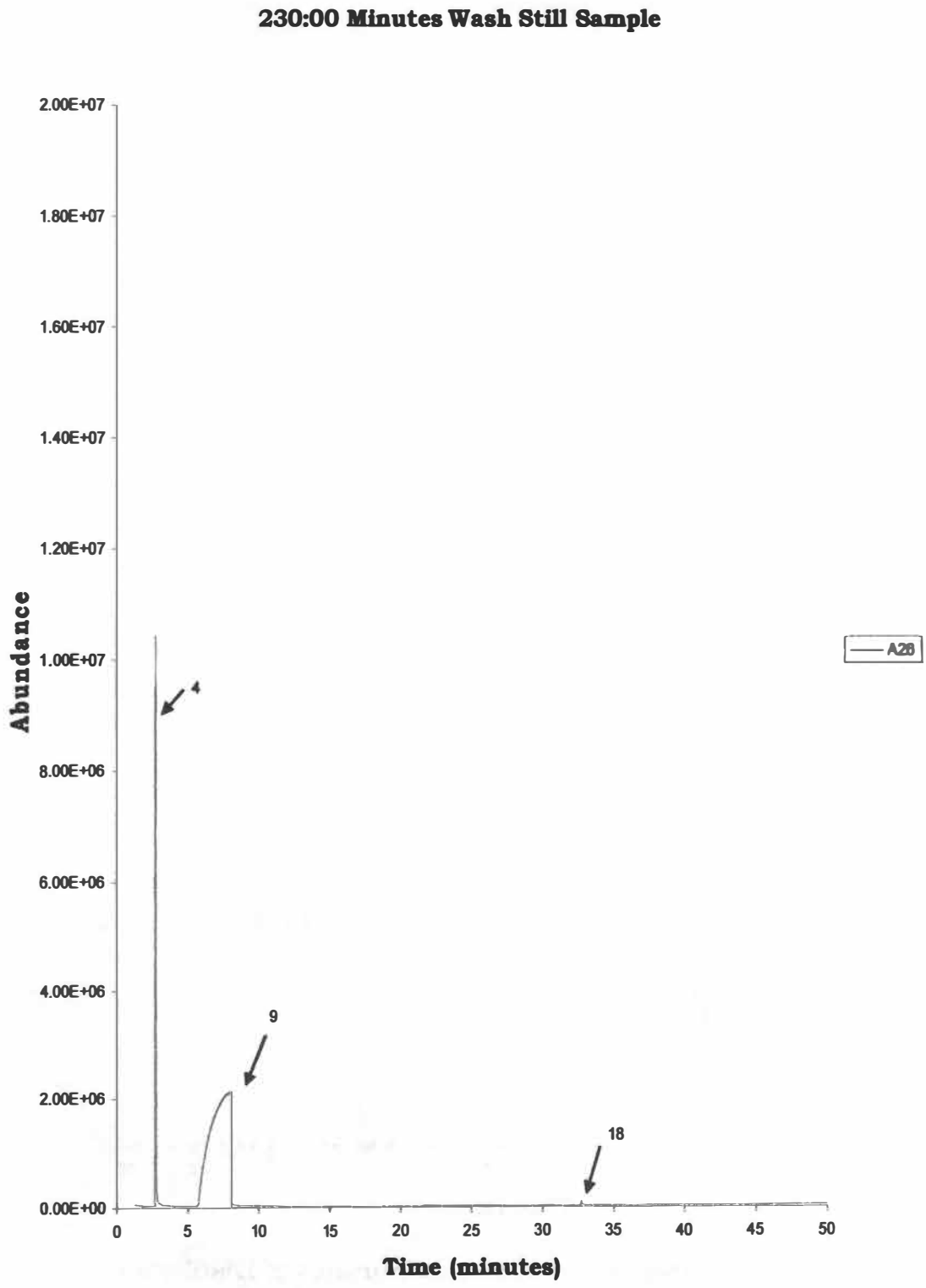

Figure 42: Wash Sample Taken at 230:00 Minutes of Distillation

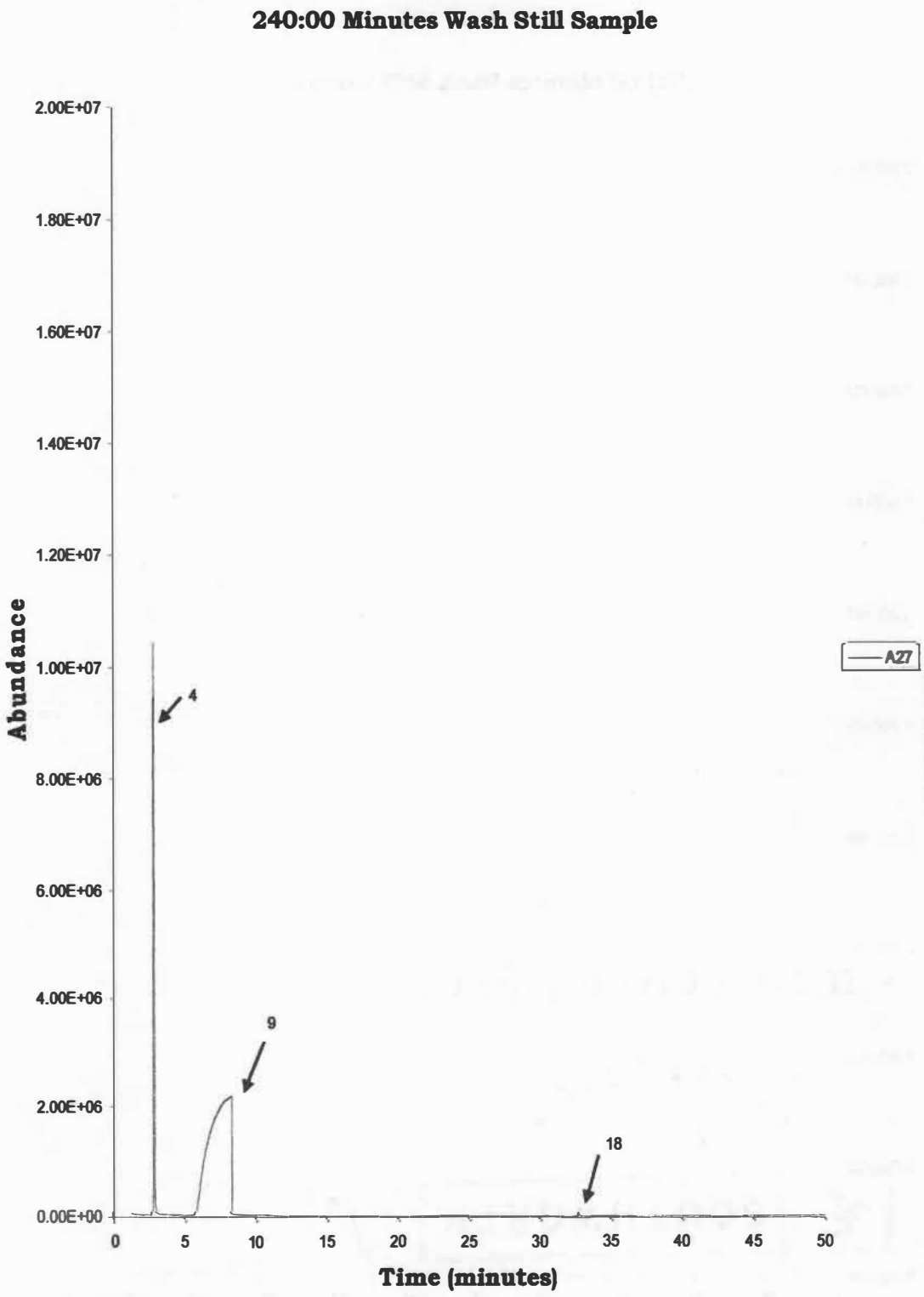

Figure 43: Wash Sample Taken at 240:00 Minutes of Distillation

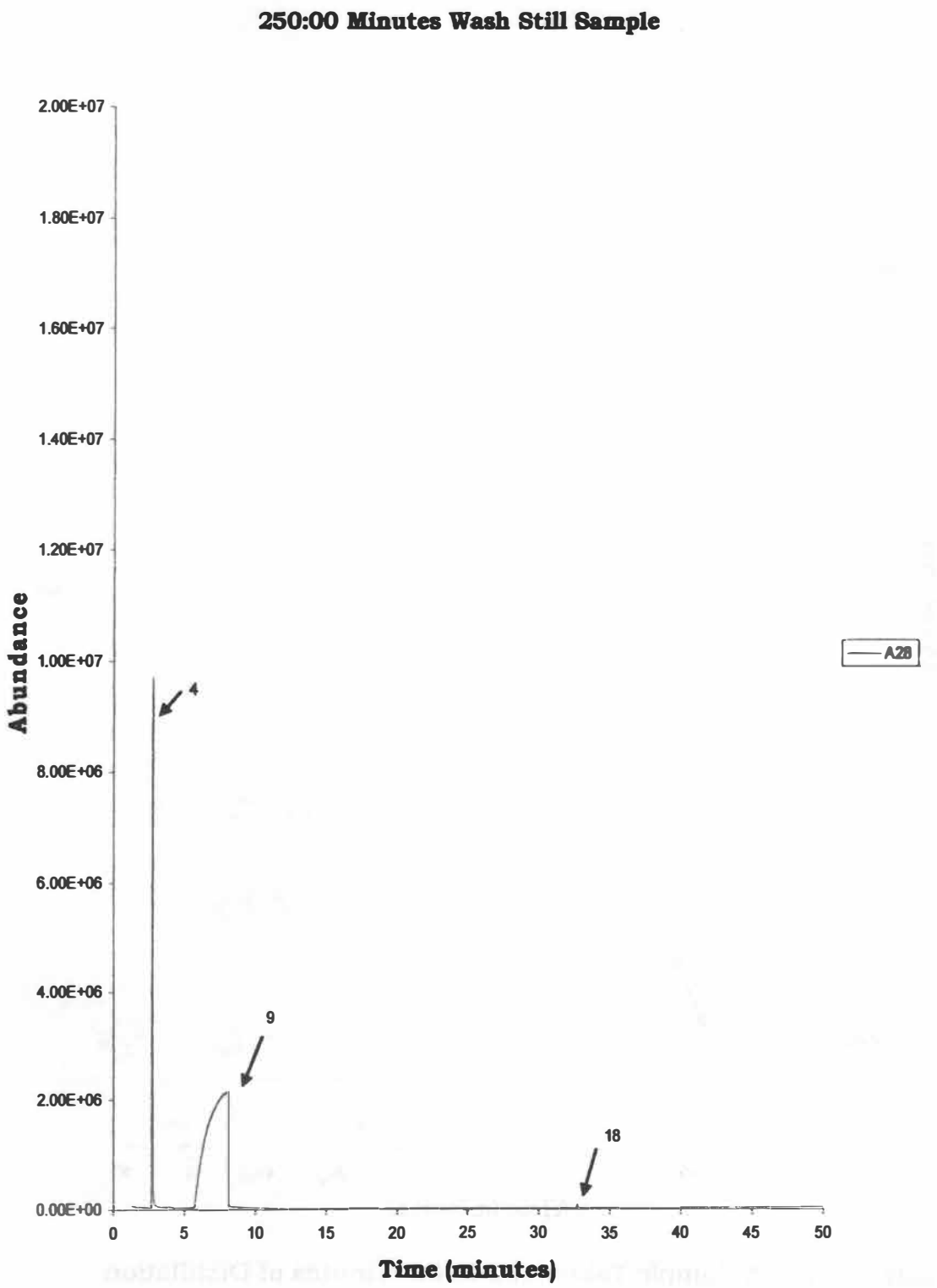

Figure 44: Wash Sample Taken at 250:00 Minutes of Distillation

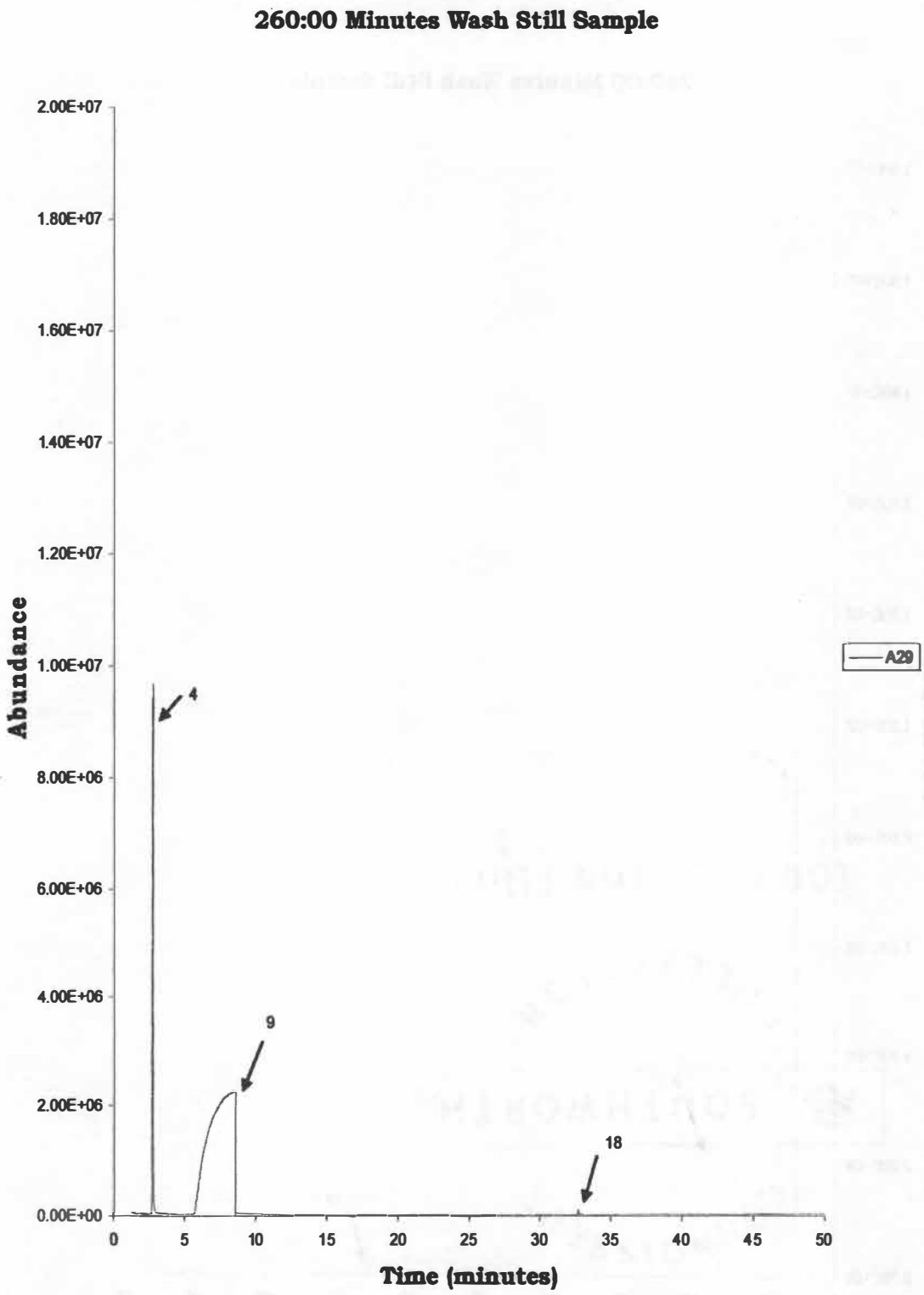

Figure 45: Wash Sample Taken at 260:00 Minutes of Distillation

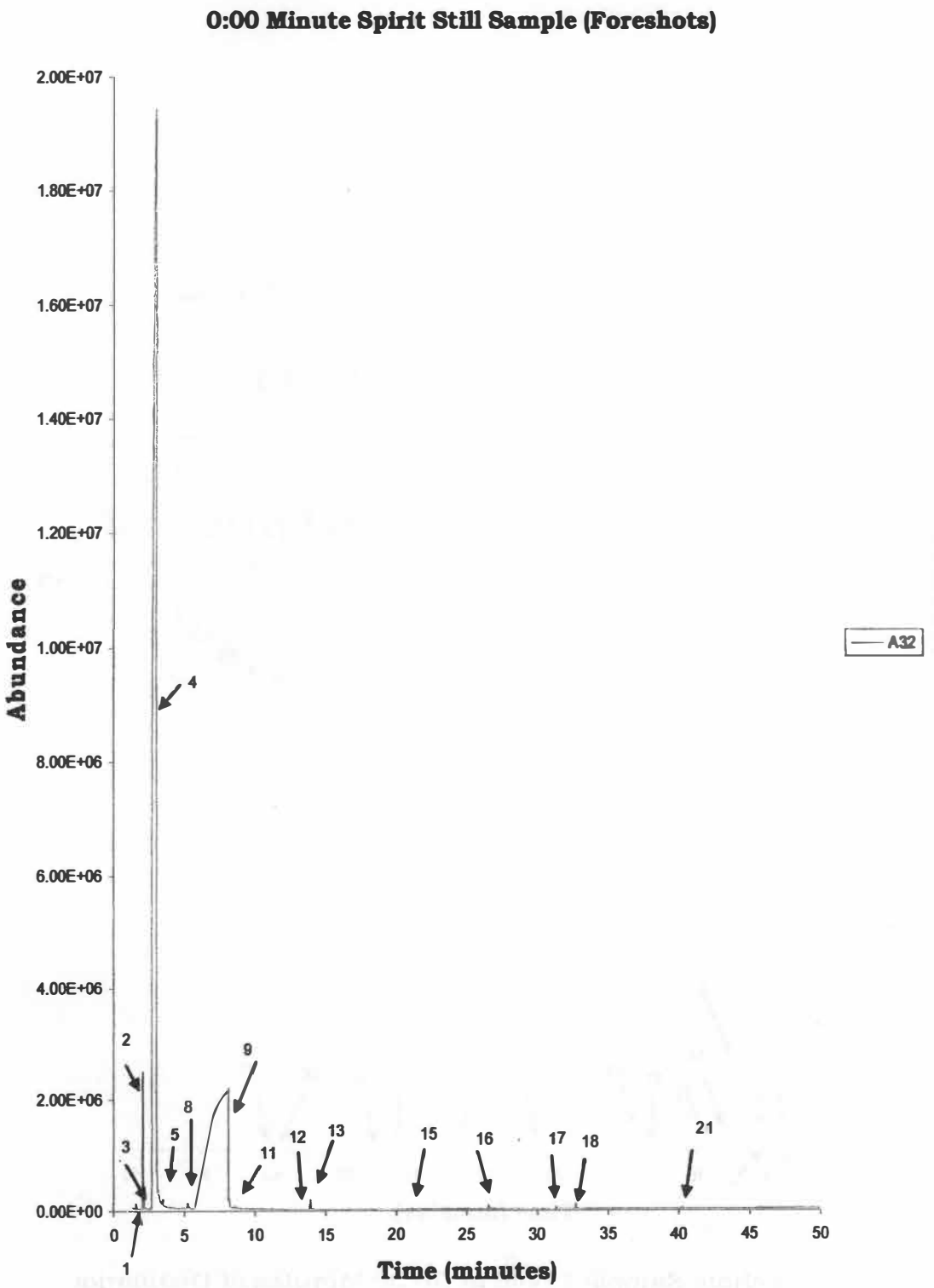

Figure 46: Foreshots Sample Taken at 0:00 Minutes of Distillation

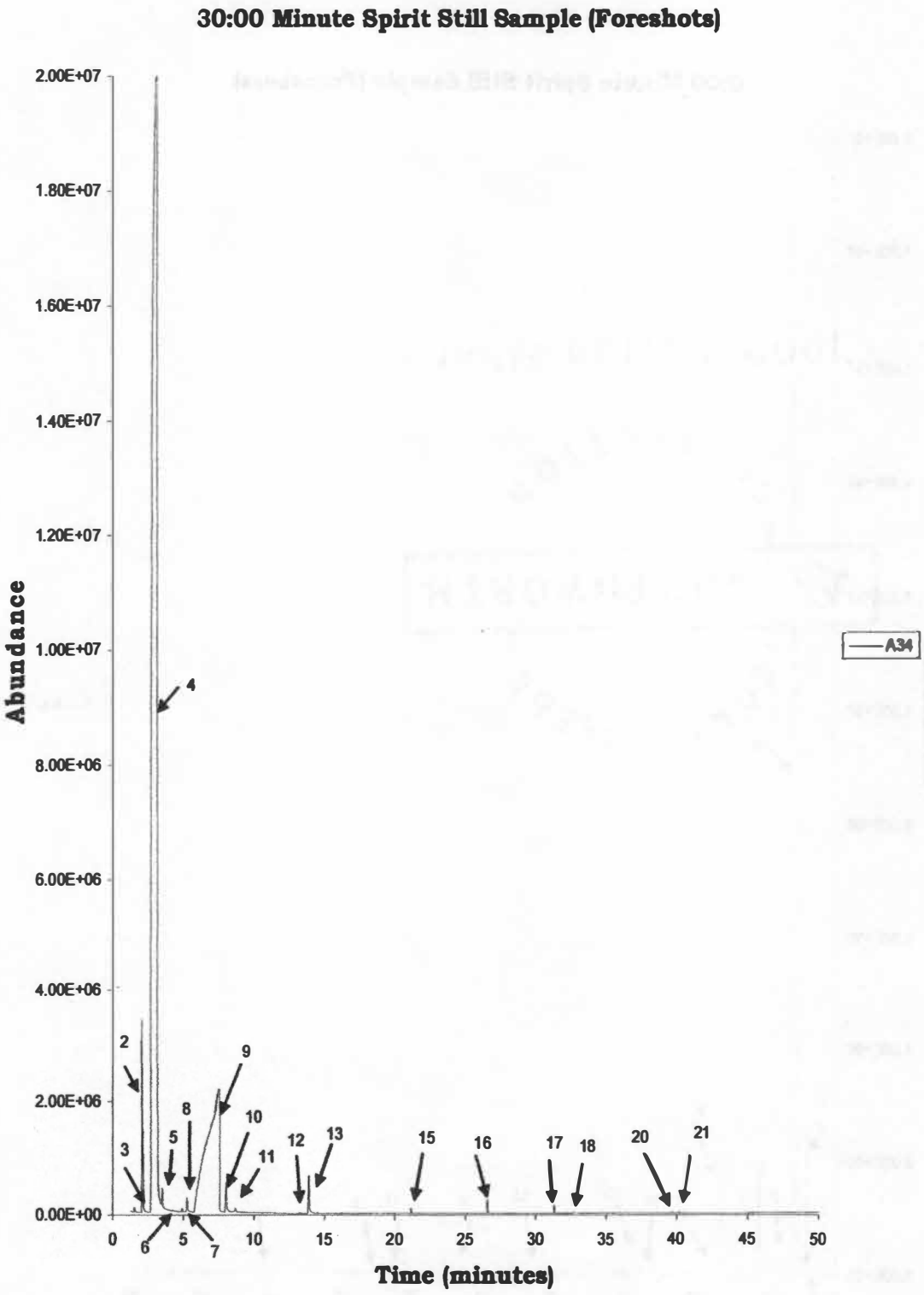

Figure 47: Foreshots Sample Taken at 30:00 Minutes of Distillation

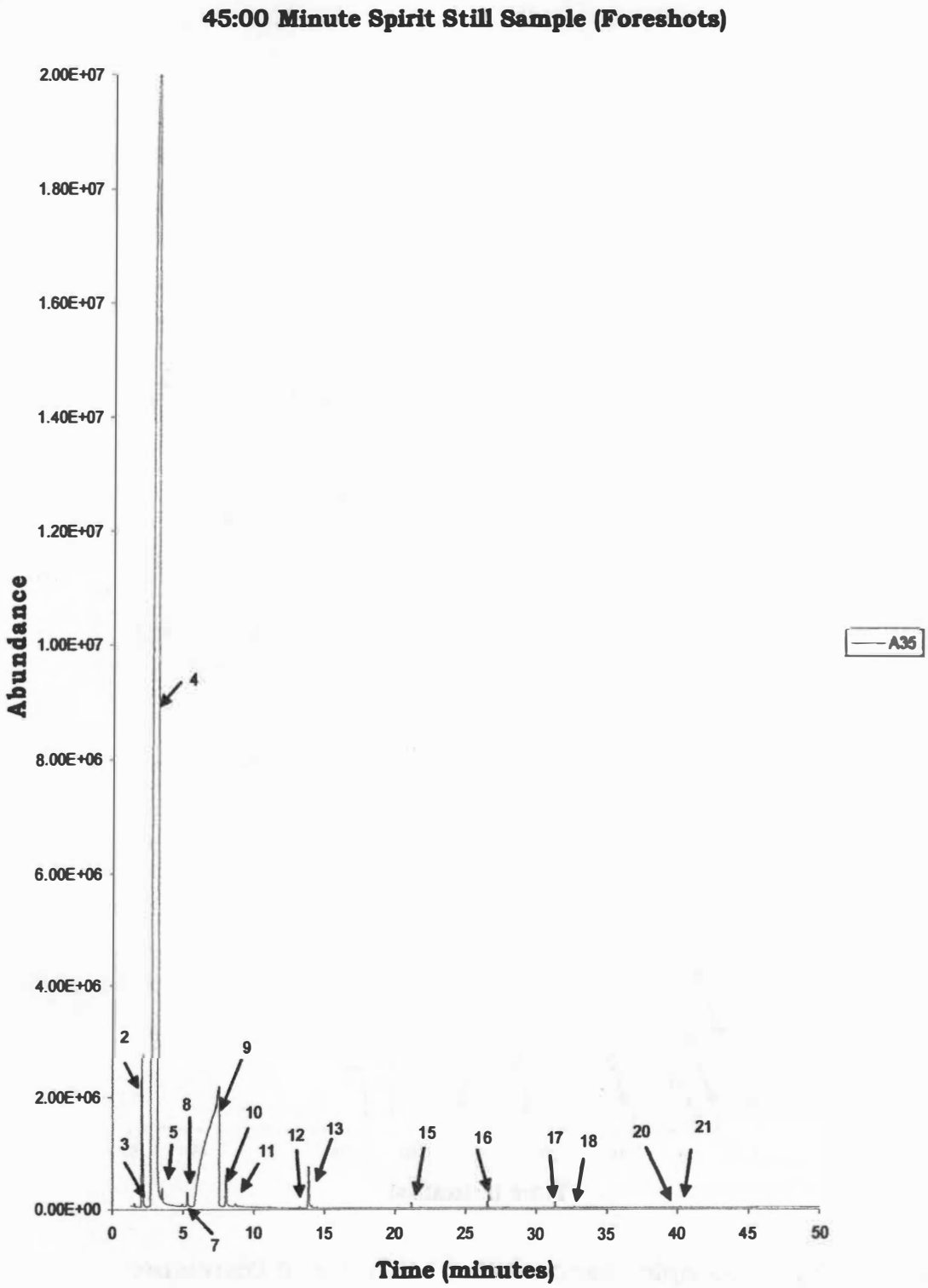

Figure 48: Foreshots Sample Taken at 45:00 Minutes of Distillation

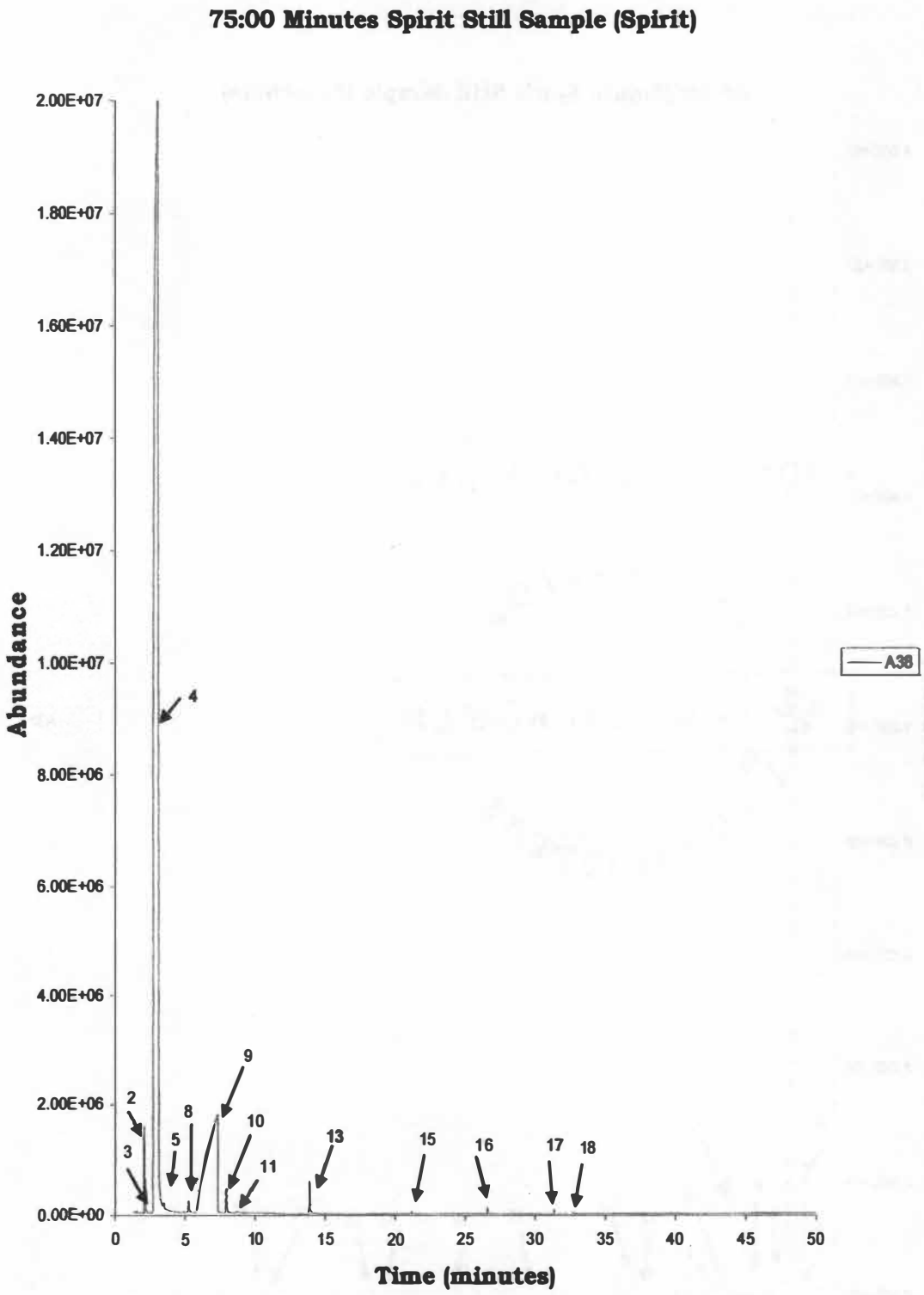

Figure 49: Spirit Sample Taken at 75:00 Minutes of Distillation

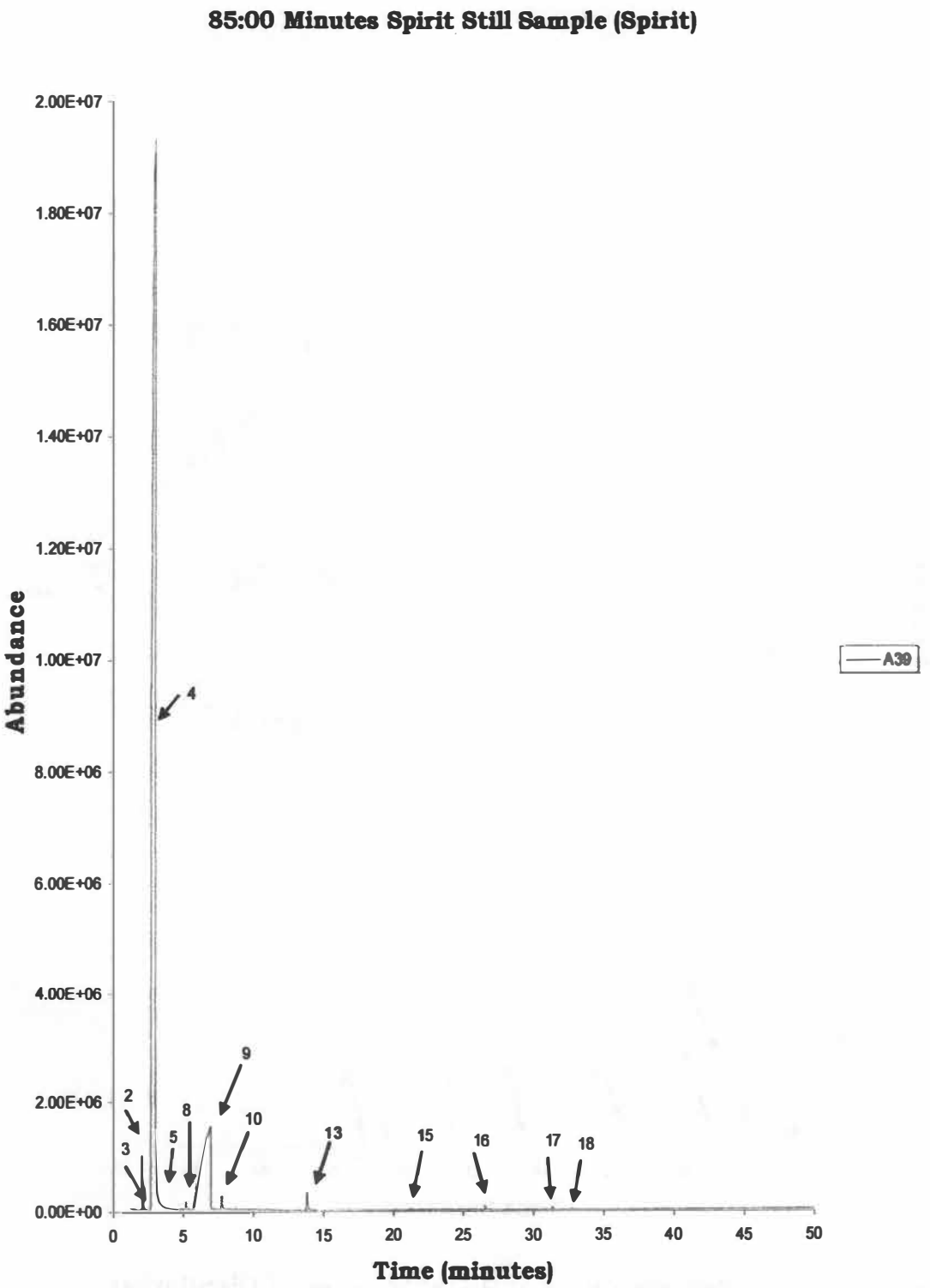

Figure 50: Spirit Sample Taken at 85:00 Minutes of Distillation

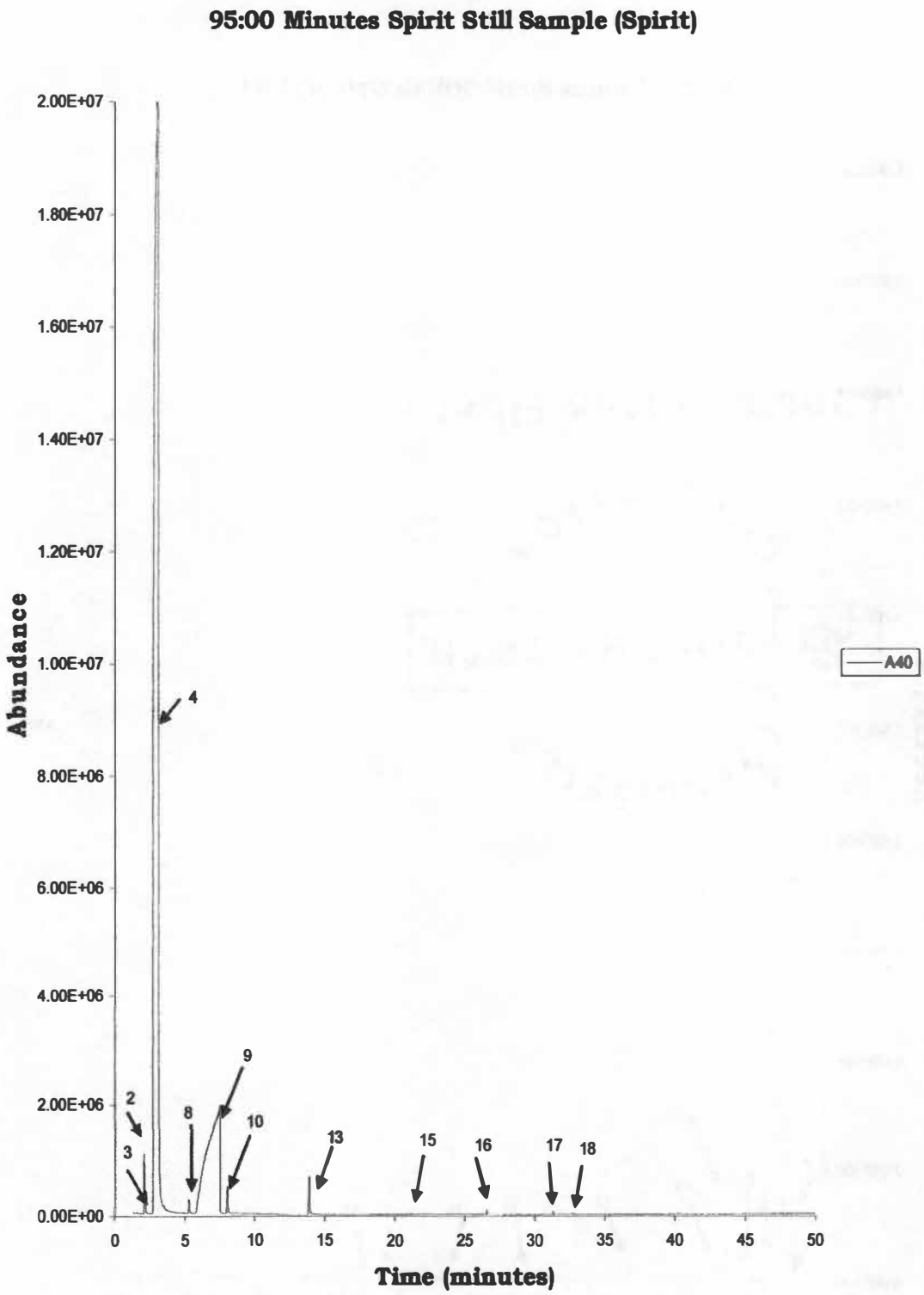

Figure 51: Spirit Sample Taken at 95:00 Minutes of Distillation

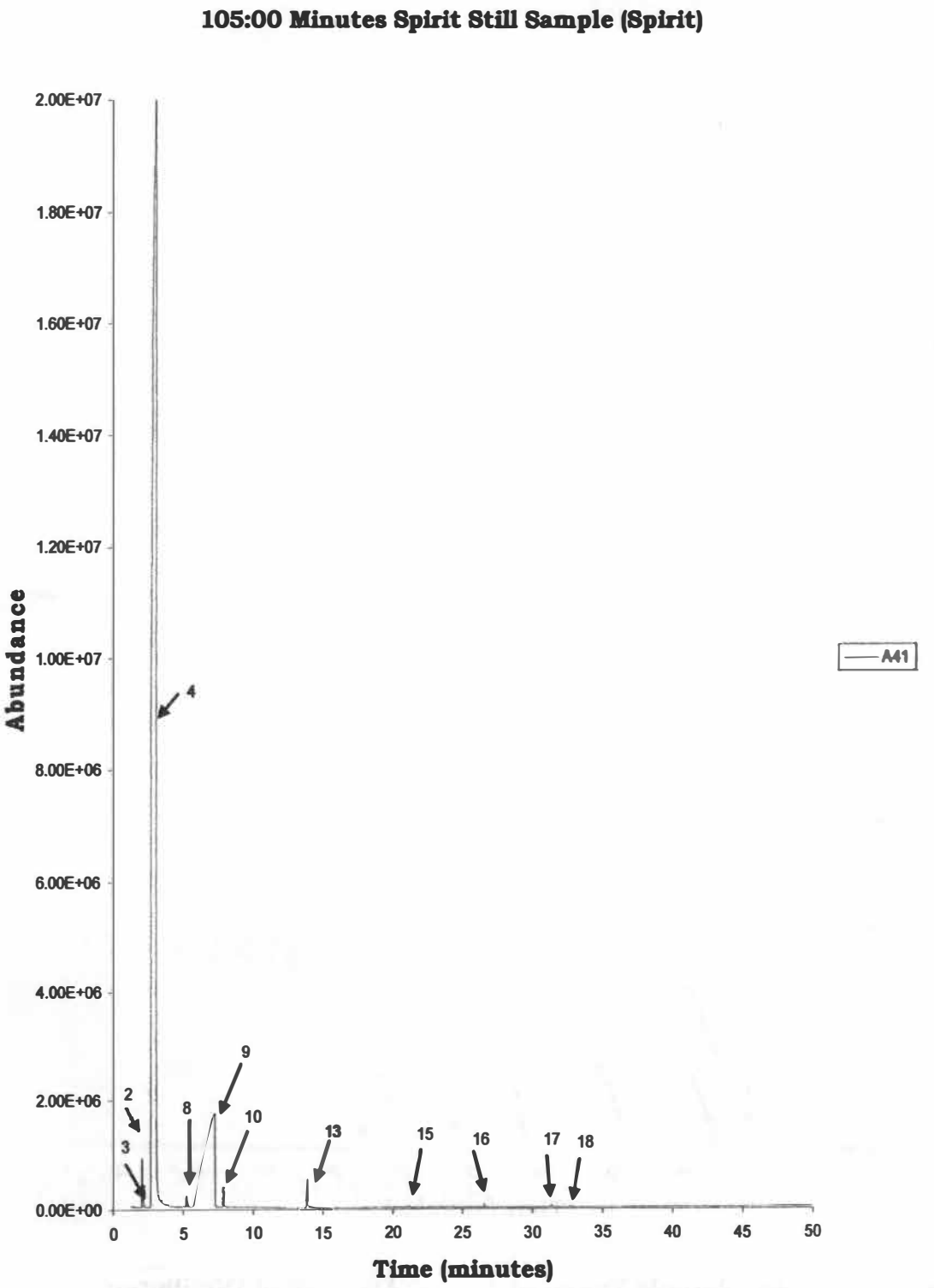

Figure 52: Spirit Sample Taken at 105:00 Minutes of Distillation

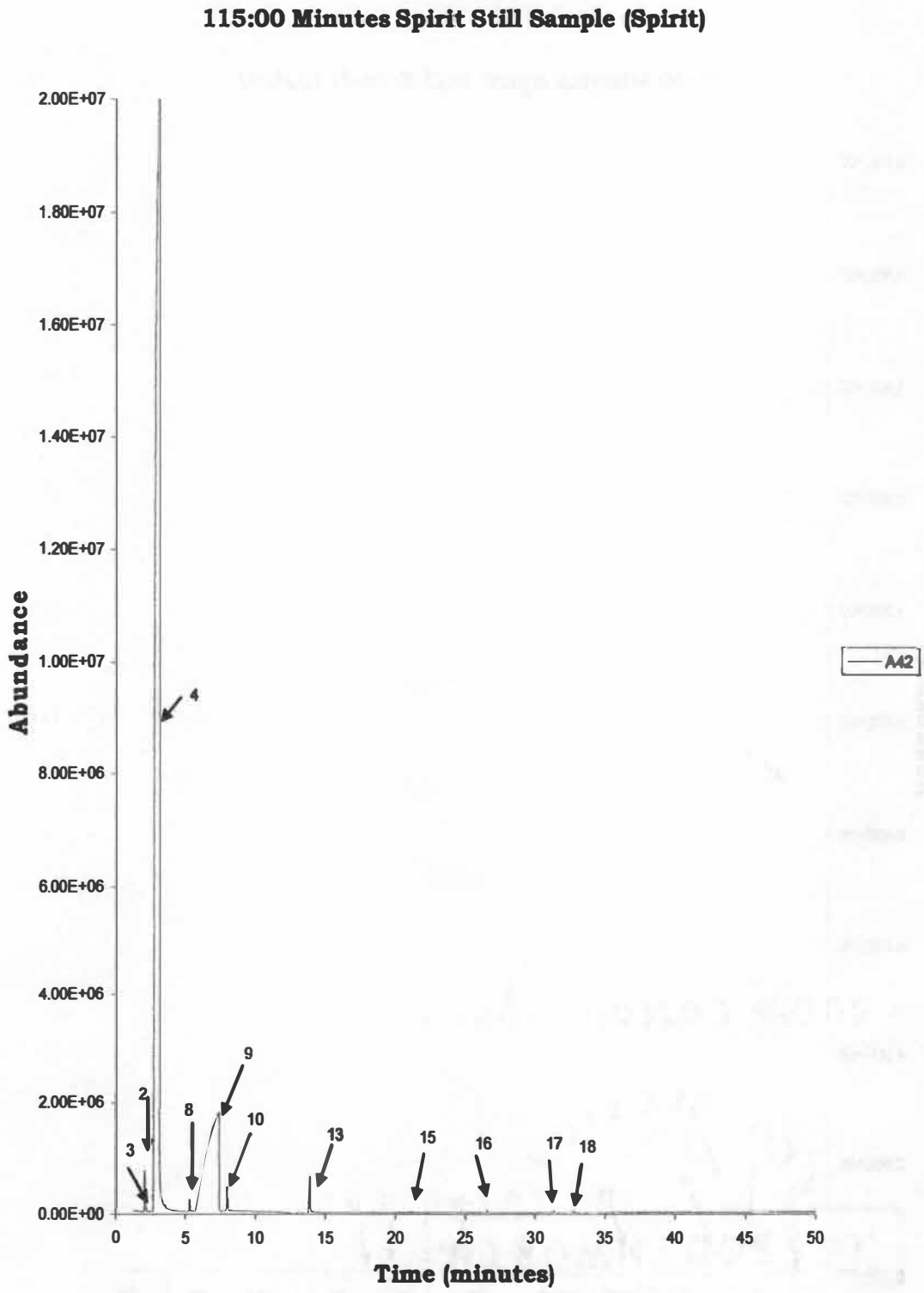

Figure 53: Spirit Sample Taken at 115:00 Minutes of Distillation

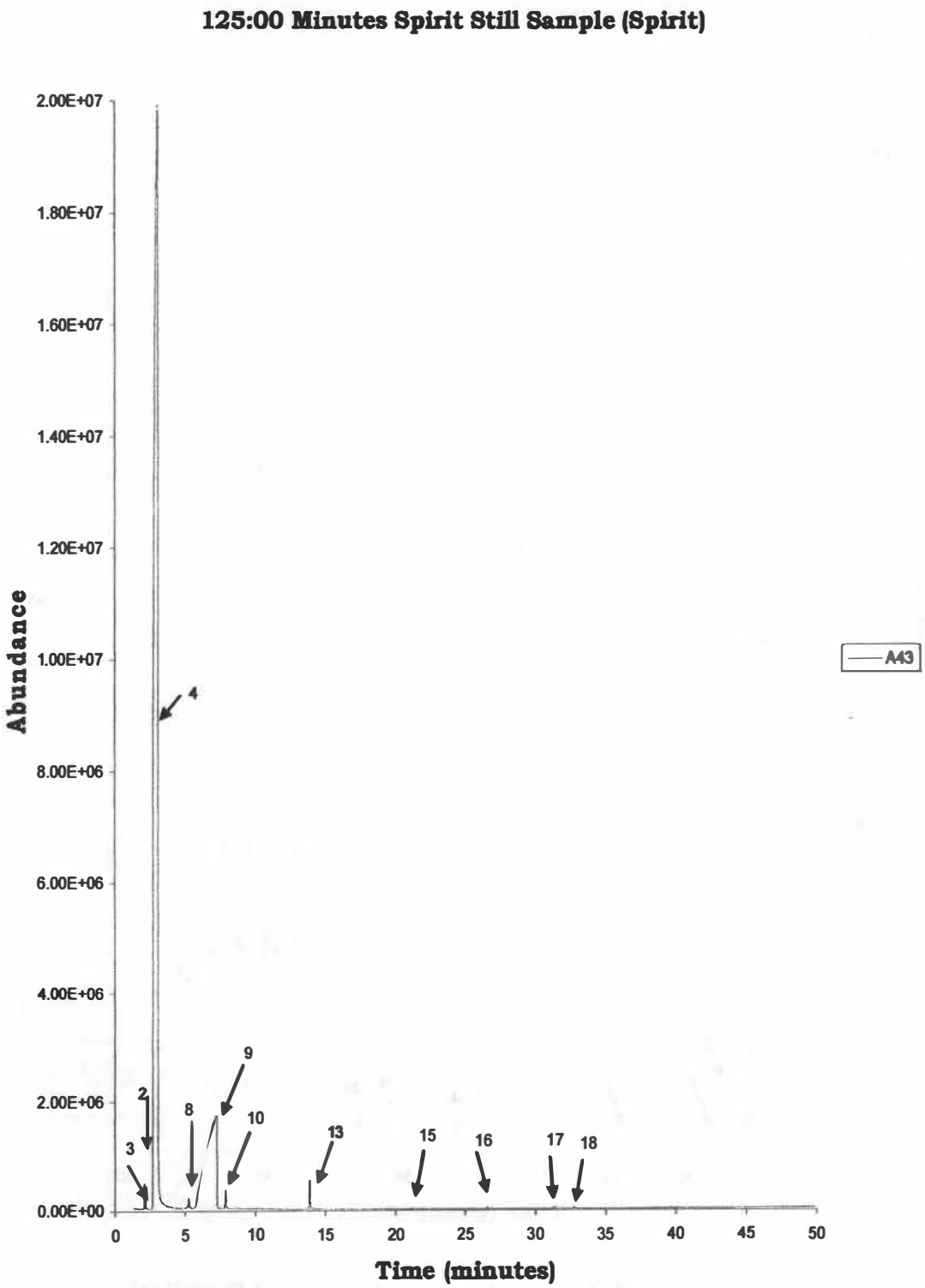

Figure 54: Spirit Sample Taken at 125:00 Minutes of Distillation

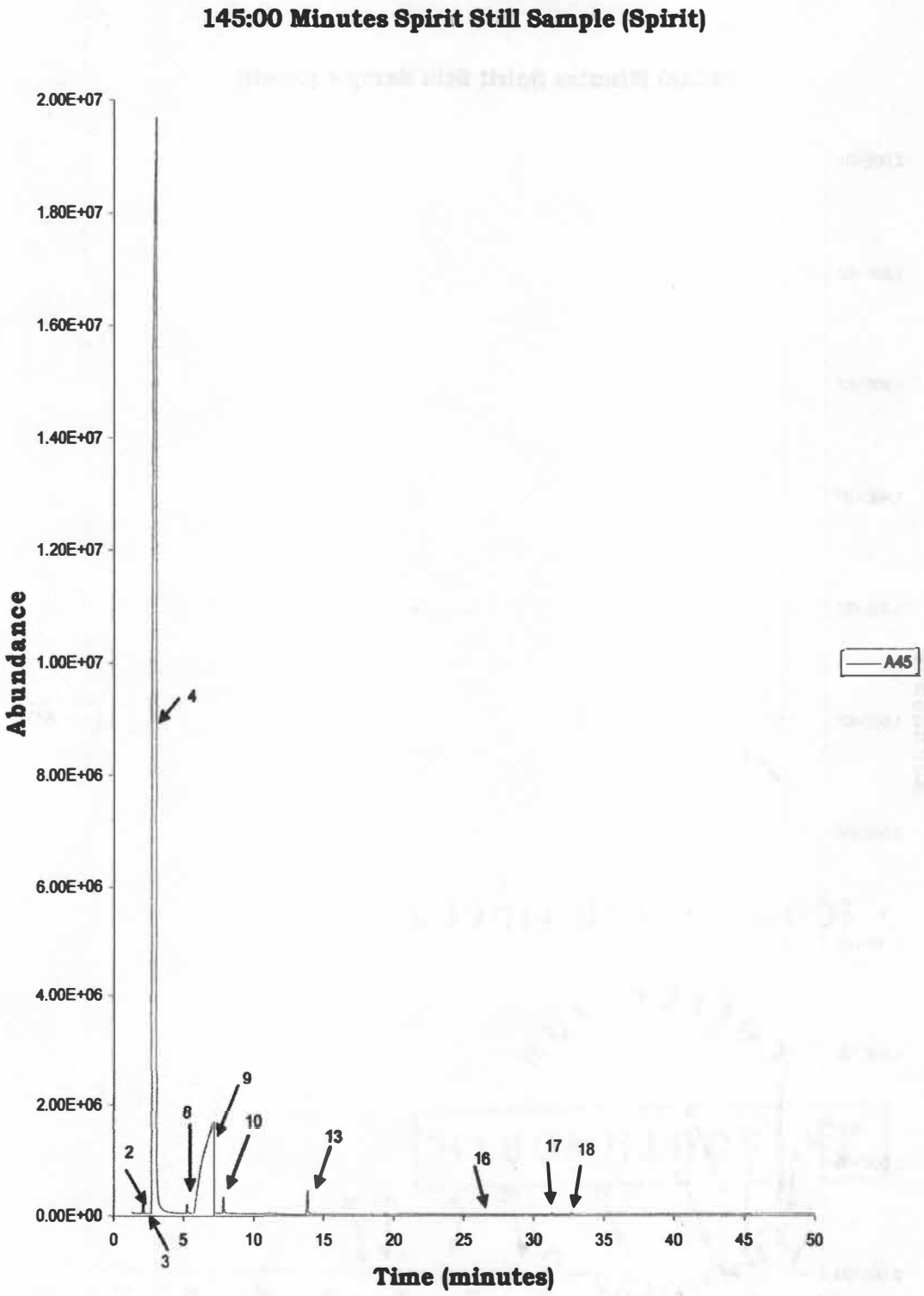

Figure 55: Spirit Sample Taken at 145:00 Minutes of Distillation

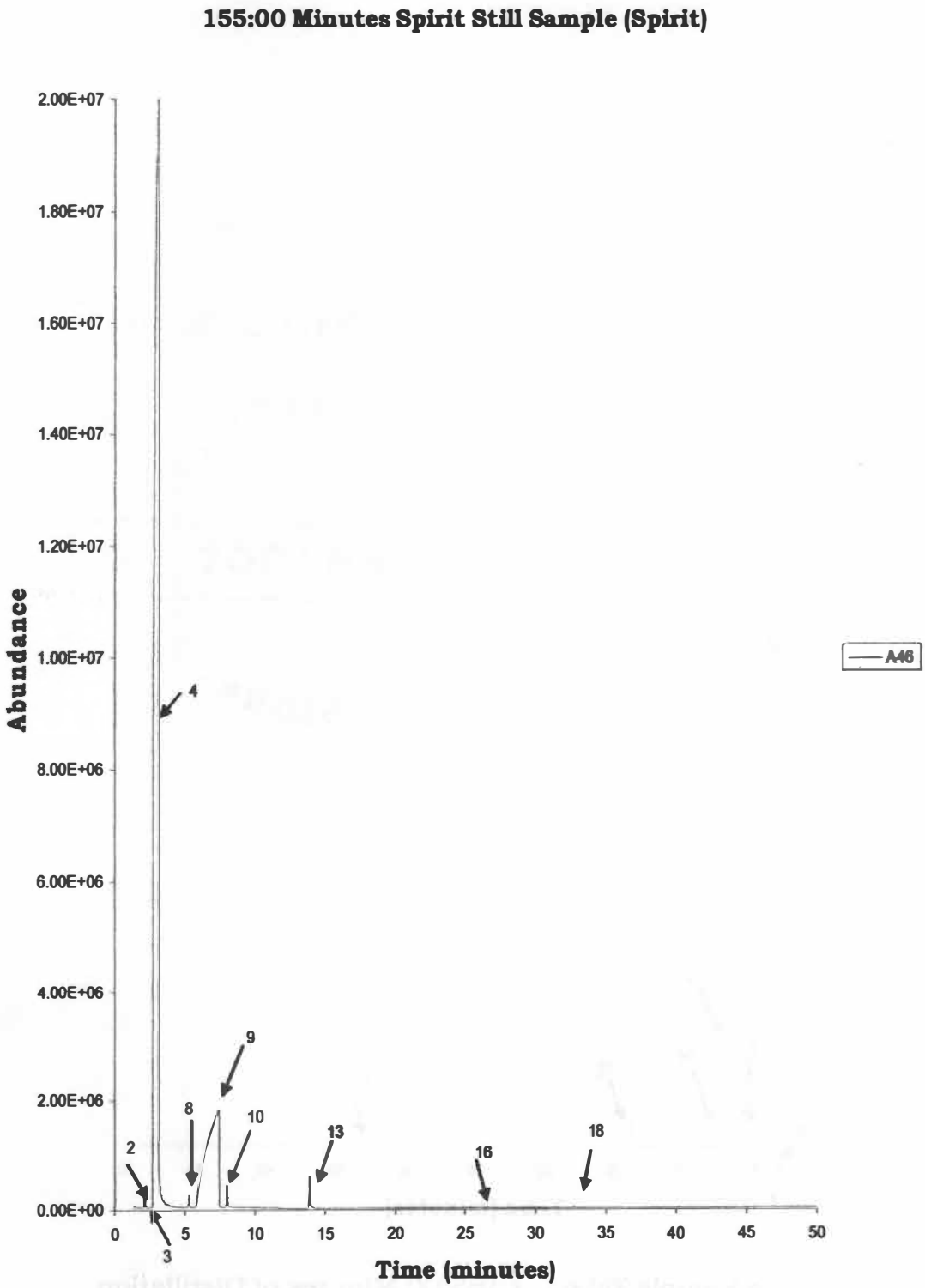

Figure 56: Spirit Sample Taken at 155:00 Minutes of Distillation

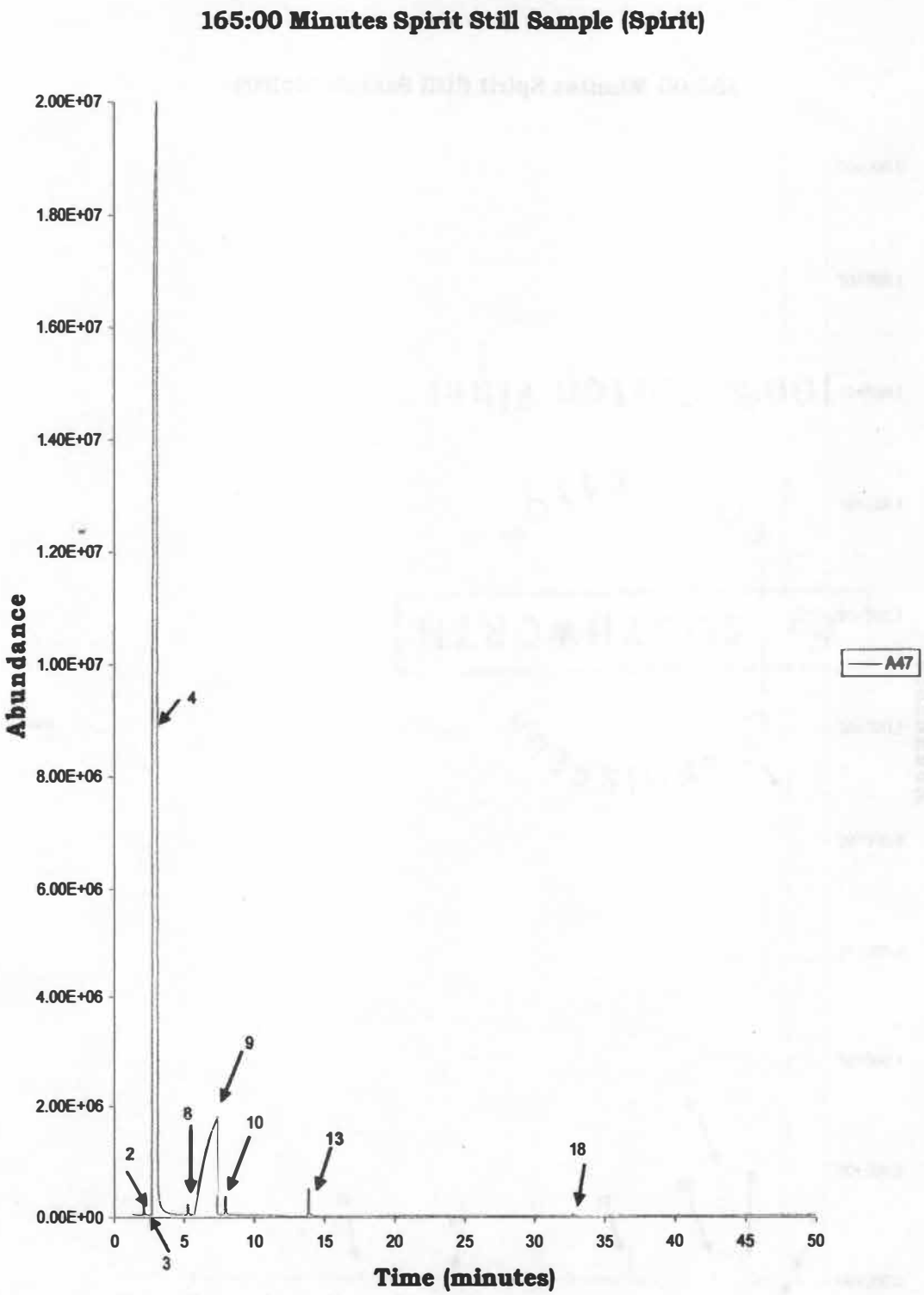

Figure 57: Spirit Sample Taken at 165:00 Minutes of Distillation

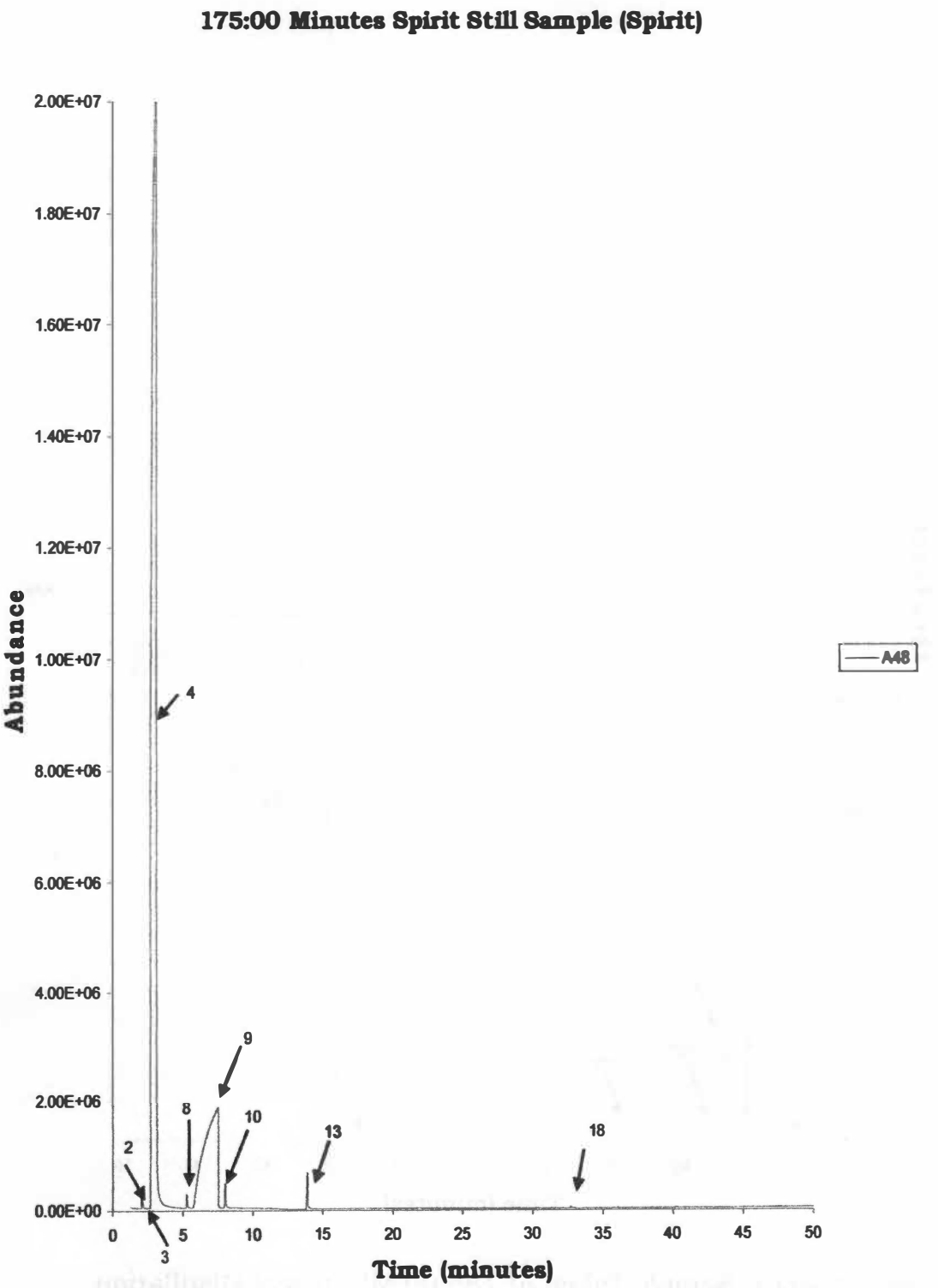

Figure 58: Spirit Sample Taken at 175:00 Minutes of Distillation

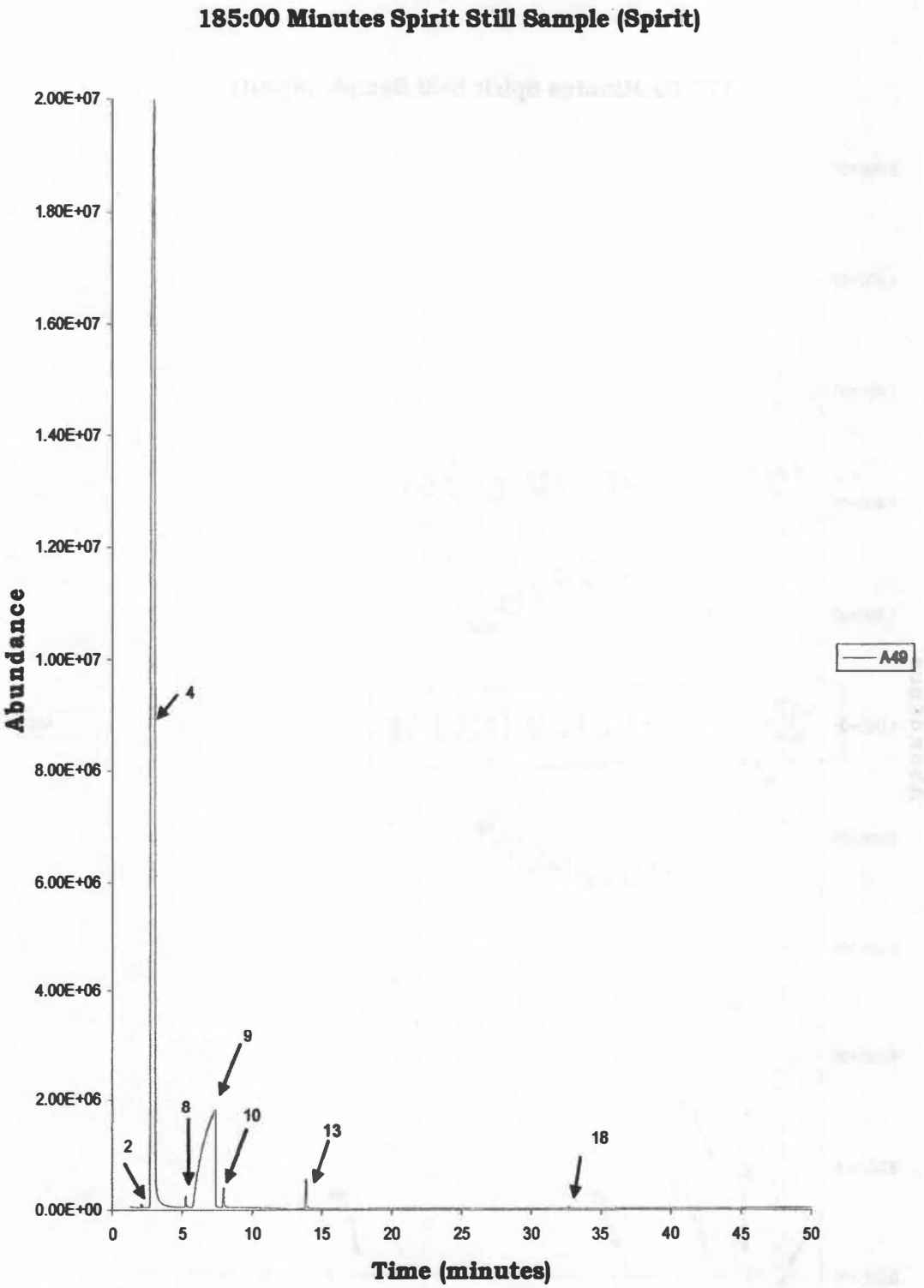

Figure 59: Spirit Sample Taken at 185:00 Minutes of Distillation

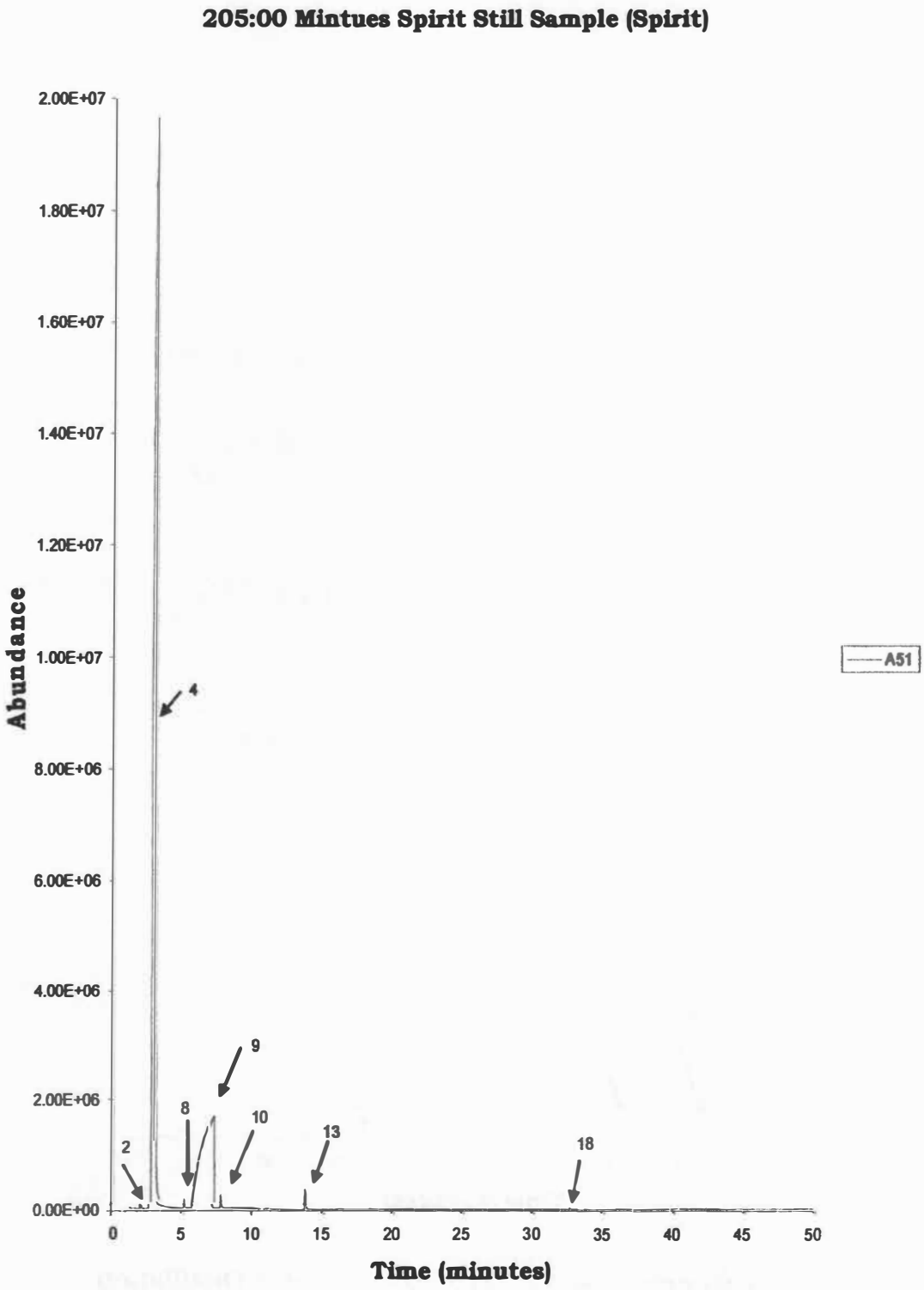

Figure 60: Spirit Sample Taken at 205:00 Minutes of Distillation

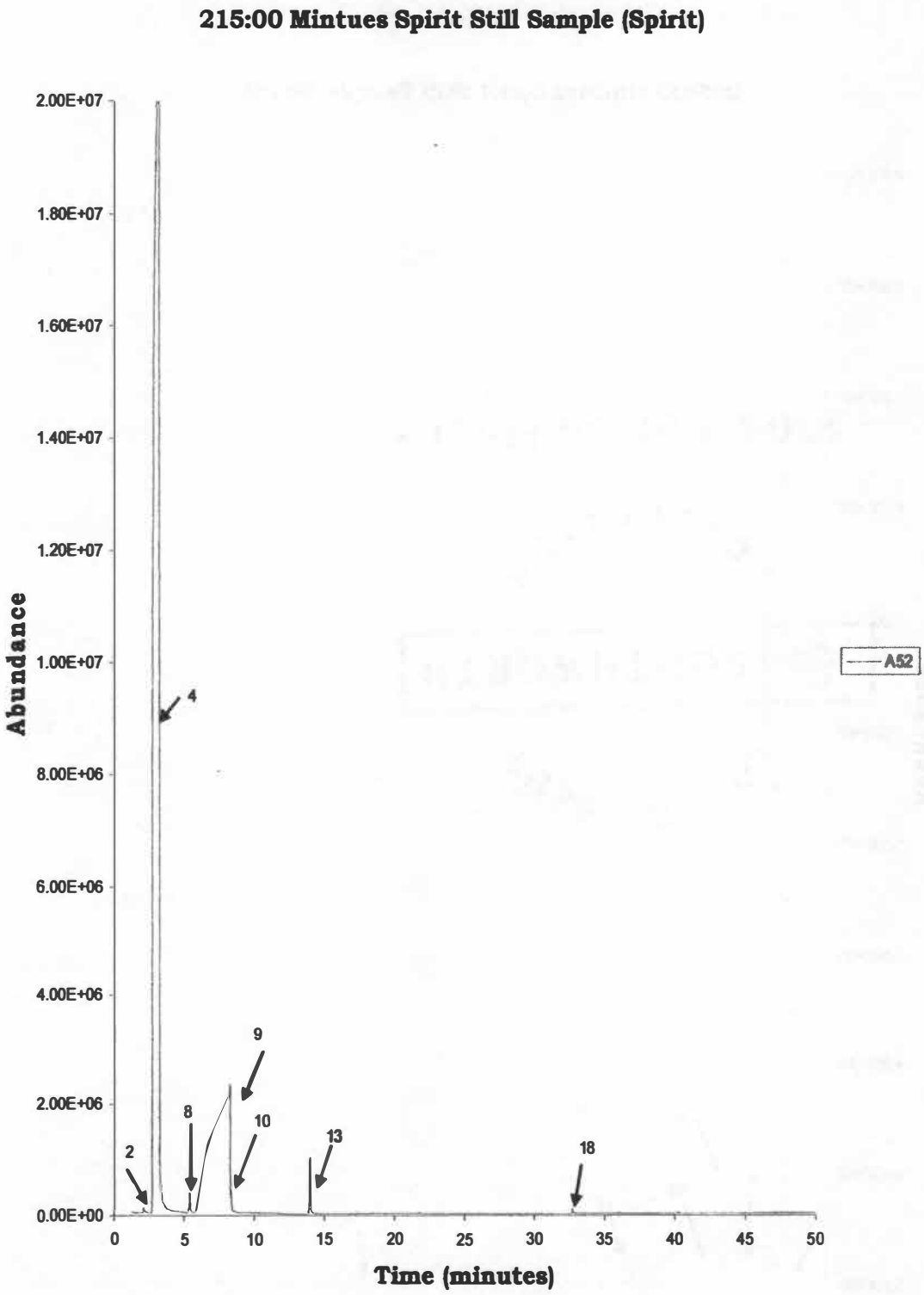

Figure 61: Spirit Sample Taken at 215:00 Minutes of Distillation

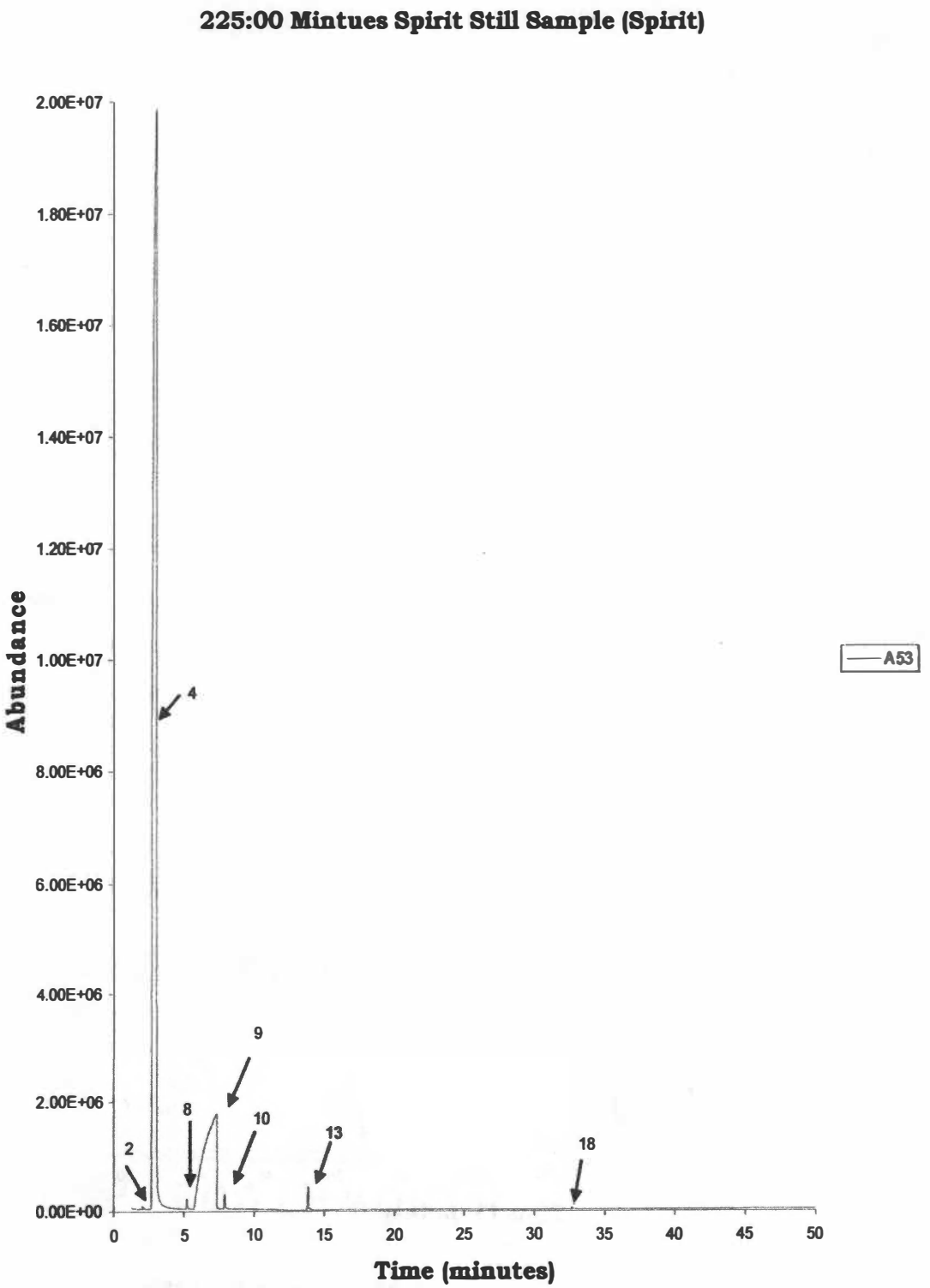

Figure 62: Spirit Sample Taken at 225:00 Minutes of Distillation

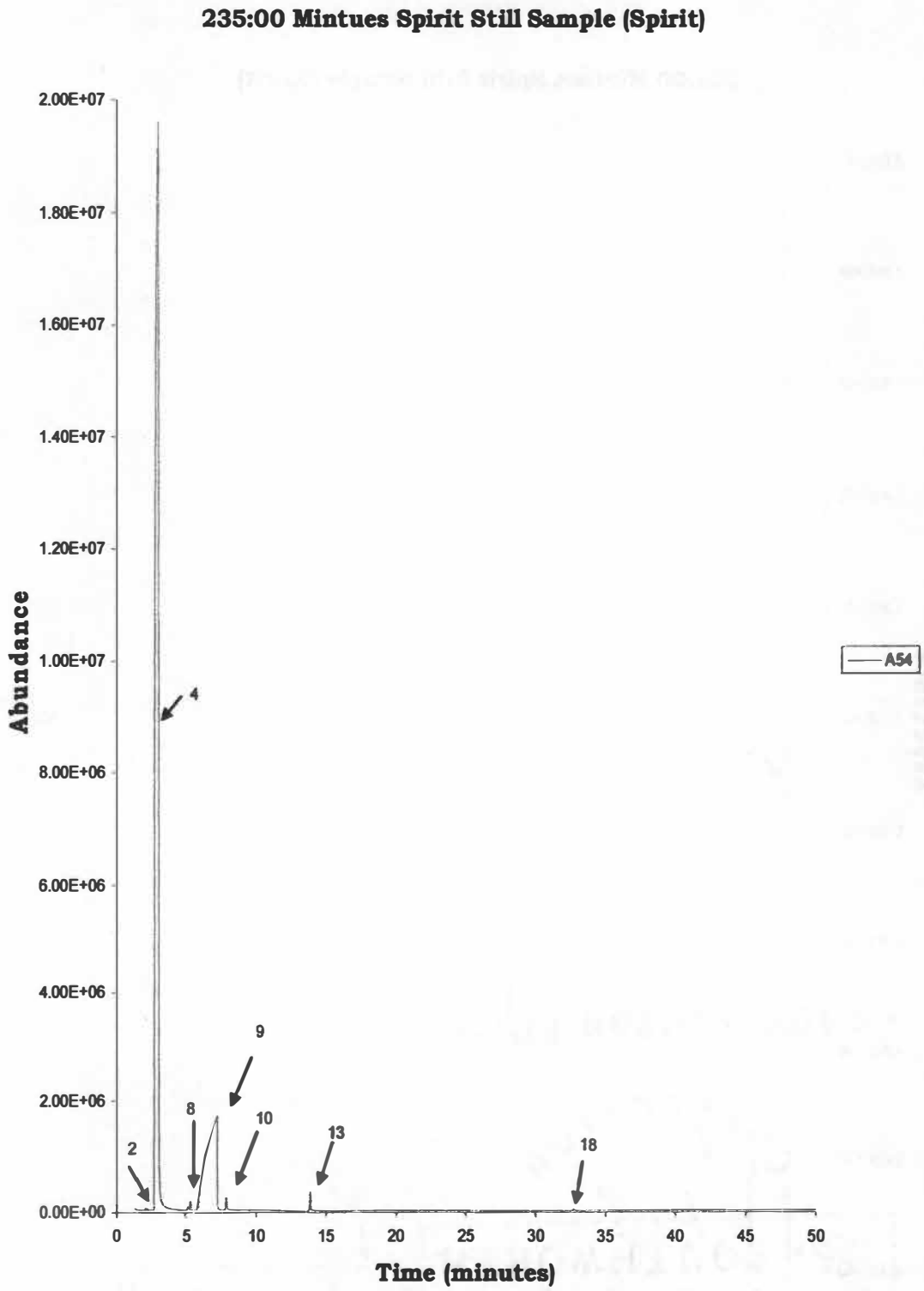

Figure 63: Spirit Sample Taken at 235:00 Minutes of Distillation

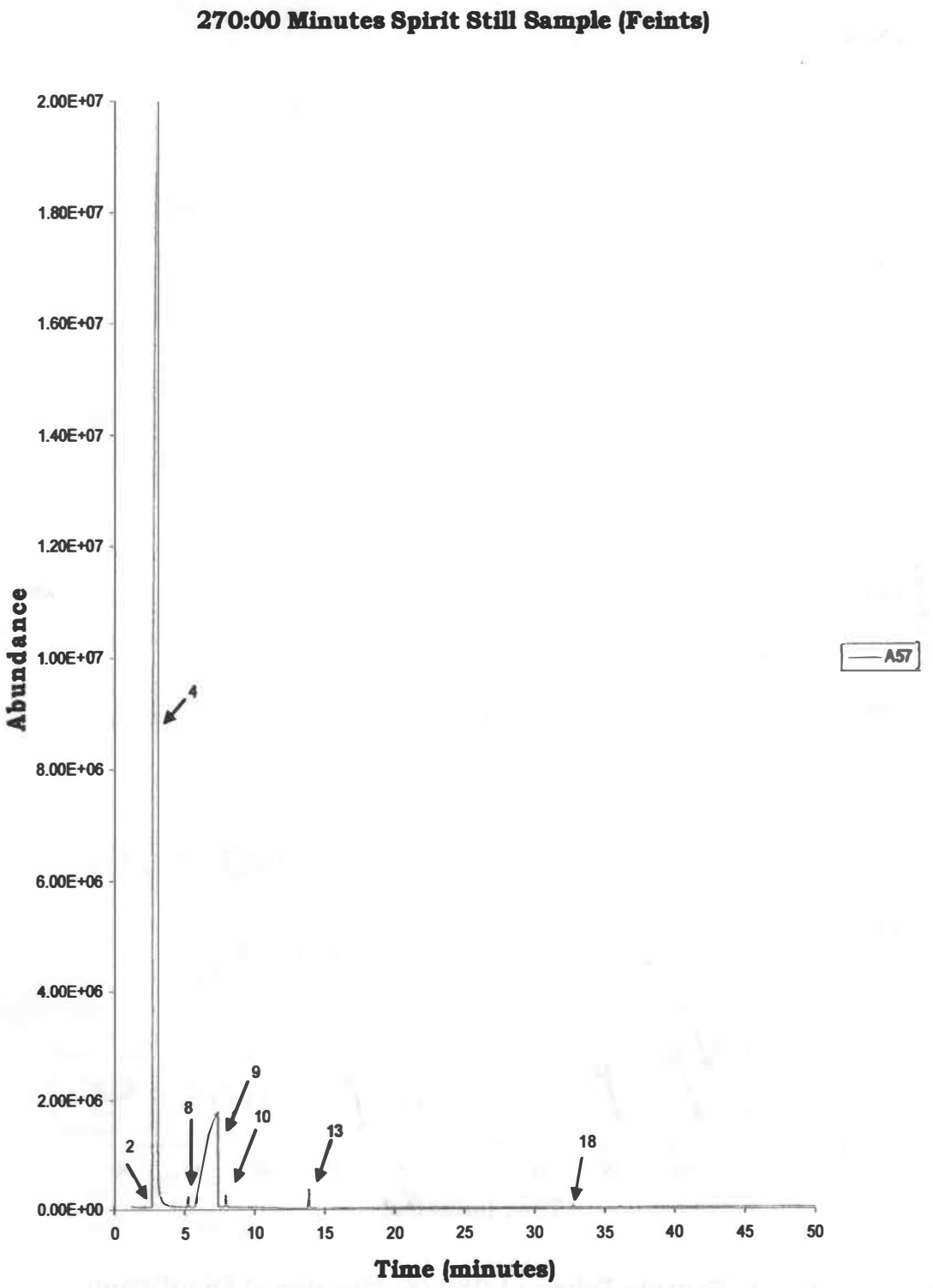

Figure 64: Feints Sample Taken at 270:00 Minutes of Distillation

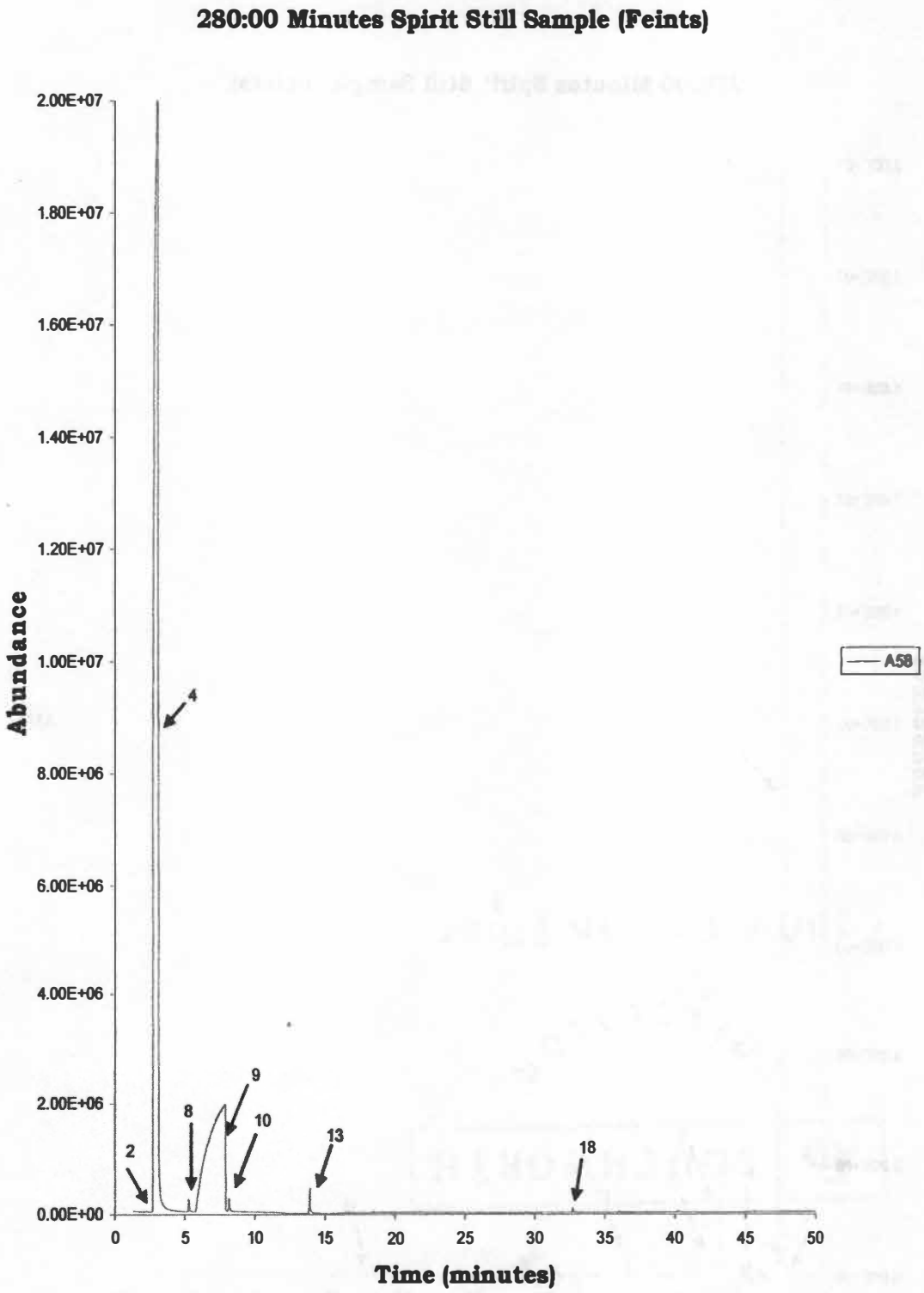

Figure 65: Feints Sample Taken at 280:00 Minutes of Distillation

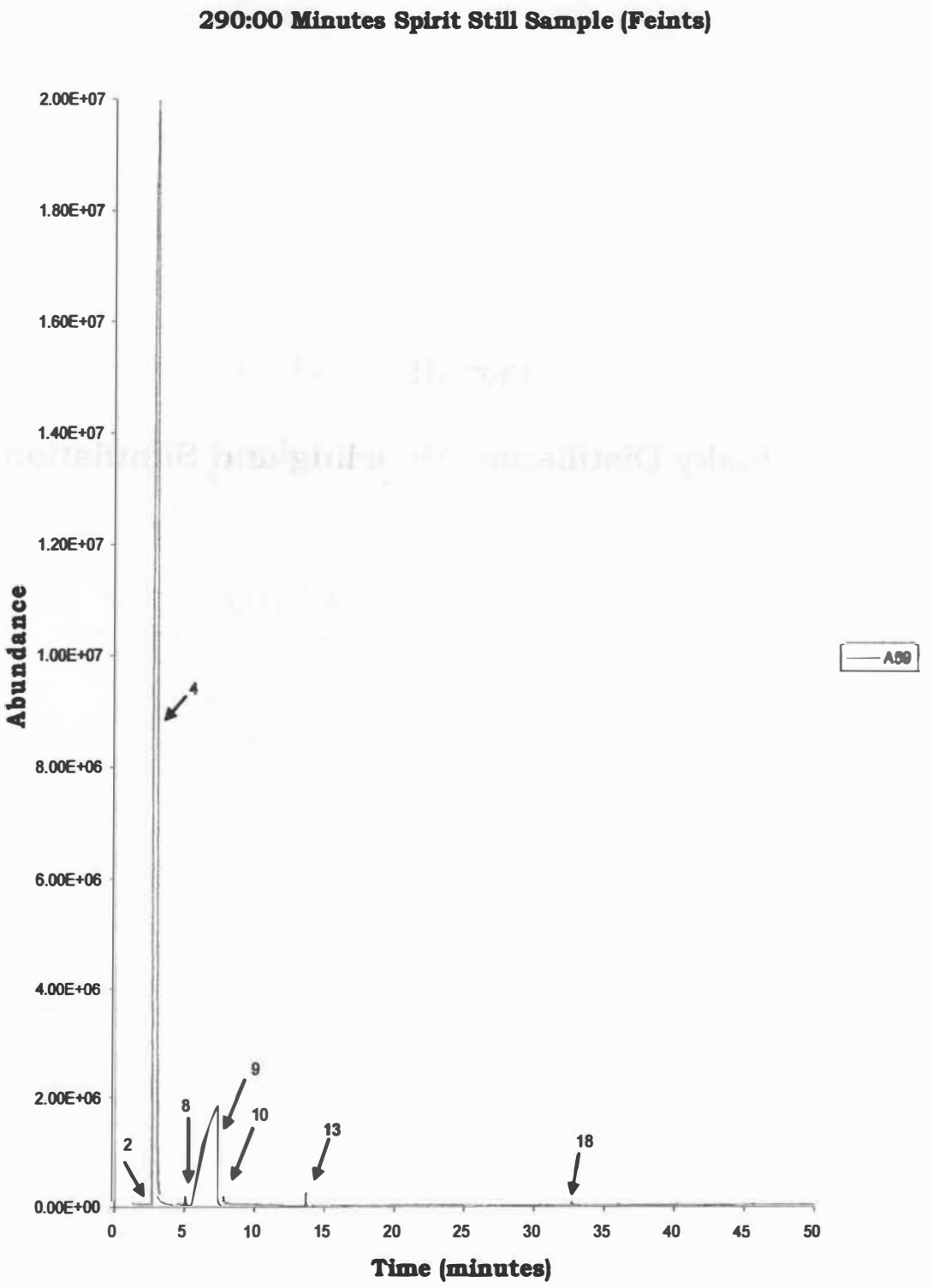

Figure 66: Feints Sample Taken at 290:00 Minutes of Distillation

Part III

Scotch Whisky Distillation Modeling and Simulation

Part III of this thesis is a copy of a paper by the same name to be submitted for publication in the Journal of Agricultural and Food Chemistry in 2004 by Ben Rogers, Charlie Moore, Samuel Morton, and John Collier. This article was written in its entirety by Ben Rogers. Charlie Moore contributed to the work as an advisor, consultant on the computer simulation software, and editor. Samuel Morton contributed in the literature search and as an editor. John Collier contributed as an advisor and editor. The authors reserved the right to publish this article in this thesis.

ABSTRACT

Scotch whisky is produced in a two step distillation process that has remained relatively unchanged for decades, even centuries. Much work has been done to analyze and study the final composition of different whiskies. However, to date little work has been published that studies the composition of the distillate with respect to distillation time. Samples collected during the distillation process were analyzed using gas-chromatography mass spectrometry to develop composition curves for several components found in whisky. The experimental data developed during the chemical analysis provided a physical basis for development of a process simulation. The simulation was done using the HYSYS® Simulation software. The batch distillation process was modeled using a tray distillation column with a large reboiler and low reflux. The simulation successfully modeled the experimental data for both the major and minor components. Simulation studies have also been able to produce suggestions for process improvements that could increase the economic yield of the distillery.

INTRODUCTION

The manufacture of whisky can be done in a number of different ways. Some bourbon such as Jack Daniels Tennessee Whiskey is made in a continuous distillation process, while other whiskies are made in a batch distillation process. Irish whiskies are produced in a series of three distillation steps. This work focuses on the Scottish process which is a two step distillation. Two major goals of this work are to develop a process simulation capable of reproducing experimental data collected from the operation of a Scotch whisky distillery and to determine if this can be accomplished using a tray distillation model to approximate the performance of a pot still.

Whisky production in Scotland has a long history that is kept alive by the many distilleries that have been in continuous, or near continuous, production for more than a century. Many distilleries have gone to a modernized production scheme leaving behind the traditional methods of manufacturing. Some distilleries have preserved the methods used to produce Scotch for a hundred years or more. Despite the vast difference in the approach and equipment used to produce the whisky the two systems are essentially the same. This is not true of grain distilleries which operate a continuous Coffey distillation. Distilleries of this type will not be addressed in this work. Figure 1 is a diagram of the production process from malting to aging.

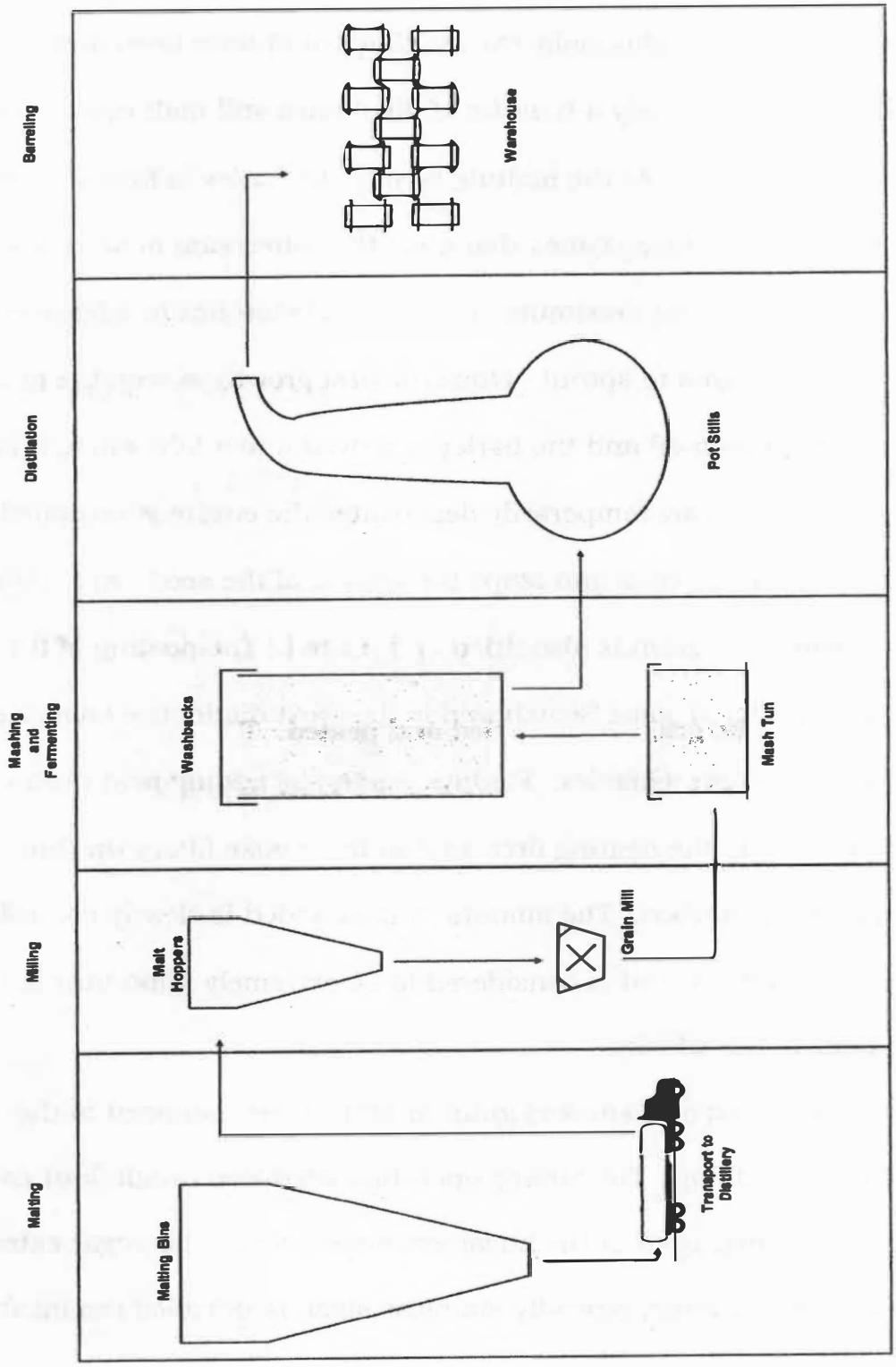

Figure 1: Production Process Diagram

The production of Scotch whisky is done exclusively with barley as the source for fermentable sugars. The barley is harvested and sent to a malting facility. Traditionally the malting would have been done at the distillery but today only a handful of distilleries still malt even a fraction of their total needs. At the malting facility the barley is first soaked in water to activate the enzymes that start the conversion of starches in the grain to sugars. The maximum conversion of starches to sugars occurs as the grain begins to sprout. Once the first growth is seen the grain shoots are broken off and the barley is moved into a kiln where it is heated. The heating temporarily deactivates the enzymes responsible for converting the starches and stops the growth of the seed. In addition to being heated the grain is also dried and peated. The peating of the barley is typical of some Scotch and is the most distinctive characteristic of some particular whiskies. Peating is done by adding peat during the initial kilning to the heating fires so that the smoke filters up through the grain and is absorbed. The amount of peat added is closely controlled by the malting facility and is considered to be extremely important in the final taste of the whisky.

The heated and smoked grain or malt is then shipped to the distillery for milling. The milling operation produces rough flour called grist that is then used in the sugar extraction step. The sugar extraction takes place in a large, typically stainless steel, tank called the mash tun

that is equipped with a mixer. Traditional distilleries often have crawling or crab mixers while modern distilleries often have stirring arm mixers. The sugar extraction is performed by washing the flour with hot water three or four times to extract as much sugar as possible. The first two washes are relatively high in sugar content and are sent over to the washbacks for fermentation. The second two washes are too low in sugar to be fermented economically so they are recycled and used as the first two washes for the next batch of grist. The remaining material in the mash tun, the draff, is typically sold for animal feed as it has been almost completely leached of fermentable sugar but still has value as feed. The sugar water or worts from the mash tun are pumped through a heat exchanger to cool them and then stored in a large vat or washback. The washback is the reaction vessel where fermentation takes place.

Washbacks are large tanks made of either Oregon pine or stainless steel where the fermentation takes place. The worts are pumped into the washback and yeast is added and allowed to ferment for up to 3 days. Two kinds of yeast are typically used in the fermentation; distiller's yeast and brewer's yeast. Brewer's yeast is quick to begin conversion of sugar to ethanol but does not perform well in high alcohol concentration. Distiller's yeast is slow in the early stages but performs much better in high alcohol environments. Distillers typically use both kinds of yeast during fermentation.

Alcohol is produced during the fermentation by yeast converting sugars to ethanol and carbon dioxide. After the malting process most of the barley starch has been converted to sugars that are fermentable. Equation 1 shows a typical reaction of glucose to ethanol and carbon dioxide in the anaerobic state. [1]

(1) $C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$

The reaction in Equation 1 shows the mechanism responsible for the production of the ethanol. The fermented mixture or beer has a maximum alcohol content of roughly 18% ethanol. The yeast used to ferment the sugars will not produce any more ethanol at those concentrations. The simplified reaction predicts only ethanol and CO2 as products of the fermentation. In reality, several alcohols are produced along with other esters, ketones, and acids. The ethanol is significantly preferred in the conversion but the other components are present and are important to the flavor of the final product. [2-4]

The reaction shows that ethanol and CO_2 are produced in equal molar amounts from the fermented sugars. The CO_2 produced bubbles up through the mixture and can produce foam on the top of the fermenting liquid. The foam is knocked down either with a defoaming agent or with mechanical action such as a rotating bar. The CO_2 that is produced typically is vented to the atmosphere although at large scale distilleries recovery and purification can be profitable.

The resulting mixture of water, yeast, alcohols, minor components, and whatever fraction of sugar remains is called the beer and is pumped into the wash still for the first distillation. The wash still is simply the first distillation vessel. It is used to concentrate the alcohol to a point where subsequent distillation will yield the desired spirit. After distillation in the wash still the distillate is sent to a holding tank where it mixes with the first and third spirit cuts from the spirit still. The mixture of newly distilled wash and recycled spirit it then fed into the spirit still for distillation. The unused spirit is recycled to increase alcohol recovery, the single most important factor in the profitability of the distillery. The spirit still distillation is split into three separate phases. The first phase comprises roughly the first third of the distillation and is called the foreshots. It is the portion of the distillation highest in alcohol content and is recycled to the low wines and spirit receiver. The second phase of the distillation is the spirit cut and comprises roughly the middle third of the distillation. The spirit cut is sent to the barreling vat where it will be held until the spirit is casked and sent to the warehouse for storage and aging. The final third of the distillation is the feints and is also recycled to the low wines and spirits receiver.

The use of pot stills is the most characteristic aspect of the Scotch malt production. Every malt distillery in Scotland operates batch

distillation in pot stills. Individual distillers often patent the design of their pot stills to protect the specific manufacturing process they use.

After the spirit cut from the spirit still has been collected it is pumped over to the barreling facility. In the barreling process the spirit is placed into previously used casks. Used casks are preferred because new oak would overpower the flavors found in scotch. Bourbon casks from the United States are used since Kentucky law requires bourbon to be aged in new oak casks. Other types of casks that are used are sherry, port, madeira, rum, and cognac although rum and cognac have only recently been used.

The spirit, once placed in the cask, is left there for a minimum of three years. Scottish law requires that scotch be aged at least three years in Scotland to be considered authentic. Typically the spirit will be aged a minimum of 8 years to be considered for bottling as a single malt. If the malt is to be used for blending it may not be aged as long in the warehouses. As the spirit ages in the casks the ethanol content slowly decreases at about .8%/yr and the total volume decreases by about 2%/yr. This effect, sometimes referred to as the angel's share, increases the cost of aging the whisky beyond the cost of merely storing the casks. By common consensus the longer the malt is aged the better it becomes. However, it is uncommon to see single malts older than 25 years because the positive effect of aging virtually vanishes after that length of time.

Further explanation of each step of the production process is available in the literature. [5]

This work will use experimentally derived information about a malt distillation process to evaluate the feasibility of a computer simulation that correctly models the whisky production process. Computer simulations of continuous whisky distillation processes have been successful but little work has been done on simulation of batch processes. [6] This computer simulation of a batch process will utilize a tray column approximation of the pot still. The aim is to be able to propose process improvements based on our ability to simulate a wide range of operating conditions.

MATERIALS AND METHODS

The experimental basis for this study comes from the prior work of Rogers et al. [7] The work develops experimental data from a single production run of a traditional scotch whisky distillery. The data developed in the work included concentration values for ethanol, water, and some minor components. These values were of particular use in this work. The work provides the simulation targets for evaluating simulation accuracy. However, the work does not include an experimentally determined set of initial feed conditions.

The computer tools used for this work were HYSYS v3.0.1 (Build 4602) by Hyprotech Ltd. The software was used to simulate both the initial steady state and dynamic modes of operation. The HYSYS help documentation was used extensively as a source for simulation guidance and troubleshooting. [8] HYSYS was run on a Windows XP machine. Based on information collected from the distillery in Scotland a preliminary distillation design was developed. The fluid modeling package used for this simulation was selected based on the available literature for ethanol-water binary mixtures. [9-10] The Non-Random Two Liquid property package was selected for use in this model. The components included in the simulation based on experimental evidence and literature review were water, ethanol, 1-propanol, 2-methyl-1-butanol, isoamyl alcohol, and ethyl acetate. Unknown binary interaction

parameters were estimated using the UNIFAC VLE estimation method provided in the software package.

A pot still is a batch distillation vessel that is steam heated to precipitate the boiling of the mixture. HYSYS does not have a predefined batch distillation unit so it was necessary to approximate such a process with the available unit operations. It was decided to simulate the pot still with a trayed distillation tower using a large reboiler and a small rectifying section.

Pot stills used in the production of Scotch whisky have specially designed geometries that are often patented. The geometry of the still affects the heat transfer from the vessel to the surroundings and also affects the reflux of the vessel. The batch distillation vessels do not have a reflux stream from the condenser so the only reflux is from condensation at the walls of the vessel. To approximate the internal reflux of the pot stills the reflux from the condenser of the tray tower was adjusted.

Using the steady state solver the initial condition of the pot still was solved to approximate the values determined in the experimental analysis of the distillate in Rogers et al. [6] The initial conditions of the dynamic model were determined by trial and error analysis of the steady state solution. Flow valves and process controllers were added to allow the dynamic simulation of the model from the initial conditions

determined by the steady state model. The dynamic model was then tuned to reproduce the experimental data as nearly as possible. The tuning was done on only a few variables in order to maintain consistency with the actual operation of the process. The manipulated variables were reflux ratio and heat added to the reboiler.

RESULTS AND DISCUSSION

The first process to be simulated was the wash still. The wash still model along with the experimental data was being used to predict the feed composition to the spirit still.

Wash Still Feed Conditions. The initial composition of the weak beer in the wash still is the most important variable in the distillation process. There was no experimental basis for predicting the beer composition at the start of the distillation process. It was therefore necessary to determine the feed composition by trial and error. In order to consider the model successful it had to reasonably predict the composition of the distillate at each point in time. As discussed by Rogers et al. [6] the ethanol concentration of the first data point from the analysis of the wash still distillate is probably inaccurate due to water remaining in the condenser or pipes between runs. Because the first data point was likely to be inaccurate it was determined that it was more important to fit the second data point than the first for the feed conditions. This also held true for the minor components. The feed compositions were altered systematically until the predicted compositions from the steady state model were reached. The final distillable feed compositions are shown in Table 1.

Table 1 - Wash Still Feed Composition

Feed Composition	
Compound	% by vol
Ethanol	14.000
Water	83.725
Ethyl Acetate + Acetal	0.900
1-Propanol	0.125
2-M-1-Butanol	0.250
Isoamyl Alcohol	1.000

The wash still configuration is shown in Figure 2. As shown the model of the process included a tray distillation column with a partial condenser, a storage tank for the distillate, and four PI controllers. The controllers are designed to control the condenser level and pressure, the reboiler level, and the charging tank pressure. The reboiler level is controlled to ensure that bottoms flow is zero during the distillation simulation. The condenser pressure and level and the charging tank pressure are controlled to maintain dynamic stability. The controllers do not significantly affect the model aside from maintaining numerical stability during the simulation.

Wash Still Model Ethanol Tuning. The first decision that was made was to tune the model to accurately reflect the ethanol composition profile. Ethanol is the species of interest and it was therefore determined that ethanol was the most important variable for the model.

The first attempt to model the system was done with a constant flux of heat into the reboiler. Constant heat flux is different from the

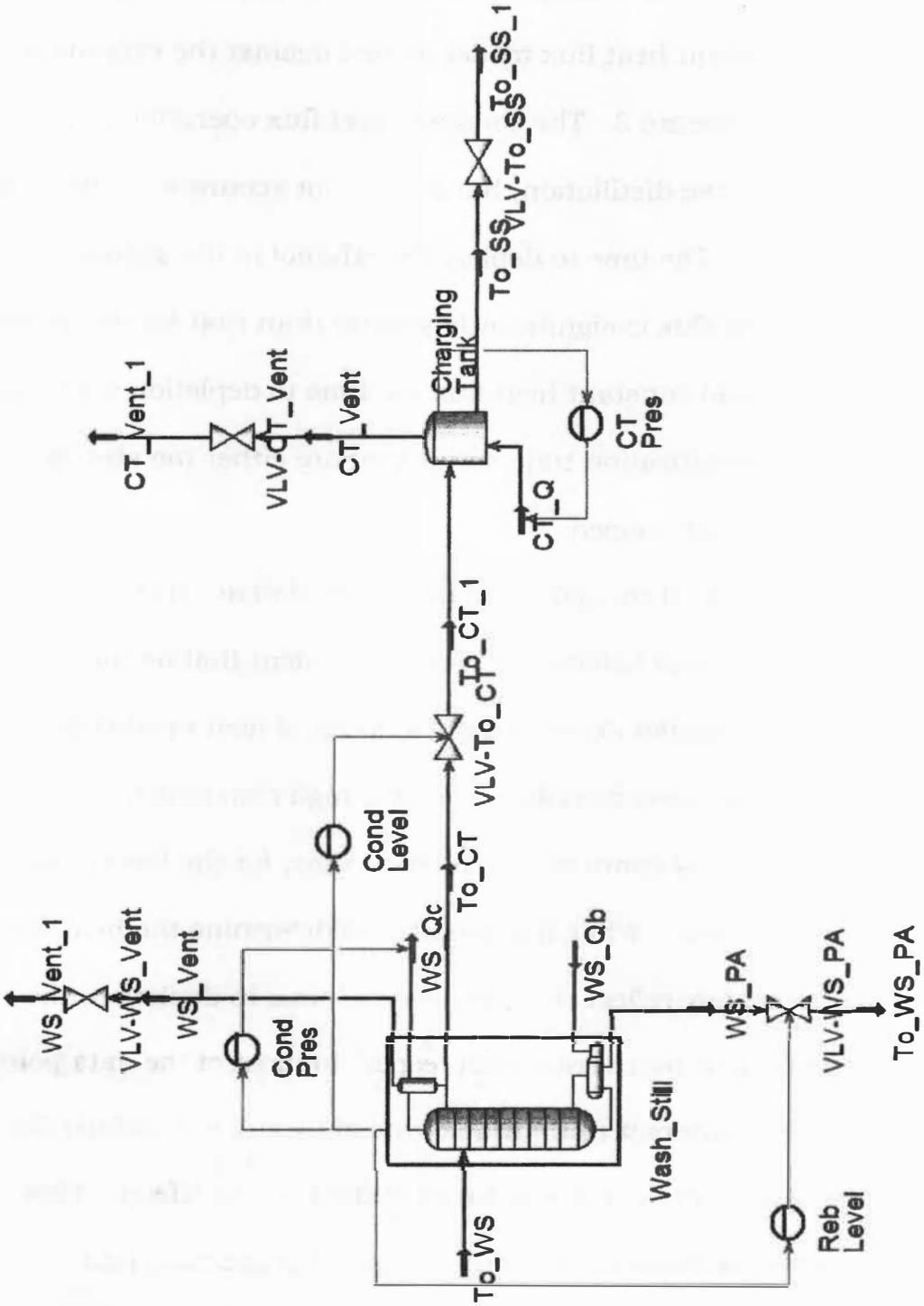

Figure 2: Wash Still Simulation Schematic

normal operation of the distillery but was simulated to gain a rough approximation of the wash still performance. The ethanol concentration results of the constant heat flux model plotted against the experimental data are shown in Figure 3. The constant heat flux operation mimics the overall behavior of the distillation, but it does not accurately reflect the experimental data. The time to deplete the ethanol in the system for a large constant heat flux is significantly shorter than that for the actual process. For a small constant heat flux the time to depletion is too short. This results in concentration trajectories that are either too steeply sloped or too shallowly sloped.

This is a result of the nature of batch distillation. If you consider the energy and material balances it becomes evident that as the amount of material in the reboiler decreases the amount of heat needed to boil the remaining liquid also decreases. For the high constant heat flux model this results in a shortened distillation time, for the low constant heat flux a longer time. While it is possible to determine the heat flux that would accurately reflect the experimental time to depletion, the model is significantly inaccurate with respect to most of the data points. One method to counteract this variable rate of boiling is to adjust the reflux of the system in such a way to offset the heating effects. This solution however is inconsistent with the actual production and mechanisms of the process. It therefore was not attempted.

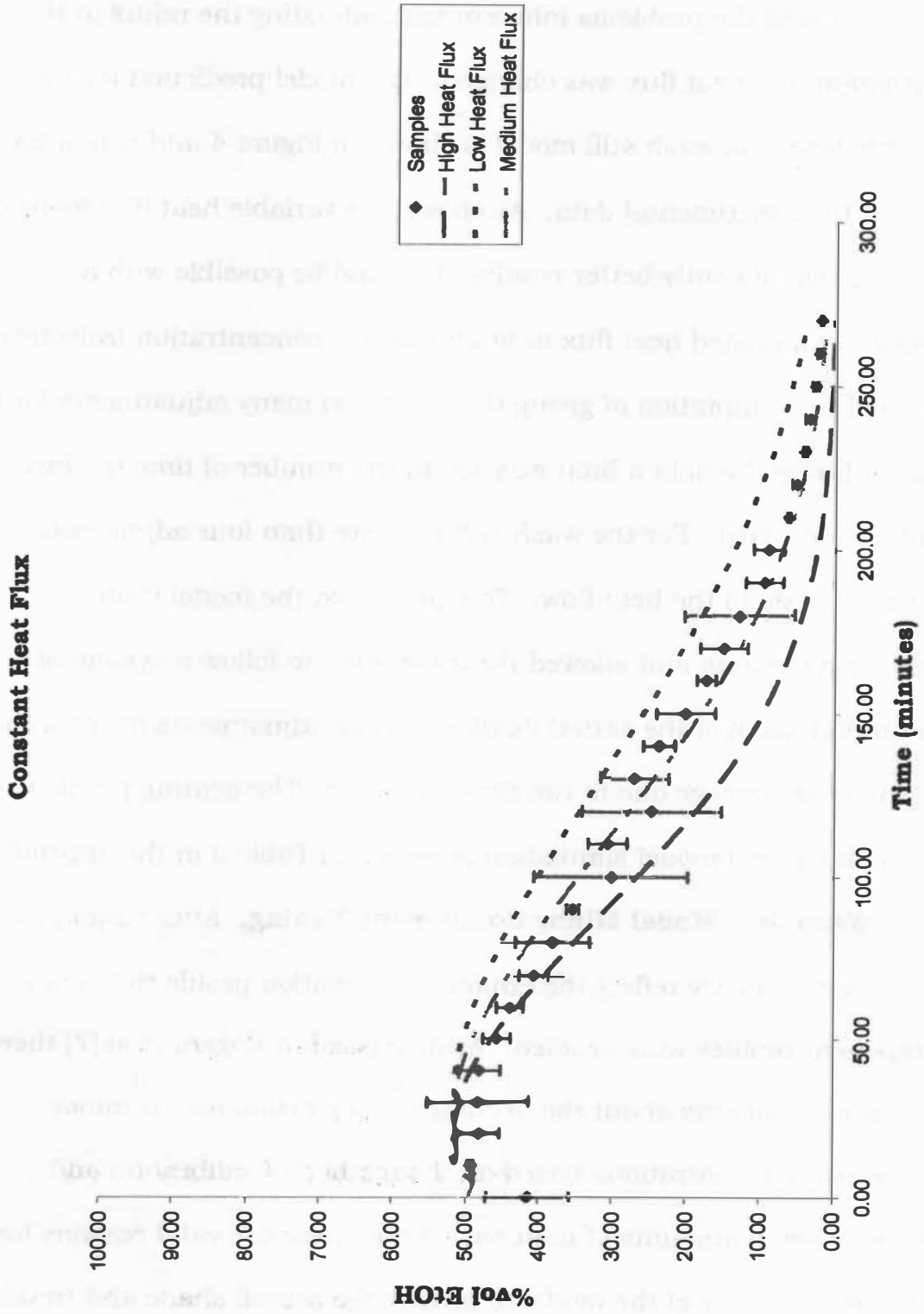

Figure 3: Constant Heat Flux Simulations of Wash Still

To avoid the problems inherent with adjusting the reflux in the simulation, the heat flux was changed. The model prediction for the variable heat flux wash still model is shown in Figure 4 and is plotted against the experimental data. As shown the variable heat flux method produces significantly better results. It would be possible with a constantly adjusted heat flux to fit almost any concentration trajectory. To avoid the temptation of giving the model too many adjustments for the sake of fitting the data a limit was set on the number of time the heat could be adjusted. For the wash still no more than four adjustments could be made to the heat flow. This prevented the model from overfitting the data and allowed the simulation to follow a system of operation typical of the actual distillery where adjustments to the steam are made on average one to two times an hour. The heating profile used for the wash still model simulation is shown in Table 3 in the appendix.

Wash Still Model Minor Component Tuning. After tuning the model to accurately reflect the ethanol composition profile the minor component profiles were studied. As discussed in Rogers et al [7] there were some concerns about the accuracy of the estimates for minor component concentrations based on the method of calibration and relatively small amounts of material. While these are valid reasons for concern the ability of the model to predict the overall shape and trends

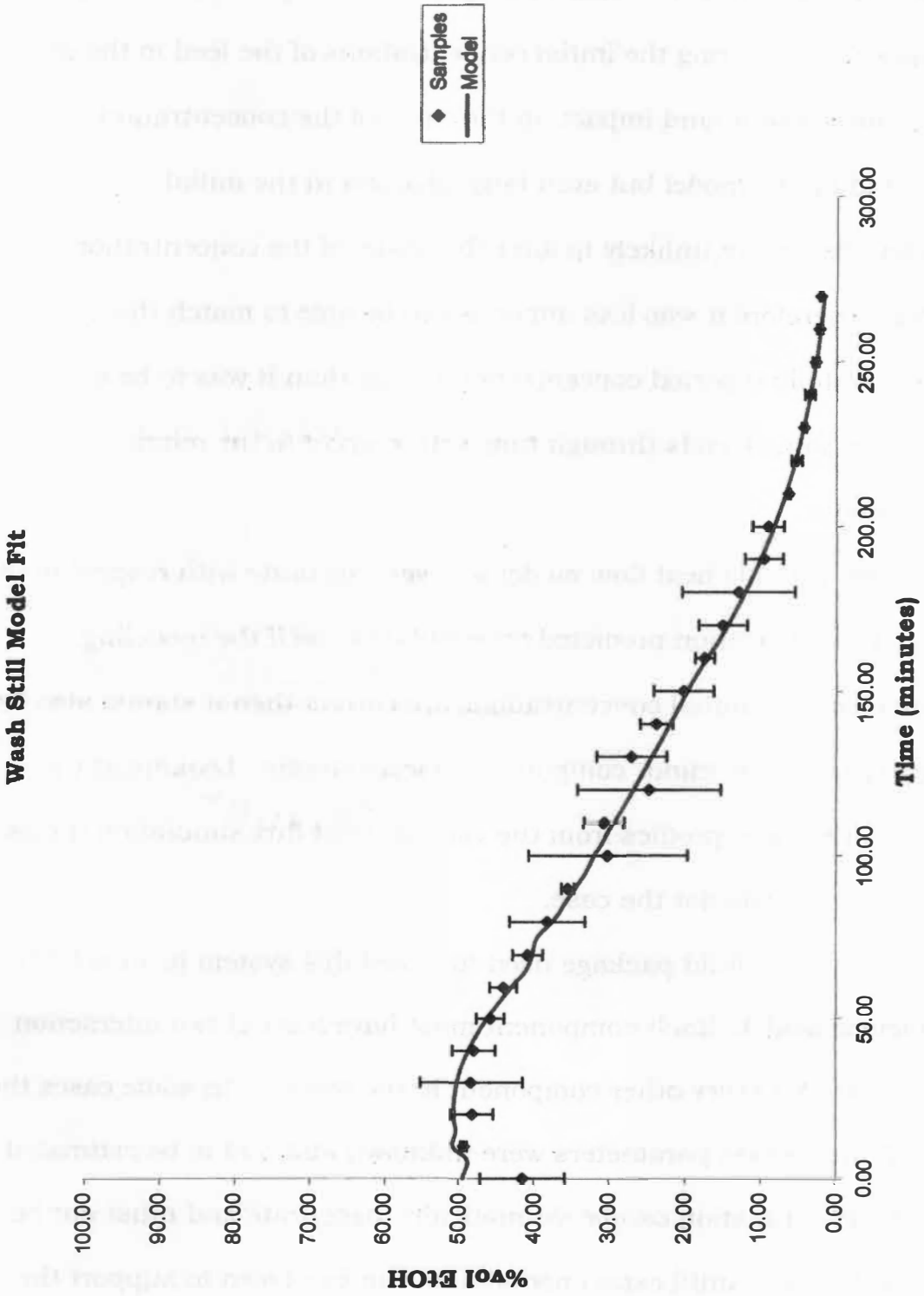

Figure 4: Experimental Data with Variable Heat Flux Simulation

observed in the minor component profiles was determined to be a reliable measure of the model's ability to accurately simulate the minor components. Altering the initial concentrations of the feed to the still would have a profound impact on the value of the concentration predicted by the model but even large changes in the initial concentrations are unlikely to alter the shape of the concentration profile. Therefore it was less important to be able to match the experimentally reported concentration values than it was to be able to follow the same trends through time with respect to the minor components.

The variable heat flow model was very accurate with respect to the ethanol concentration predicted by simulation, so if the modeling parameters and initial concentrations are correct then it should also be able to predict the minor component concentrations. Looking at the minor component profiles from the variable heat flux simulation it was apparent this was not the case.

The NRTL fluid package used to model this system is an activity coefficient model. Each component must have a set of two interaction parameters for every other component in the system. In some cases the HYSYS interaction parameters were unknown and had to be estimated. Parameter estimation can be dramatically inaccurate and must not be accepted as true until experimental data can be shown to support the

estimation. [11-12] The estimated parameters were insufficient to accurately model the behavior of the wash still system. The minor component concentration profiles did not reflect the overall trend in the experimental data. Figures 5-8 show the results of the original interaction parameters compared with the results of the adjusted interaction parameters. Again it is important to note that the actual concentration values of the minor components are less important to the quality of the model than the overall shape of the curve. With better chemical analysis of the minor components accurate concentration values can be obtained and the current model adjusted accordingly.

Final Wash Still Model. The final wash still model accurately predicts the composition profile of the ethanol and gives the correct shape for each of the minor components. The model was a success based on its ability to meet both of the stated criteria. Using the results of the wash still simulation the spirit still was undertaken.

Spirit Still Simulation. The operation of the spirit still is very similar to that of the wash still. Figure 9 shows the simulation schematic. The spirit still feed is taken from the low wines and feints receiver. This means that the feed to each run of the spirit still is related to the recycled distillate from the sprit still. Modeling the spirit still therefore required a sample from the low wines and feints receiver (LWFR). A sample was taken and analyzed. Comparing the sample from

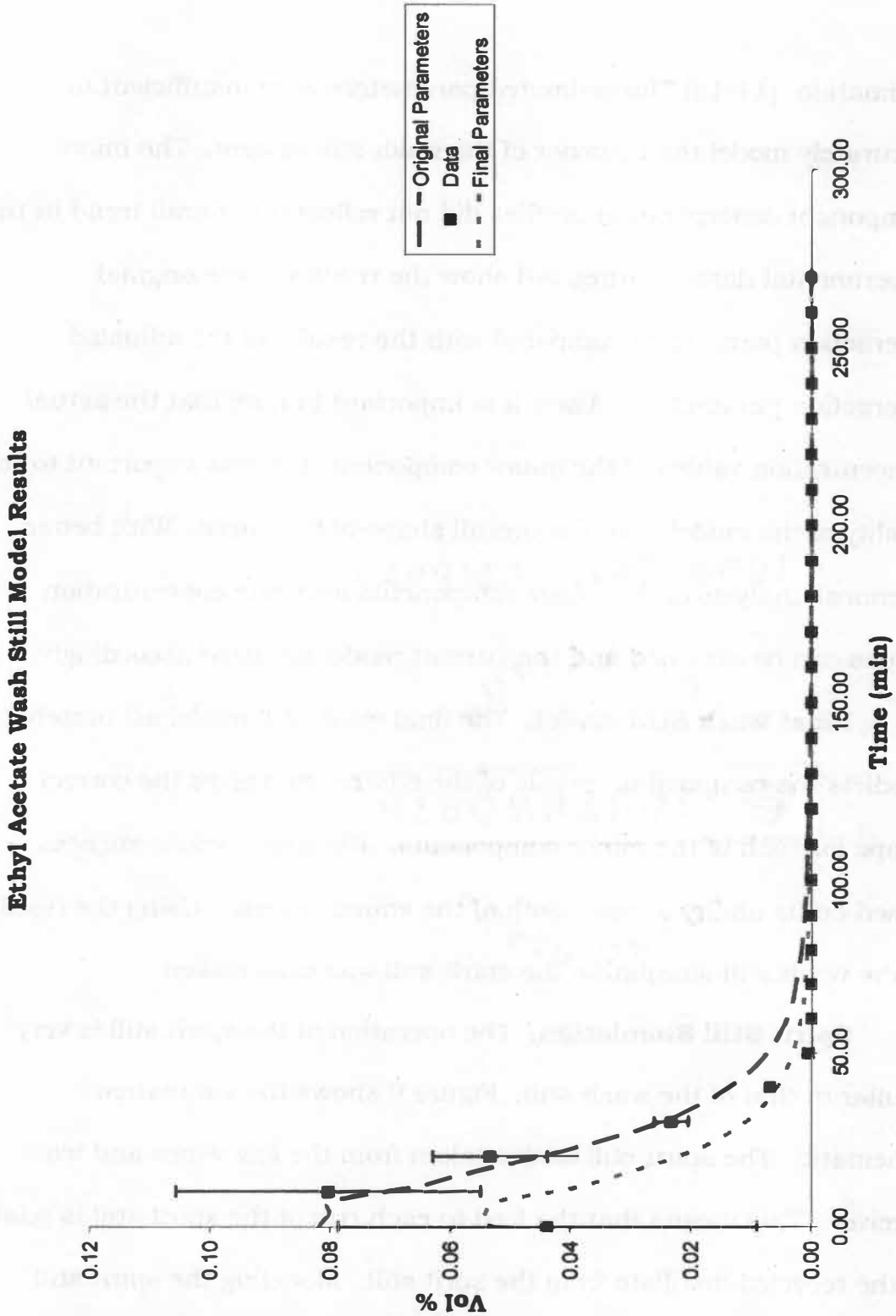

Figure 5: Interaction Parameter Adjustment for Ethyl Acetate

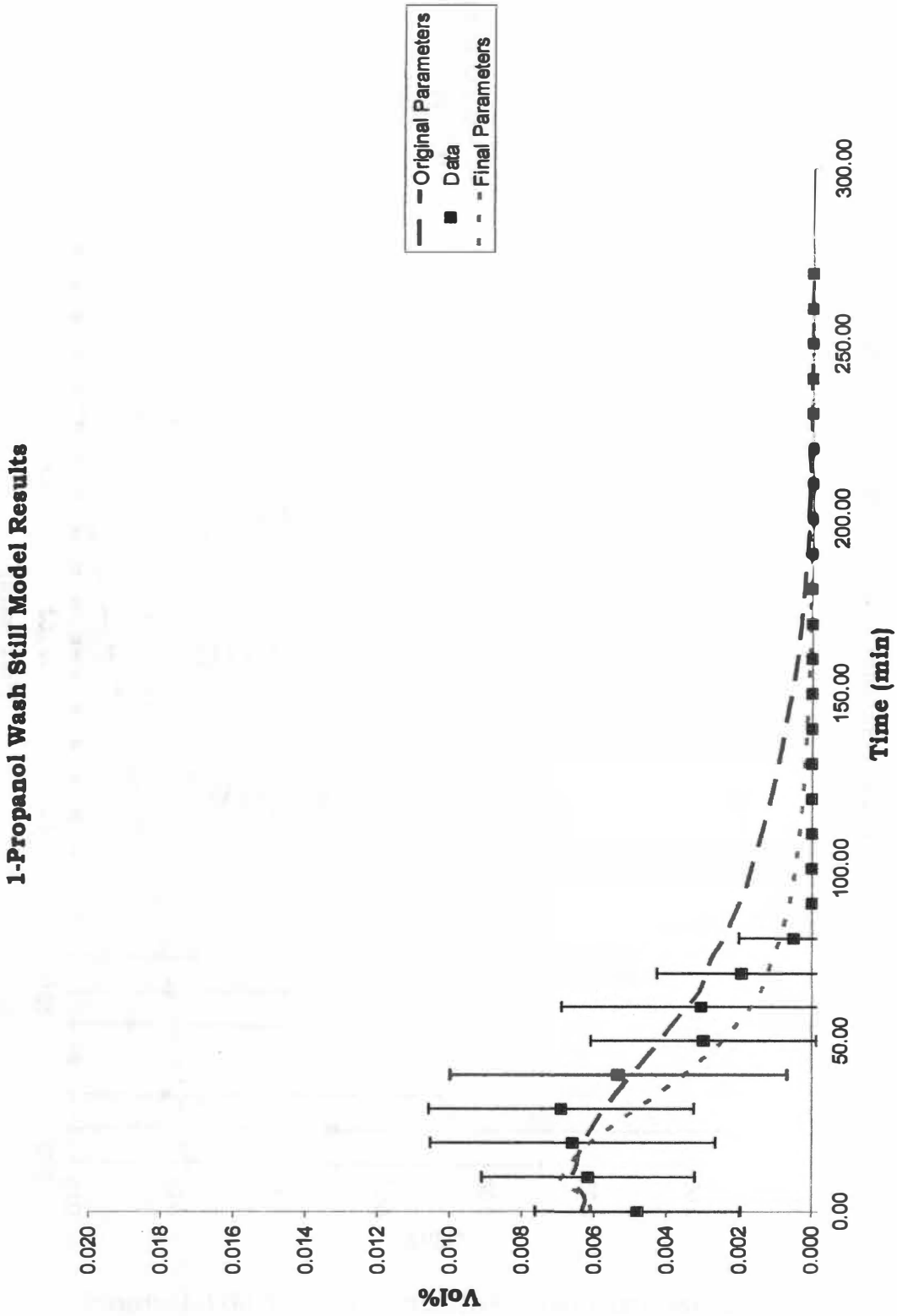

Figure 6: Interaction Parameter Adjustments for 1-Propanol

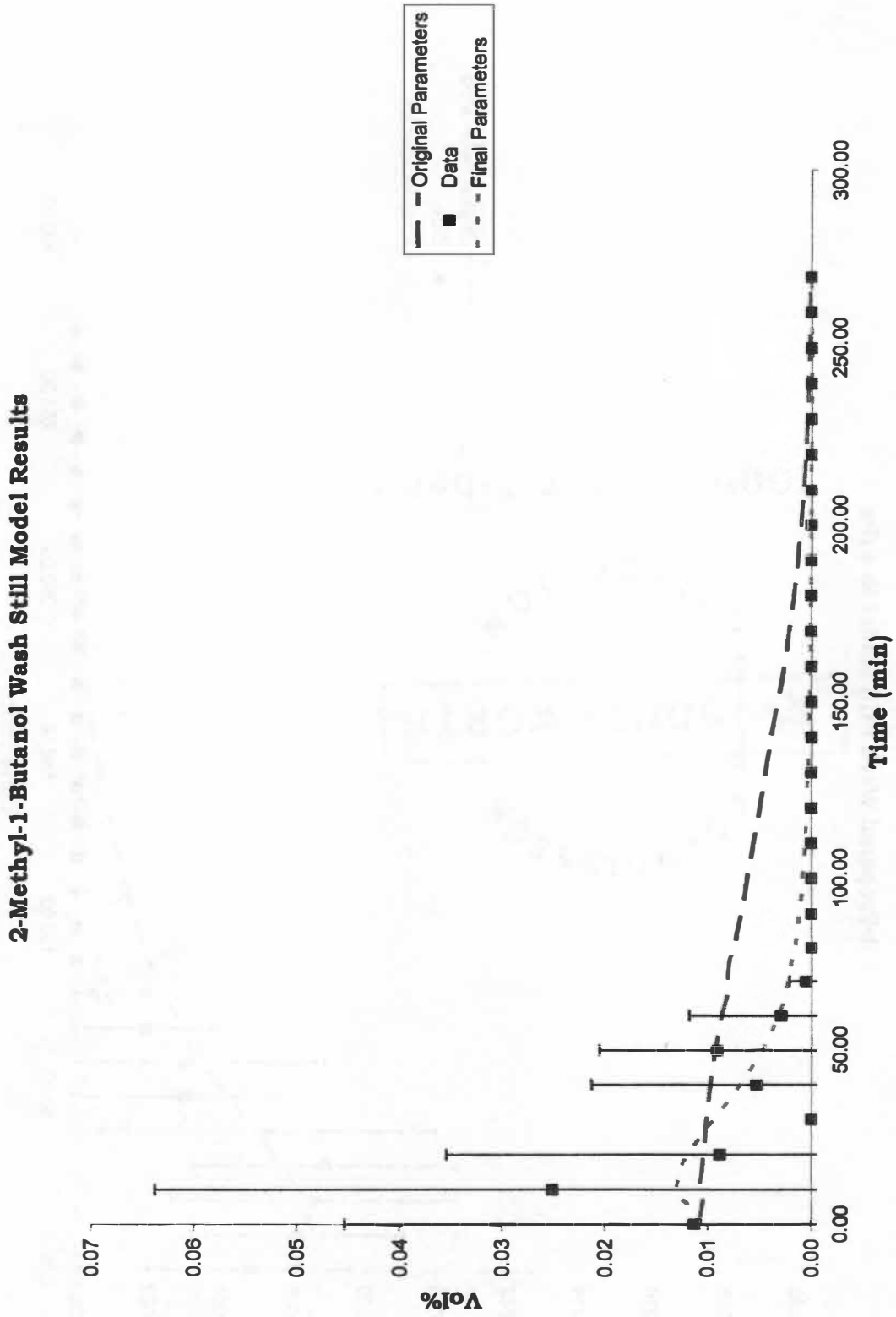

Figure 7: Interaction Parameter Adjustments for 2-M-1-Butanol

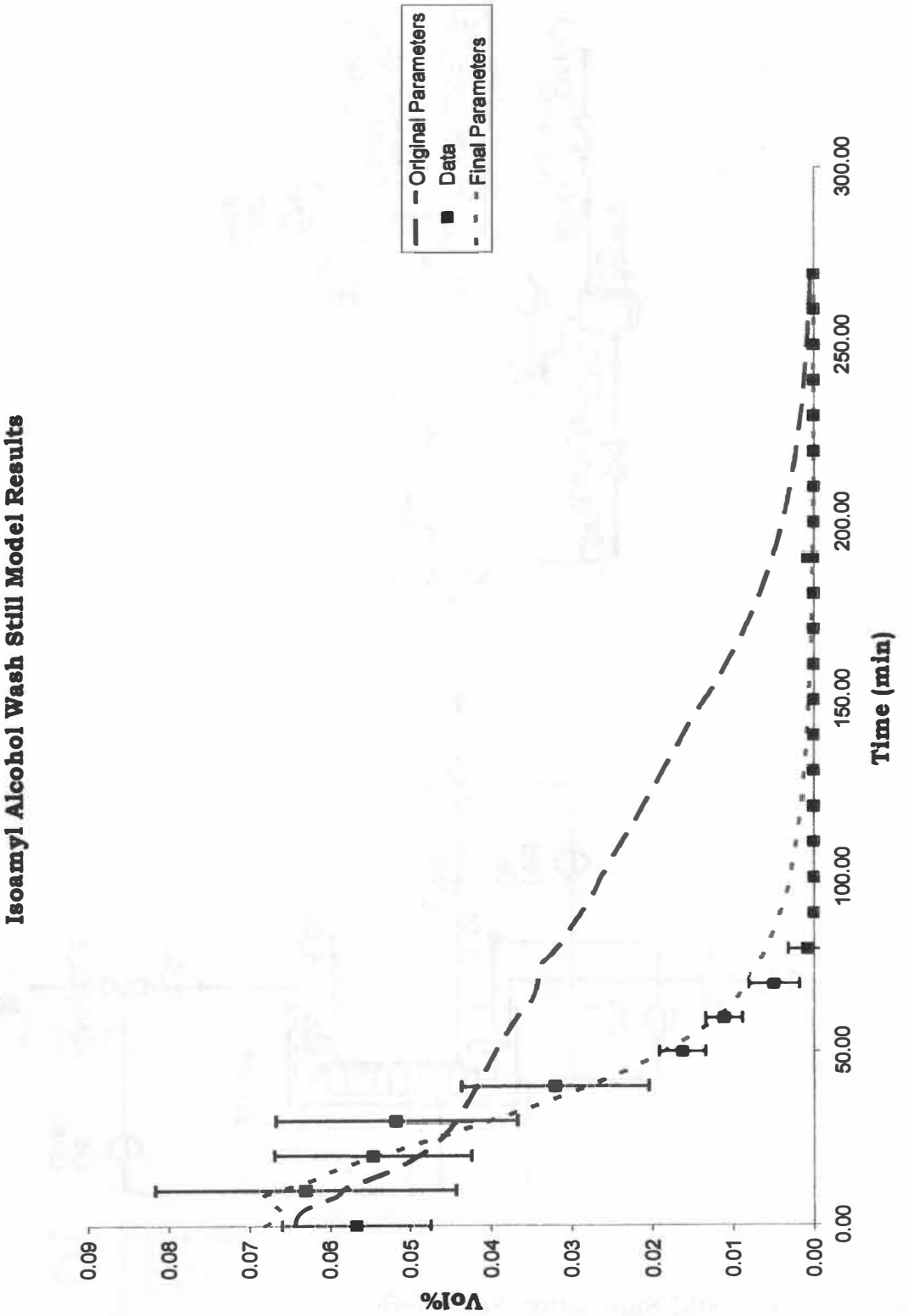

Figure 8: Interaction Parameter Adjustments for Isoamyl Alcohol

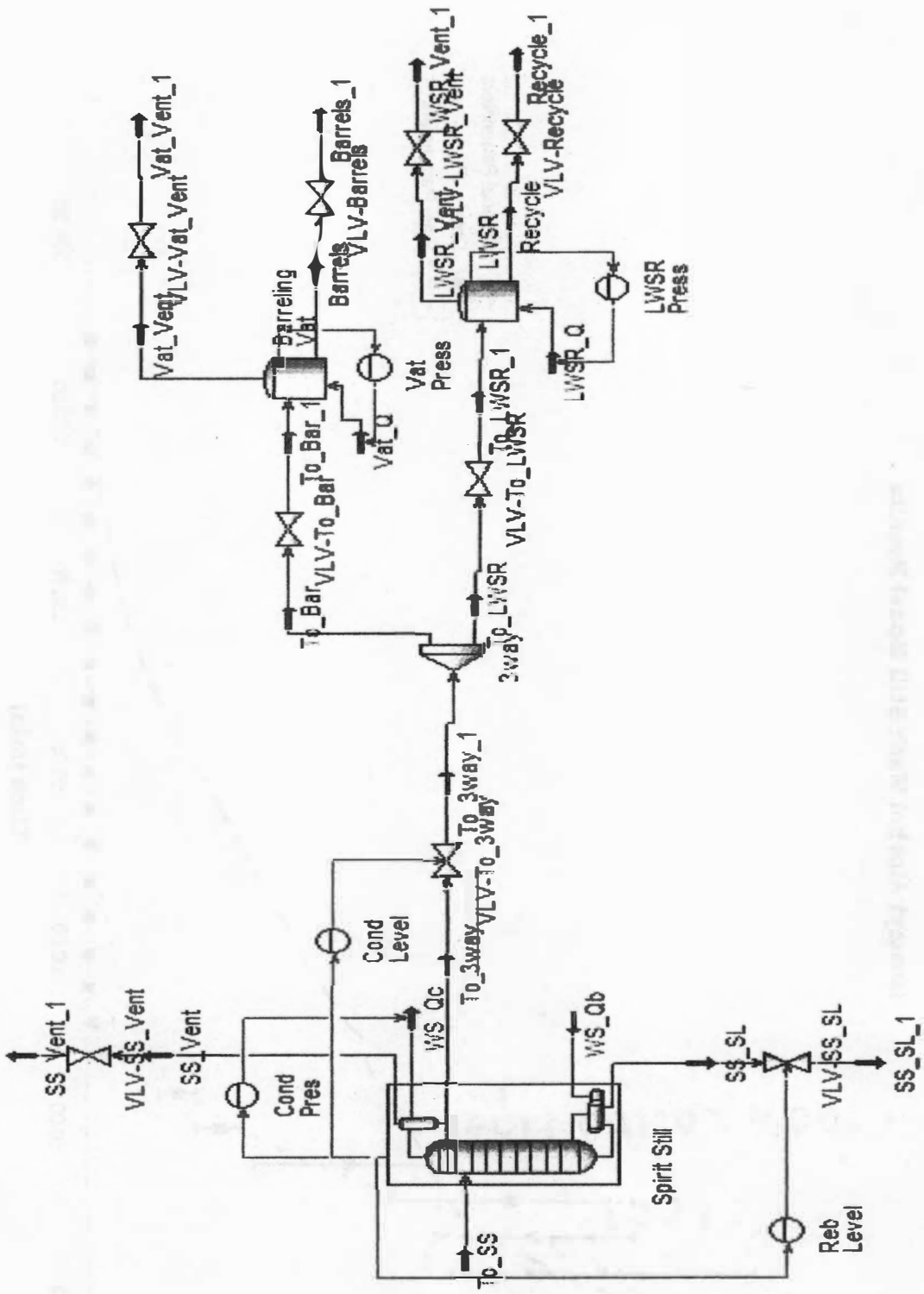

Figure 9: Spirit Still Simulation Schematic

the LWFR to the analysis of the spirit still distillate it was evident that the sample was poorly mixed and could not be relied upon as an accurate source of information about the concentrations of the minor components. It was also evident that the results of the wash still model could not be relied upon as an accurate measure of those concentrations either. It was necessary to consider the spirit still models ability to reflect the ethanol concentration curve while focusing on the shape of the minor component profiles.

Spirit Still Feed Conditions. The sample of spirit still feed taken at the distillery and analyzed proved unreliable for use in the modeling. Without a reliable method for determining the actual compositions of the feed an estimation of the feed composition was determined. Even though the LWFR sample was evidently ill mixed the ethanol concentration should be close to the actual ethanol concentration. The wash still model prediction for the final concentrations of the wash distillate should also be nearly correct for the amount of ethanol coming into the LWFR. Therefore a value between that of the LWFR sample and the predicted wash still contribution was chosen. It was selected close to the LWFR concentration on the belief that the LWFR ethanol concentration was likely to be close to the actual concentration. The minor component

concentrations of the LWFR were deemed less reliable than the model results. To account for this discrepancy an average of the model prediction and the LWFR value was used. The final composition is listed in Table 2.

Spirit Still Ethanol Tuning. The original spirit still model, much like the wash still model, could not be run as a constant heat process. The distillery process is run at relatively low heat. The distillate comes off slowly for the first few hours and the total amount of material sent over the top is relatively small. The second distillation leg is essentially a slow simmering of the feed to separate the alcohol and take as little of the water over as possible. Also of much concern in the spirit distillation are the minor component concentrations.

To simulate the slow simmering process it was necessary to adjust the heat to the system drastically over the first hour or so of the

Table 2 - Spirit Still Feed Composition

Spirit Still Feed Composition	
Ethanol	26.08
Water	72.08
Ethyl Acetate	0.66
1-Propanol	0.11
2-Methyl-1-Butanol	0.24
Isoamyl Alcohol	0.82

simulation. The simulation initializes with a relatively high heat flux which must be reduced quickly to simulate a slow boil. Once the heat was adjusted to a low heat flow the heat did not need to be adjusted until near the very end of the simulation. Near the end of the simulation the heat was increased drastically. The drastic increase is observed in the experimental data and in the normal operation of the spirit still. After completing the spirit cut of the second distillation the heat is increased to increase the rate of boiling and recover the remaining alcohol quickly.

After adjusting the simulated heat flow to the spirit still the model was able to accurately reproduce the ethanol concentration curve from the experimental data. Figure 10 shows the simulation results. The ability of the model to reflect the trends and concentrations observed in the experimental data indicated that the model was sufficient for accurate simulation of the process.

Spirit Still Minor Component Profiles. The minor components concentrations of the distillate were known to be unreliable for the reasons discussed earlier. Therefore it was difficult to determine the effectiveness of this model for predicting the minor component behavior in the spirit still distillation. Figures 11-14 show the minor component concentrations as a function of reflux ratio. As seen in the figures the minor components again follow similar trends as the experimental data without being able to accurately reflect the concentrations at specific

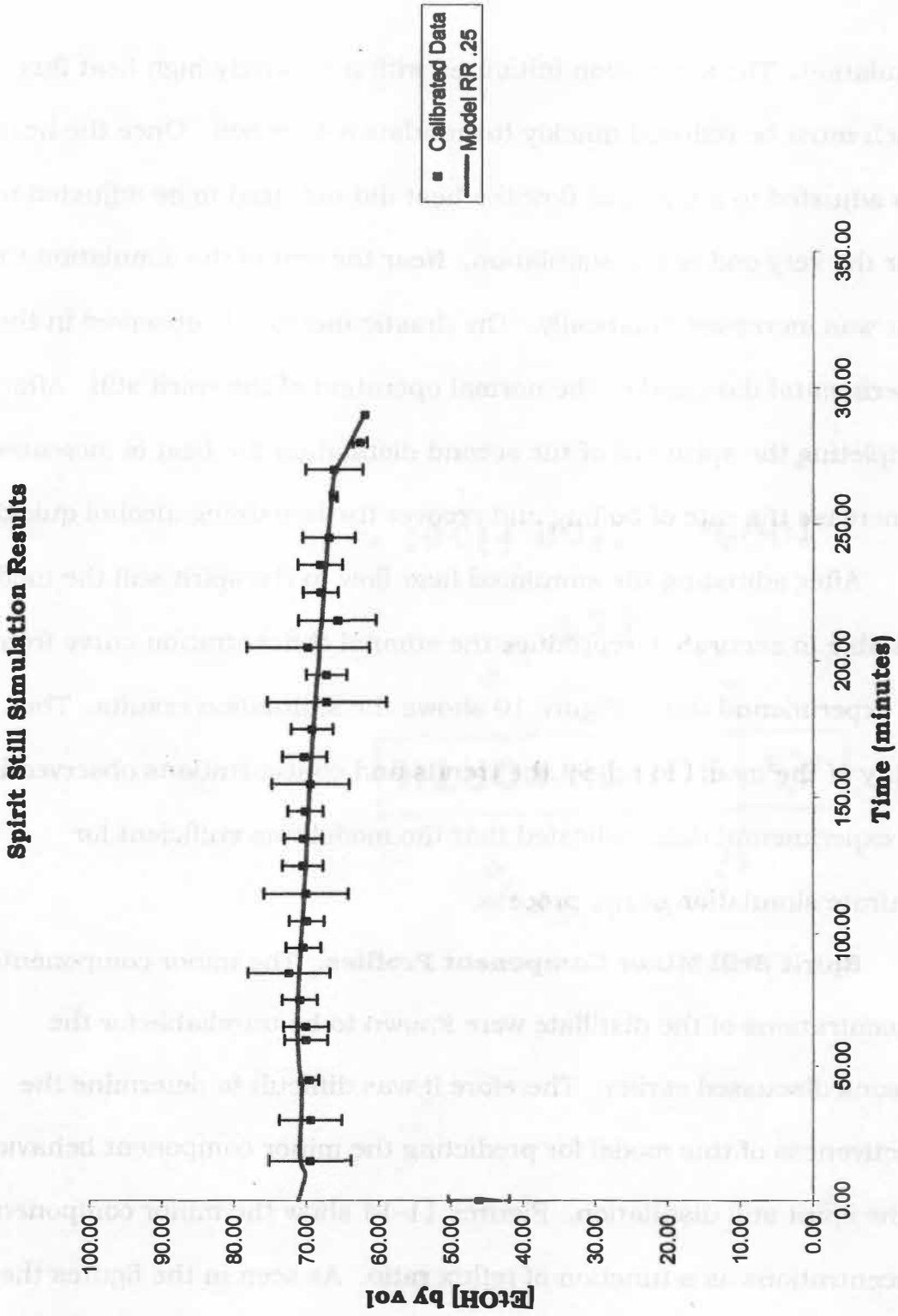

Figure 10: Spirit Still Simulation Results

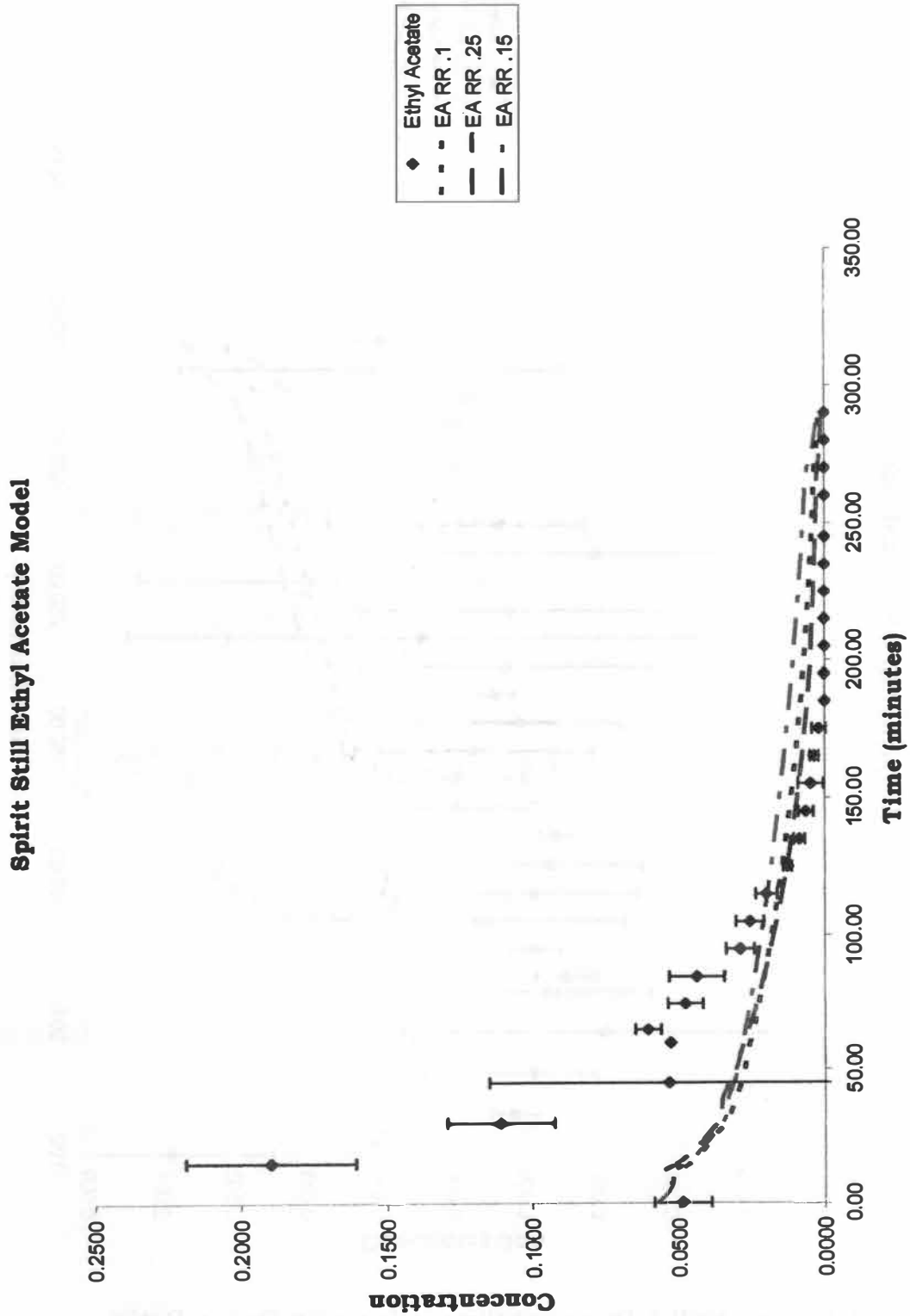

Figure 11: Spirit Still Ethyl Acetate Simulation with Reflux Ratio

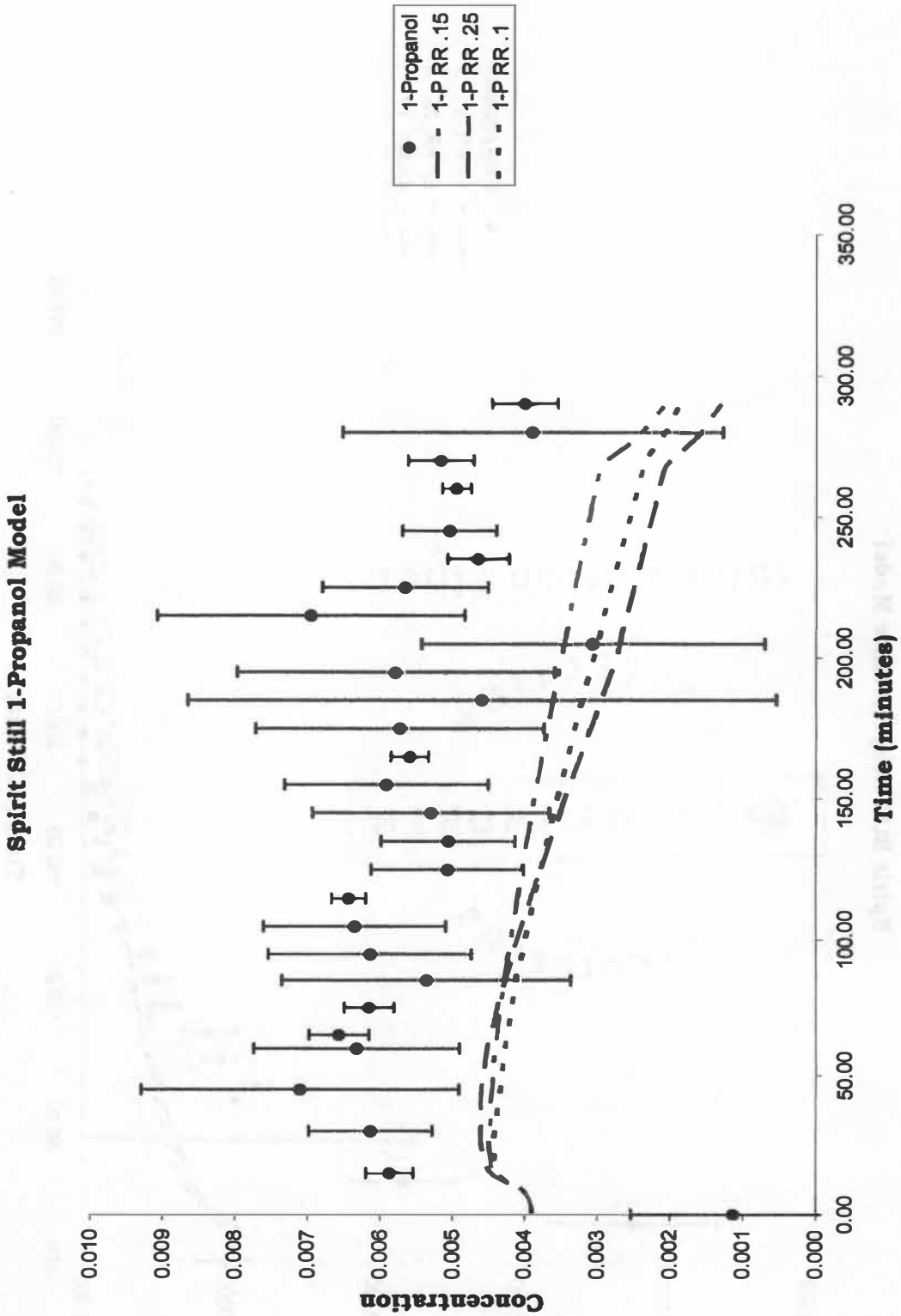

Figure 12: Spirit Still 1-Propanol Simulation with Reflux Ratio

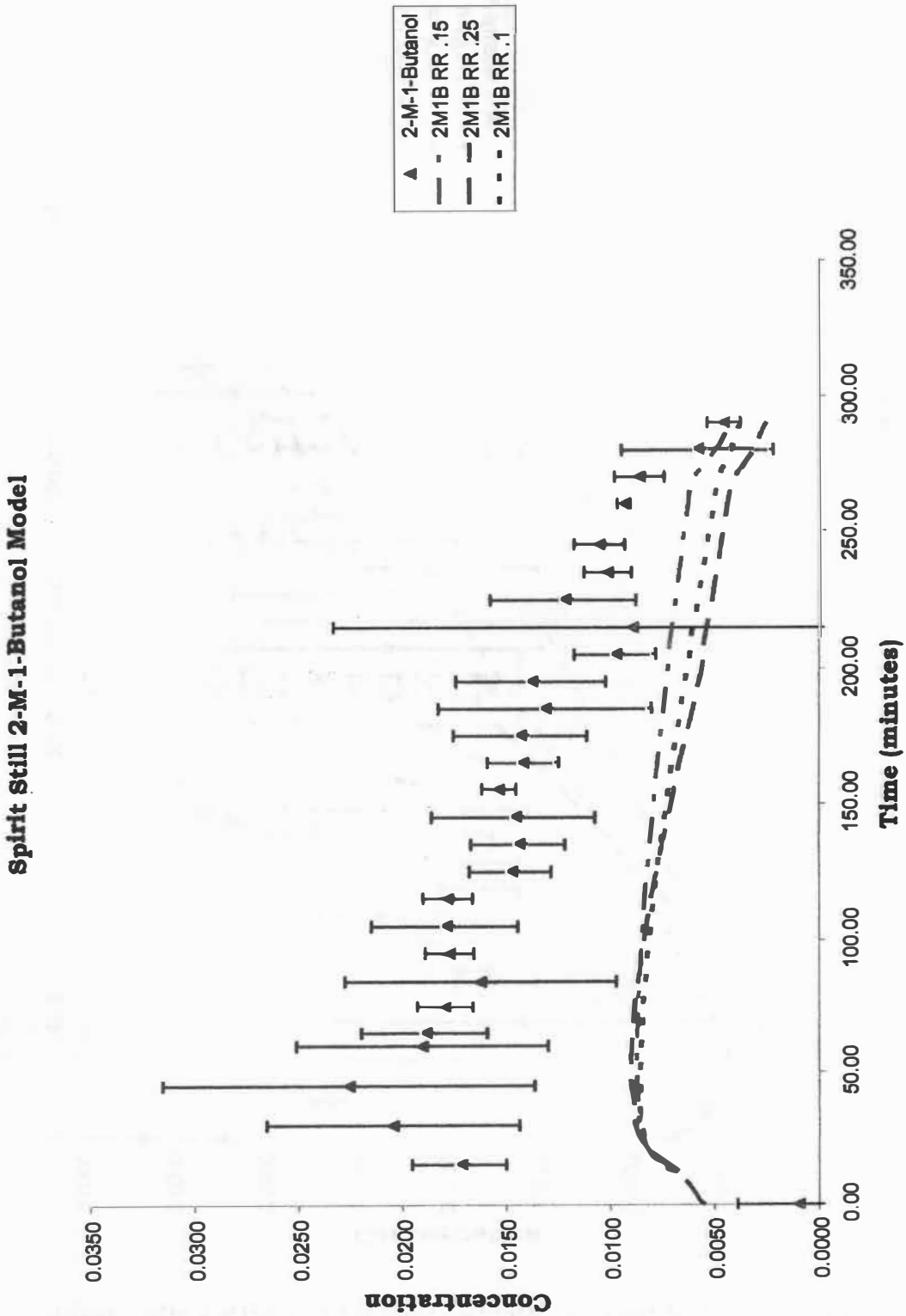

Figure 13: Spirit Still 2-M-1-Butanol Simulation with Reflux Ratio

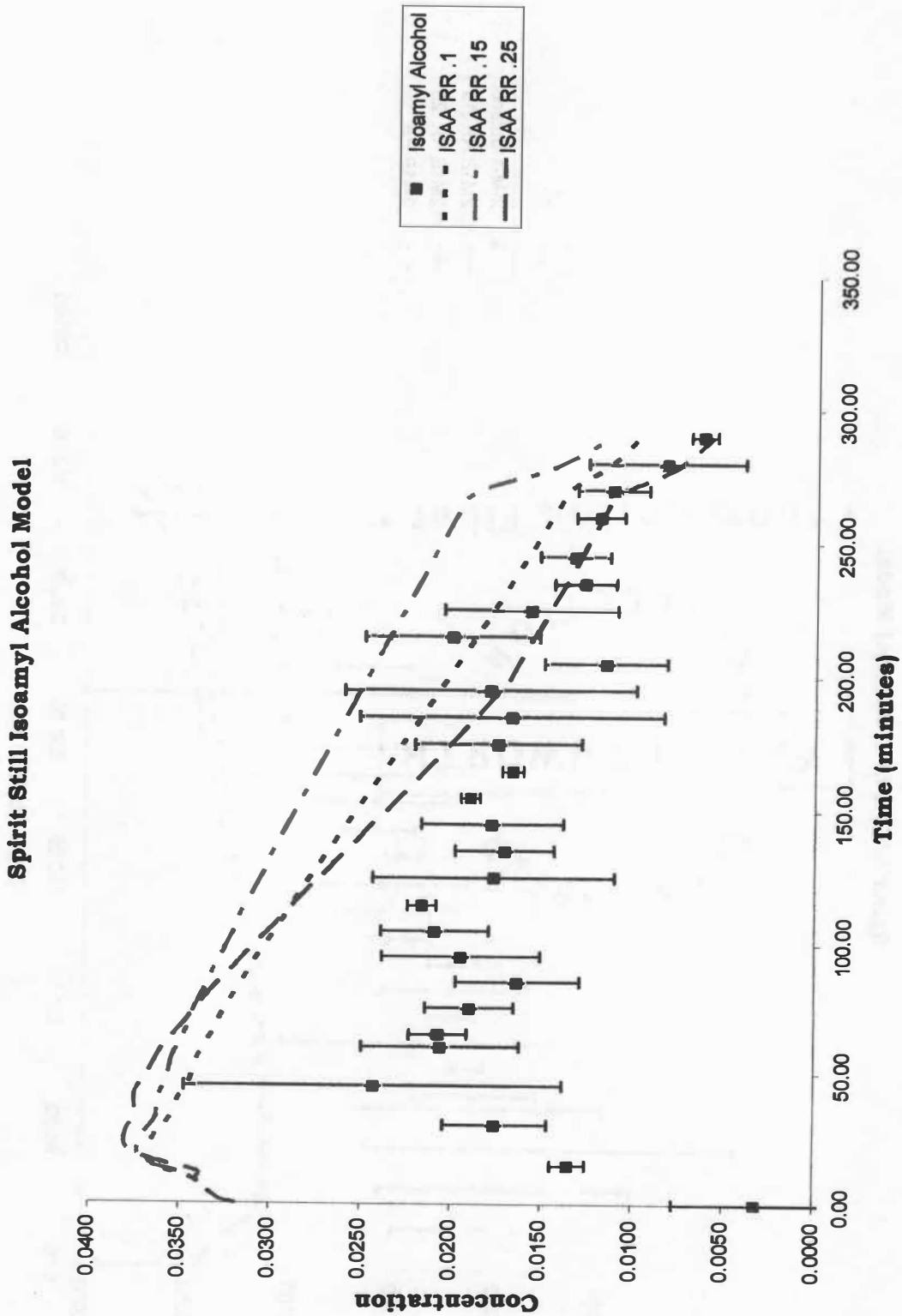

Figure 14: Spirit Still Isoamyl Alcohol Simulation with Reflux Ratio

times. The ability to simulate the trends in the data indicates that the model will be sufficient to accurately model the system when accurate feed concentrations are known.

The model interaction parameters determined in the wash still model were used for the spirit still model as well. The ability of both models to replicate the experimental data so closely is a solid indication of the model's fitness for use as a tool to study the process.

Process Improvements. With a working model of both the wash and spirit stills it was possible to begin considering ways to improve the process. The first aspect of the process to be considered for improvement was the heating system. The distillery relies on steam heating for both distillations as well as for the mashing operations. It is possible to installheat exchanger systems that would allow for the recovery of a significant portion of the heat used in the process. The savings on total energy expenses should more than offset the capital costs of the heat exchanger system and the resulting piping and pumping equipment.

Another possible improvement to enhance energy efficiency would be to insulate the copper pot stills from the environment to help minimize heat loss to the surroundings. This proposal is significantly more dangerous however. The heat loss at the walls of the pot stills are the only source of reflux in the system. The cooling film of liquid along the inside wall of the still is the source of the systems reflux. By

insulating the system to prevent much of that heat loss the system's operation would change. From simulations done with the model developed in this research it seems probable that the changes to the operation of the system would be minimal. However, there are many more minor components present in the actual distillate than are represented in this model. Some of the minor components have a distinct impact on the final flavor of the whisky even at very small concentrations. For the case of the spirit still, further study is necessary to determine the effect of any changes in operation on those other components not included in this work.

Further study is unlikely to be needed to determine the effect of insulation on the wash still. Because only the middle cut of the spirit still is taken as product the time at which each component distills is important to the final spirit cut. This is not true for the wash still. The wash still is operated to separate ethanol and water. Little thought is given to the minor components since the time at which they come over the top of the wash still is immaterial. Therefore altering the reflux in the system is unlikely to affect the final composition of the wash still product. With a minimal chance of altering the product the energy savings to be had by insulating the wash still would seem to be sufficient reason to consider doing so.

Related to the energy savings is the issue of reflux in the stills. Currently both the wash still and the spirit still are of the same design. The spirit stills are slightly smaller than the wash still but the necks of the stills have the same overall shape and presumably the same reflux pattern. Since the wash still is larger it necessarily has a larger heat transfer area and a correspondingly greater volume of reflux. Because the reflux is less important to operation of the wash still than to the spirit still it would be possible to replace the wash stills with pot stills whose design is such that it minimizes the reflux in the system. By minimizing the reflux you would cut down on energy costs and the pot still itself is likely to be smaller and less expensive than the current model. While it would be unwise to replace the stills currently in use with a new still to minimize reflux, when it is time to replace the current still a different still design should be considered. Implementing the insulation suggestion and replacing the wash stills with lower reflux designs at the next opportunity should result in significant savings in the long term.

The other area of possible process improvement is the spirit still. Process simulations using the model developed in this work would seem to indicate that the distinction between the foreshots, spirit cut, and feints is largely superficial. For the minor components included in this model there seems to be little difference between distillate deemed spirit

cut and the spirit deemed foreshots or feints. This would seem to indicate that it would be possible to increase the amount of spirit recovered for bottling in each distillation, thereby increasing the amount of product possible. This in turn should lead to higher revenues and profits from the same materials as are currently being used.

However, this model is admittedly incomplete in that it does not include information on all of the minor components of interest. As stated before, it is possible for some minor components even in very small amounts to have dramatic effects on the quality and taste of the whisky. The possibility of altering the flavor and character of the whisky by expanding the spirit cut are evident. It is therefore necessary to conduct further analysis of the samples to quantitatively determine the composition of the distillate and include the other minor components in the simulation.

Future Work. The most pressing area for future work is in the chemical analysis of the distillate samples. It is important to determine the other minor components present and quantify their concentrations. Rogers et al discussed the possibility of conducting solid phase microextraction (SPME) analysis on the distillate samples to evaluate the presence of other minor components that appear in GC/MS spectra. They also discussed repeating the analysis of the distillate samples in the GC/MS in splitless mode with adjusted mass spectrum scanning

parameters to filter out the water and ethanol peaks from the analysis. This analysis could produce quantifiable results that would allow for the inclusion of more minor components in the process simulation.

Another area for future work is in the determination of the binary interaction parameters for the system of interest. It was evident throughout the work that the estimation method for the binary interaction parameters is not effective for predicting the actual values of the parameters. Fitting the parameters from experimental data in the model will allow us to get close to the desired system but is still in adequate. Laboratory experiments to determine the interaction parameters would be useful for future work on this topic.

LITERATURE CITED

1. Bioprocess Engineering Basic Concepts, 2nd Edition, Shuler, M.L.; Kargi, F.; Prentice Hall, Upper Saddle Rive, New Jersey, 2002

2. Guichard, H.; Lemesle, S.; Ledauphin, J.; Barillier, D.; Picoche, B.; Chemical and Sensorial Aroma Characherization of Freshly Distilled Calvados 1. Evaluation of Quality and Defects on the Basis of Key Odorants by Olfactometry and Sensory Analysis. *J. Agric. Food Chem.* **2003**, 51, 424-432

3. Ledauphin, J.; Guichard, H.; Saint-Clair, J.F.; Picoche, B.; Barillier, D.; Chemical and Sensorial Aroma Characterization of Freshly Distilled Calvados 2. Identification of Volatile Compounds and Key Odorants. *J. Agric. Food Chem.* **2003**, 51, 433-442

4. Aroma of Beer, Wine and Distilled Alcoholic Beverages, Nykanen, L.; Suomalainen, H.; D. Reidel Publishing Company, 1983, Boston USA

5. Lyons, T.P.; Production of Scotch and Irish whiskies: their history and evolution. In The Alcohol Textbook, 3rd edition.; Jacques, K.; Lyons, T.P.; Kelsall, D.R.; Nottingham University Press: Nottingham, United Kingdom, 1999

6. Gaiser, M.; Bell, G.M.; Lim, A.W.; Roberts, N.A.; Faraday, D.B.F.; Schulz, R.A.; Grob, R.; Computer simulation of a continuous whisky still. *J. Food Eng.* **2002**, 51, 27-31

7. Rogers, B.; Morton, S.; Collier, J.; GC/MS Analysis of Scotch Whisky Distillate Samples, *In Preparation for Submission*

8. HYSYS Help Documentation

9. Vapor-Liquid Equilibrium Data Collection Aqueous-Organic Systems Vol I, Part 1, J Gmehling, U Onken, DECHEMA Chemistry Data Series Vol.1 Part 1, 150-196

10. Vapor-Liquid Equilibrium Data Collection Aqueous-Organic Systems Vol I, Part 1 (Supplement 1), J Gmehling, U Onken, W Arlt, DECHEMA Chemistry Data Series Vol.1 Part 1a, 116-157

11. Agarwal,R.; Li,Y.K.; Santollani, O.; Satyro, M.A.; Vieler, A.; Uncovering the Realities of Simulation. *Chem. Engr. Prog.* **2001**, 97, 5, 42-52

12. Agarwal,R.; Li,Y.K.; Santollani, O.; Satyro, M.A.; Vieler, A.; Uncovering the Realities of Simulation. *Chem. Engr. Prog.* **2001**, 97, 6, 64-72

APPENDIX

Table 3 - Heat Flux to Reboiler Wash Still

Heat to Reboiler	
Time (min)	**Heat Flow (KJ/hr)**
0	3,500,000
60	2,500,000
90	2,200,000
150	2,900,000

Table 4: Heat Flux To Reboiler Spirit Still

Heat to Reboiler	
Time (min)	Heat Flow (KJ/hr)
0	2,000,000
10	1,500,000
27	1,000,000
40	700,000
270	1,200,000

PART IV

CONCLUSIONS AND FUTURE WORK

1. SUMMARY

The work presented in this work was done with the intention of developing a useful computer simulation of a traditional scotch whisky distillation process. Through extensive distillate sampling, sample analysis, and study an experimental basis for a computer simulation was developed. The experimental analysis of the distillate samples reliably identified 16 separate components found during the distillation of the whisky. As many as 23 separate chromatographic peaks were observed in the data analysis but only 16 could be reliably identified. This laboratory analysis served as the basis for the computer modeling and simulation that followed.

The simulation of the whisky batch distillation process was accomplished using HYSYS simulation software. The computer model was developed along the lines of the actual process whenever possible. This helped retain the physical significance of the simulation parameters in relation to the distillery process. A thermodynamic system was chosen based on literature review of the topic and successfully allowed the accurate simulation of the ethanol distillation. In addition to the ethanol several minor components were also simulated. The minor component interactions were not as well understood as those of ethanol and water, however the parameter estimation method utilized allowed for the simulation of the minor components. When the minor components

behaved differently in the simulated system than in the experimental data the parameters were adjust to bring the simulation closer to the experimental data.

Not all of the experimental data was deemed reliable and therefore simulation and prediction of actual concentration values of the minor components was impossible. Simulation did allow comparison of trends in the experimental data with the simulated data. Comparing the two the trends observed in simulation were substantially similar to those observed in the analysis data. The simulation could accurately model the concentration of ethanol during the distillation and modeled the observed trends in the minor component concentrations. The model was therefore deemed successful.

2. PROPOSED IMPROVEMENTS

The successful simulation models were then studied to address possible process improvements. Simulation and study provided several possible ways to improve the batch distillation process. The first proposed improvement was for implementation of a heat recovery system. Anecdotal evidence suggests that such a system could be very valuable in terms of cost savings. The second improvement suggested was for insulation of the distillation vessels. Currently each distillation vessel generates significant amounts of heat that is radiated by the vessel into the ambient environment. While there are some legitimate concerns about the effects of insulating the vessel and the influence that would have on the internal reflux of the system, the idea is sound. Insulation is of particular interest for the wash still, where composition of the distillate at any given time is relatively unimportant.

A third proposed improvement is for a redesign of the wash still and spirit still. With more knowledge of the process it would be possible to determine the approximate needed reflux for each operation. If insulation of the stills is rejected, or even if it were implemented it would be more effective if the stills were designed in such a way to minimize heat loss that exceeds the reflux needs of the still. This type of improvement would prevent energy waste.

The final process improvement stems directly from the simulation and analysis of process model. It seems likely that using the process model, particularly if it is extended to include more of the minor components, there will be enough evidence to justify extending the spirit cut of the second distillation to increase product recovery. Extending the spirit cut by just 20 minutes both before and after the current process cutoffs would likely make a significant difference in product recovery and profitability for a distillery of similar size and nature to the one studied here. The current spirit cut lasts approximately 200 minutes. Extending that time by 40 minutes should realize an increase in product recovery of close to 20%.

3. FUTURE WORK

The most pressing area for future work is in the chemical analysis of the distillate samples. It is important to determine the other minor components present and quantify their concentrations. Knowing the minor component concentrations more accurately would allow us to compare the compounds found in the distillation to those known to have either favorable or unfavorable flavors and aromas. It would also allow for the extension of the current model to include more of the minor components and more accurately predict the behavior of the distillation process.

Extension of the model to include the other process equipment would also allow for reliable estimation of the amount of heat that could be recovered from a heat integration and recovery system. Inclusion of the other process equipment would also allow studies of batch scheduling to increase production efficiency and reliability.

VITA

Thomas Benton Rogers was born in South Pittsburg, TN on July 8, 1980. He attended his first year of high school at South Pittsburg High School in South Pittsburg, TN. He attended his final three years of high school at Baylor School in Chattanooga, TN. He continued his education by attending the University of Tennessee, Knoxville where he became a member of Tau Beta Pi in 2001. He went on to graduate Summa Cum Laude and received a Bachelor of Science degree in Chemical Engineering in 2002. Ben then continued his education and received his Master of Science degree with a major in Chemical Engineering from the University of Tennessee in 2004.

1331 4702 59
10/28/04 MSB