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**A STUDY OF EXPERT PROBLEM-SOLVING
IN QUALITATIVE ORGANIC ANALYSIS
USING A COMPUTER SIMULATION**

by

Keith A. Schramm

**A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Mallinson Institute for Science Education**

**Western Michigan University
Kalamazoo, Michigan
August 2002**

**A STUDY OF EXPERT PROBLEM-SOLVING
IN QUALITATIVE ORGANIC ANALYSIS
USING A COMPUTER SIMULATION**

Keith A. Schramm, Ph.D.

Western Michigan University, 2002

A qualitative case study of eight doctoral level organic chemists from academia (6) and industry (2) solved eleven qualitative organic analysis problems using the Identification of Organic Compounds* software computer simulation. Think-aloud protocols were analyzed for content knowledge and strategic knowledge to account for expert performance.

Each of the eleven qualitative organic analysis problems included a variety of functional groups and structures and was solved in a computer-simulated environment to allow for extensive problem-solving by the experts and to evaluate the simulation's ability to model the problem-solving environment. The data provided consisted of the typical instrumentation available to university undergraduate students, including infrared, proton nuclear magnetic resonance, carbon-13 nuclear magnetic resonance, and mass spectral data. Traditional wet chemistry data were also provided in the software, including solubility tests, fusion tests, classification tests, and derivatives. The subjects from industry did not effectively utilize the wet chemistry techniques, whereas the subjects from academia emphasized spectrometric techniques but also used wet chemistry techniques.

Only two of the subjects made the determination of an empirical formula an initial part of their problem-solving strategy. This strategy was used on 24 percent of the

problems. On 16 percent of the problems the subjects reverted to calculating an empirical formula when the problem became difficult to solve. The most effective strategy for utilizing the percent composition was to check the answer's percent composition with the elemental analysis. This was 100 percent successful and was used on 15 percent of problems. The elemental analysis was not used quantitatively by these experts on 45 percent of the problems.

Problem-solving was idiosyncratic in that subjects utilized a particular experimental method that they were the most comfortable interpreting as their initial experimental space search. Then subsequent problem-solving largely consisted of a series of explorations of the experimental space with subsequent searches for confirmation of model-building conclusions drawn from the data. Derivatives were used exclusively by the academic chemists both to search for solutions and to confirm proposed solutions.

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Keith A. Schramm, Ph.D.

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CHAPTER I

INTRODUCTION

Research in Problem-Solving

When behaviorism was the dominant psychological paradigm, it was believed that little could be known about the thought processes that a subject used when solving problems. The human mind was considered a “black box” which was unavailable to probing by the researcher. Consequently, research consisted primarily of the study of stimulus-response mechanisms, with little or no attempt to understand the cognitive processes used by subjects as they solved problems.

With the emergence of cognitive psychology, the mind was no longer considered “off limits” to the researcher. One cognitive model of the human mind is that of an information-processing system similar to a computer (Newell & Simon, 1972). Ericsson and Hastie (1994) state that “the central claim of the human information-processing theory is that cognitive processes and thinking can be described as a sequence of states, each defined by a limited amount of information active in attention (short-term memory). Each state provides the necessary input for access or generation of information in the following state” (p. 46). According to this model, while information is in short-term memory, a subject may attend to that information as he or she solves problems of various types. Consequently, this information in the short-term memory can be probed by the researcher via techniques such as observing eye fixations, monitoring keystrokes, and analyzing think-aloud protocols (Ericsson & Hastie, 1994; Ericsson & Simon, 1980). This data can then be used to infer much of the thought process used by the subject while solving the problems.

Early research in human problem-solving was primarily in knowledge-lean prob-

blems such as the Tower of Hanoi. Solving these types of problems required no prerequisite knowledge by the subject, except the ability to read and understand the problem. The results of this knowledge-lean problem-solving led to the information-processing theory of Newell and Simon (1972). Using their theory, researchers shifted their attention to how people solve problems in domain-specific areas such as chess (Simon & Chase, 1973; Charness, 1976), physics (Larkin, McDermott, Simon, & Simon, 1980; Chi, Feltovich, & Glaser, 1981; Reif & Heller, 1982), and biology (Collins, 1986; Hafner & Stewart, 1995).

A major purpose for studying problem-solving is to enhance the teaching and learning of science. The teaching of science problem-solving skills has traditionally been made through explanation and examples followed by a time in which students practice solving problems of the type discussed in class. The hope was that students were “blank slates” upon which the teacher could write the domain. Research in alternative conceptions has clearly demonstrated this is not the case (diSessa, A., 1982; Driver, Squires, Rushworth, & Wood-Robinson, 1994; McCloskey, M., 1983). Theories have been proposed to explain the reasons for the difficulty that students have in learning, as well as the conditions needed for conceptual change to occur (Posner, Strike, Hewson, & Gertzog, 1982; Strike & Posner, 1992). Alternative conception research has shown that the teaching of science concepts and problem-solving skills is much more complicated than writing the domain on the mind of a student.

One consequence of this research has been an emphasis upon “unpacking” the cognitive structures and problem-solving strategies of experts and novices as they solve problems within various science domains. Reif (1983a) proposed that the teaching of science should be done in a systematic way, based upon this type of research. He elaborates upon four components that must be developed and understood to achieve the goal

of improved teaching and learning of problem-solving. These four components are (1) a model of novice students' performance, (2) a model of desired performance, (3) a model of learning, and (4) a model of teaching. If education practice is to be designed upon theory, it is important to have an understanding of the knowledge structures that students bring to the problem-solving environment. It is important to know what knowledge structures are desired in the student if he or she is to gain expertise in the domain. It is also important to have a model of how students might proceed in learning, advancing from their initial novice status to a state of greater expertise. Finally, a theoretical model of how to teach the domain must be developed. This model would take into account the other models, and it would include the curriculum, learning environment, and teaching strategies that might be implemented to increase the likelihood that students would gain expertise in the domain. This belief, that studying problem-solving can enhance the teaching and learning of science domain problem-solving, has been the motivation for the problem-solving research tradition in science education.

This research was an attempt to develop an account of expertise within the domain of organic chemistry. Until now, little research has been conducted in organic chemistry problem-solving. Bowen (1990) and Bowen and Bodner (1991) studied the representational systems and processes used by graduate students in organic synthesis. Gonzalez (1998) examined the influence of concepts of molecular structure, that students possessed, and its impact on how they learn to interpret proton NMR data. Little else has been studied, and no research has been conducted concerning how qualitative organic analysis problems are solved. It was hoped that this research would provide specific knowledge and strategies about how people solve problems within a science domain which has been an understudied area of problem-solving research so that undergraduate instruction in qualitative organic analysis may be improved. For a primer on

the experimental methods used in the domain of qualitative organic analysis, see Appendix E.

Problem-Based Instruction

Science instruction often revolves around developing lessons and activities which help to explain the structure of the domain to students. The emphasis in this type of curriculum is usually upon content knowledge rather than upon the ability of the student to solve problems within the domain. A different approach to science education is to base instruction around problem-solving. Why would it be important for students to engage in a problem-based curriculum? Stewart (1988) proposed four potential learning outcomes from solving problems in genetics. Furthermore, according to Stewart, these learning outcomes may be applicable to other science domains as well. When applying these principles to qualitative analysis, the student may gain (1) a better understanding of the conceptual structure of the domain; (2) a better understanding of problem-solving heuristics not specific to this particular science discipline; (3) a better understanding of the problem-solving heuristics and algorithms specific to qualitative analysis; and (4) a better understanding of the nature of science as an intellectual activity. A problem-based approach to teaching qualitative analysis has the potential to enhance these learning outcomes in students. However, qualitative organic analysis is very time consuming. Extended practice, in the lab, at the undergraduate level is not practical. Therefore, one economical and time-efficient means of utilizing a problem-based curriculum is to use computer simulations.

Computer Simulations

The practice of qualitative analysis is a time-consuming endeavor. Each methodology in the process requires time for preparation of the sample, as well as time to conduct the tests and collect data. Some of the chemical tests require hours to react, not to mention the time required to prepare the proper reagents used in the process. While spectrometers are able to yield a spectrum in a short period of time, preparation of the sample may be difficult and time-consuming. Furthermore, the instruments used are very expensive and are in high demand for use by chemists within the university. Consequently, students of organic chemistry may receive limited practical exposure to determining the structures of organic compounds. Limited resources and time may prohibit students at many colleges and universities from having enough experience at collecting and interpreting data to develop any degree of competence in qualitative organic analysis.

A computer-based problem-solving environment in qualitative analysis has the potential to enhance the teaching and learning of this domain. This type of environment saves time and resources. While the technical ability to prepare a sample for an infrared spectrum may be an important skill, it does not involve the knowledge and strategies the chemist uses in the interpretation of data used while solving these problems. For the purposes of this research, the skills of competency in performing chemical tests and in using the instrumentation were not considered in developing the model of expertise in qualitative organic analysis. Only the declarative and strategic knowledge used in selecting the tests and interpreting the data were considered in this study. Since only the selection of tests and the interpretation of data was of significance here, a computer-based simulation of qualitative analysis was a viable means of investigating problem-solving. Furthermore, the time of experts is a precious commodity, and it would have been difficult and expensive to find chemists who could devote the time which would

be required to solve these problems using the actual chemicals and equipment. The difficulty of assembling a panel of experts to solve problems which would require hours of experimentation was eliminated by the use of a computer simulation. Even with the time savings, the strategies the experts employed were not eliminated since the viable tests were included in the computer software.

The use of a computer-based simulation has classroom benefits beyond this research project. As stated previously, the factors that limit students access to qualitative analysis problem-solving are the lack of time and the access to specialized equipment such as the infrared spectrometer and the nuclear magnetic resonance spectrometer. A problem-solving tool such as a computer simulation offers the student opportunities to develop a richer understanding of the knowledge structures and strategies used within the domain. As students solve numerous problems in a computer environment, they have the opportunity to refine their knowledge and develop successful strategies that can increase their competency in qualitative organic analysis long before they ever manipulate and conduct actual chemical and spectroscopic tests on an actual organic compound. This is the potential of a qualitative organic analysis computer-based simulation. For an expanded description of the Identification of Organic Compounds[®] software used in this research, see Appendix F.

Problem Statement

As discussed previously, qualitative organic analysis is an important domain within organic chemistry. Without research on how chemists solve these problems, education is founded upon beliefs based on anecdotal accounts or experience of how to teach problem-solving in the domain. If the educational process is to be systematically based on theoretical models of performance, research must be conducted (Reif, 1983a).

Furthermore, in content-rich domains most of the knowledge and strategies used in problem-solving is domain specific and, therefore, not transferable to qualitative analysis. The goal of this study was to begin an examination of problem-solving as performed by experts within the domain of qualitative organic analysis. This investigation focused on experts solving problems in qualitative organic analysis, with the goal of developing a model of desired performance within the domain. Future research can build upon this study by investigating and developing a model of novice performance, as well as developing models of teaching and learning within the domain.

The purpose of this research was to explain expert performance in the solving of qualitative organic analysis problems. Specifically, the questions for this research ask what declarative and strategic knowledge was used by experts as they solved these qualitative organic analysis problems? Declarative knowledge consists of the information that makes up the conceptual structure of the discipline. This conceptual structure is the specific concepts, theories, and models used in the domain, along with their organization. Strategic knowledge consists of those procedures that allow the chemist to solve problems. These strategies may make use of heuristics and algorithms. Heuristics may be defined as "rules-of-thumb for decision-making on how to proceed to an answer" (Stewart, 1988, p. 239). While heuristics help to direct the subject, they do not ensure a correct resolution of the problem. Furthermore, the use of a particular heuristic may not be the most efficient strategy to use in finding the solution to the problem. Heuristics can be both domain-specific and domain-general. Algorithms differ from heuristics in that they guarantee a correct solution to the problem when correctly applied. The steps of an algorithm are always completely specified; an algorithm can be used to solve any problem of its type, and an algorithm will always produce the correct answer when the proper data are used in the algorithm and the algorithm is applied

properly (Stewart, 1988).

The solving of any domain-specific problem involves the use of both declarative and strategic knowledge. It was hypothesized that the subjects in this study would utilize this knowledge as they conducted searches of the model space and the experimental space. Therefore, after the subjects solved the problem sets for this research, there were four questions to be answered:

1. When provided with a full battery of testing options (as defined by this proposal), what combinations of chemical tests and spectrometry are used by experts as they search in the experimental space that allowed them to solve these specific qualitative organic analysis problems effectively? Did the subjects utilize traditional wet chemistry techniques in combination with spectroscopy, or did they attempt to solve the problems by utilizing only the modern spectroscopic instrumentation?
2. If experts solved qualitative organic analysis problems by successive refinement of their molecular models, thus achieving the three subgoals described in this proposal, what was the nature and sequence of their model revisions? That is, what knowledge did they use that was critical in formulating and revising their models as they interpreted the results of experimental space searches?
3. What strategic knowledge, heuristics and algorithms did experts use as they searched the model and experimental spaces? When, where, and why did the experts choose to conduct particular searches of the experimental space?
4. What experimental results were used by experts to evaluate a proposed model of an unknown compound's structure as accurate? Specifically, what tests were conducted, and when were they used to evaluate various stages of the model refinement?

Significance

Accounting for expert performance in qualitative organic analysis has both theoretical significance in the problem-solving research tradition of science education and theoretical and practical significance in the teaching of qualitative organic analysis.

Qualitative organic analysis is not a new domain. There exist a few articles (McQuarrie, 1988; Ingham & Henson, 1984; McMinn, 1984; Turek, 1984; Bright & Chen, 1983; Jeffreys, 1979) and a number of textbooks (Lambert, Shurvell, Verbit, Cooks, & Stout, 1976; Breitmaier, 1993; Roeges, 1994; Feinstein, 1995; Shriner, et al., 1998; Silverstein & Webster, 1998) which describe the chemistry involved in a subset of many of the methods used in the domain. However, until now, no research had been conducted on how chemists actually solve qualitative organic analysis problems. This research has theoretical significance in the problem-solving tradition of science education because it applies the problem-solving research framework to a new domain. Previous research has indicated, with the exception of domain-general heuristics, that the knowledge and strategies used in one domain are not transferable to another domain. Much of the knowledge and strategies used in a domain are, quite simply, applicable only to that domain. This research examined a domain which, until now, had not been studied. Therefore, these findings have the potential to reveal new insights into qualitative organic analysis problem-solving. In fact, the literature review shows that there has been little problem-solving research within the domain of chemistry in general — and within organic chemistry, even less. Furthermore, most of the research that has occurred has been related to how students solve simpler, more algorithmic problems in general chemistry (Gabel & Bunce, 1994). Overall, the educational research within the domain of chemistry has lagged behind that of physics and biology. This investigation has broken new ground in the problem-solving tradition of science education by studying a rich problem-solving environment within a different domain of human cognition.

This project has theoretical significance in the teaching of qualitative organic analysis. This is the first step in developing a model for the teaching and learning of a science domain as described by Reif (1983a). If learning is defined as the transformation of a student's initial state of knowledge into a different final state of knowledge, then developing a model of desired performance is a logical first step in the process. This model provides a representation of the desired state of knowledge for students in the classroom. As discussed earlier, future research can build on this study to help develop a model of novice performance. A comparison of how a novice solves these problems to how an expert solves these problems can help to specify a model of learning, that is, the sequence of steps needed to transform the subject from his or her initial novice condition to a more expert-like knowledge state. Finally, this would allow for the specification of a theoretical model of how to teach the domain, a model that would be based upon research rather than conjecture and anecdotal experiences.

The practical significance of this research is threefold. First, it has the potential to inform the teaching of qualitative analysis as it occurs in the undergraduate classroom. The model of the knowledge and strategies used by experts has the potential to alter instruction by making explicit to students those strategies, heuristics, and algorithms that are actually used by experts as they solve problems. Second, it has the potential to make explicit the nature of expert model building in qualitative organic analysis. By making explicit the nature and sequence in which chemists search a space of models and a space of experiments to develop their structural models, we can gain insight into how knowledge is structured within the domain. Third, this study has the potential to enhance the use of computer simulation for instruction in qualitative organic analysis. The research demonstrates needed changes in the IOC[®] software, that may be applicable to other qualitative organic analysis software (Blackman, 1996). MacSQUALOR[®]

is already being used to assist in the instruction of qualitative analysis (Sundin, 1997). The conclusions drawn from this study demonstrate the need for changes in both the IOC® and MacSQUALOR® software in order to make them more viable tools in teaching qualitative analysis. Ergo, there is a potential to inform both the teaching of qualitative analysis in the classroom and to enhance the use of a computer simulation, such as IOC®, for instructional purposes.

A General Model of Problem-Solving

How do people solve problems in the context of scientific discovery? Klahr and Dunbar (1988) propose a model of Scientific Discovery as Dual Search (SDDS), which is intended to provide a framework for the interpretation of how people solve problems in a scientific manner. Scientific reasoning and problem-solving in the SDDS model occur as subjects conduct searches of two interrelated problem spaces: The first is the hypothesis space, and the second is the experimental space. The SDDS model consists of three primary phases that involve search within and between the hypothesis and experimental spaces. These phases are SEARCH HYPOTHESIS SPACE, TEST HYPOTHESIS, and EVALUATE HYPOTHESIS. SEARCH HYPOTHESIS SPACE consists of formulating an hypothesis either by evoking relevant knowledge from memory or by using the data obtained by searching the experimental space to help formulate or alter an hypothesis. The experimental space consists of those experiments that may be conducted by the subject either for the purpose of providing guidance in the formation of an hypothesis or for the purpose of testing a proposed hypothesis.

In the TEST HYPOTHESIS phase the subject makes a prediction about the expected results of an experiment based upon the formulated hypothesis. After the subject conducts the experiment or experiments, the observations are matched to the ex-

pected results. Next, these outcomes are used in the EVALUATE HYPOTHESIS phase to decide if the hypothesis in question should be accepted, rejected or revised. Evidence which indicates rejection or revision of the hypothesis would cause the subject to go back to the SEARCH HYPOTHESIS SPACE to generate a new hypothesis based upon the new experimental evidence.

The SDDS model of scientific discovery has proven to be a useful framework in problem-solving research (Hafner & Stewart, 1995). However, it was desirable to modify the model since the initial SDDS model pertained to solving problems of a domain general nature. The precedence for revising the SDDS model was established by Hafner and Stewart (1995) in their research of how subjects account for genetic anomalies.

In their research involving high school students' model revising process while solving various types of genetics problems, they modified the Klahr and Dunbar model to consist of a search of two spaces: a model space and an experimental space. In Hafner and Stewart's research the students were taught, and had opportunity to apply, Mendel's simple dominance and co-dominance models of genetics. The students became proficient in the interpretation of genetic crosses pertaining to these models. The most proficient of these students were then presented with genetic crosses that did not fit the explanatory models they had learned. Hafner and Stewart (1995) focused their research on how these students accounted for anomalous data from the genetic crosses. That is, these researchers observed how did the students revised, tested and evaluated their explanatory models. Like the model proposed by Klahr and Dunbar (1988), the problem-solving model developed by Hafner and Stewart (1995) consisted of three major components: SEARCH MODEL SPACE, TEST MODEL, and EVALUATE MODEL. This model differed from the Klahr and Dunbar model primarily in that this model was a search of a space of models, as opposed to a hypothesis space. Figure 1 is the Hafner and Stewart (1995) model-revising problem-solving in genetics model.

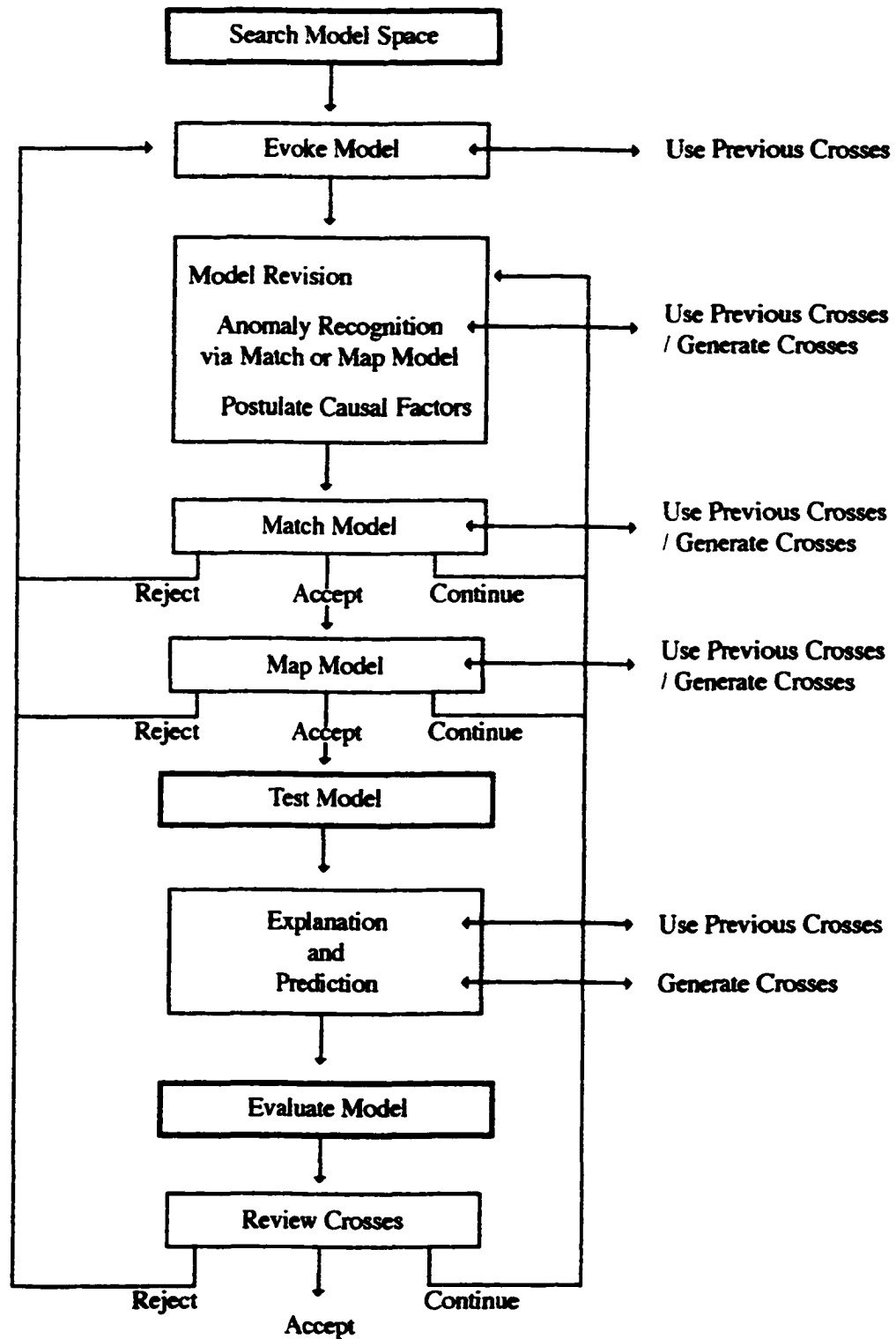


Figure 1. Hafner & Stewart's Model-Revising Problem-Solving Model in Genetics.

In the SEARCH MODEL SPACE of the Hafner and Stewart (1995) model, the subject evokes mental models of genetics to explain the results of a genetic cross. When the data set does not fit his model he begins to postulate reasons for the discrepancy. The subject may then revise the model, attempting to match or map the revised model with the data. When the subject has devised a new genetic model, he enters the next stage, TEST MODEL. In this testing stage of the problem-revising process he looks for the model's ability to explain adequately any previous genetic crosses. He also tests the predictive power of the model by postulating the results of a particular cross and then searching the experimental space of the specific cross in question. The results of these tests allows the subject to proceed to the next phase, EVALUATE MODEL. He may review a number of the crosses and in a recursive manner go back to revising or rejecting the proposed model if it did not satisfactorily answer explain the anomalous data.

While Hafner and Stewart's (1995) research pertained to explanatory model-revising research, qualitative organic analysis is model-using and model-building. Organic chemists utilize theoretical models of how chemical instrumentation work to elicit structural models of a compound. For example, infrared spectroscopy utilizes a ball and spring model to explain absorptions in the infrared region of the spectrum. The wavenumber of absorption when infrared light is transmitted through a sample of the compound is dependent upon the mass of the balls (atoms) and the stiffness (bond strength) of the chemical bond between the atoms. Consequently, particular atoms that are bonded in a specific manner evoke a definite structural model in the mind of the trained chemist. For example, a strong absorption peak near 1700 cm^{-1} in an infrared spectrum evokes a structural molecular model for a carbonyl ($\text{C}=\text{O}$) functional group, since the theoretical models of infrared spectroscopy predict an absorption at that wavenumber for atoms of carbon and oxygen joined by a double bond.

Different theoretical models are utilized for each type of instrumentation or wet chemistry used in qualitative analysis. In each case, however, the chemist has a working theoretical model of the chemistry involved, and the interpretation of the data causes the chemist to develop and refine the structural model of the unknown compound.

Consequently, instead of SEARCH HYPOTHESIS SPACE as a phase of the problem-solving process, it is more reasonable to think of qualitative organic analysis problem-solving as model building. It was assumed that experts in qualitative organic analysis solved problems by successfully building more and more sophisticated and complex models of a compound. The model refinements can be broken into three major subgoals: 1) determination of the simple molecular formula, 2) determination of functional groups within the compound, and 3) determination of the structural arrangement of the atomic fragments found within the compound. This model refinement is directly connected to the information that is obtained from experimental data. It is the chemist's understanding of this model as vibrating particles (with specific mass and bond strength) that gives this absorption peak significance. Therefore, the interpretation of data is based upon structural models of compounds and the influence of the data collected from each type of experiment conducted upon each stage of model refinement, rather than just simplistic hypothesis formation and revision. It was expected that the subjects in this study would engage in problem-solving that would consist of formulating and modifying models pertaining to the subgoals of molecular formula, functional groups, and structural arrangement. The initial models and revisions of their models according to this researcher's model, would be created by SEARCHING MODEL SPACE. Just as described in Klahr and Dunbar's (1988) SDDS model of non-domain specific problem-solving and Hafner and Stewart's (1995) model of explanatory genetics model revising, experts in qualitative organic analysis search the experimental space to collect evidence

which allows both for the formation and the evaluation of their structural models.

What is the nature of the model-building process that chemists use to solve qualitative organic analysis problems? A rational analysis of the domain was conducted prior to the research to hypothesize an initial model of this process. This model was based upon textbook descriptions of how to solve qualitative analysis problems, and this researcher's personal experience in the domain. The initial, hypothesized model consisted of three subgoals: determining the molecular formula, determining functional groups, and determining the skeletal arrangement. Each of these subgoals in the hypothesized model consisted of a complex procedural model of how an expert might proceed in the problem-solving process. In each subgoal of this model, the objective was to reduce the problem space by developing more and more specific representations of the compound. If subjects followed this initial model explicitly and in order, they would have, at the conclusion of the determination of the molecular formula (Subgoal A), a model of the compound that was very simple. Yet, a formula such as $C_6H_{14}O$ would reduce the problem space from millions of possible compounds to hundreds or less. Utilizing the second subgoal, Subgoal B, the determination of functional groups, would also refine the molecular model. When particular functional groups are determined, other functional groups are eliminated and the problem space is reduced significantly more. The final subgoal was the most complex and subtle, because the final output of this subgoal was the proposed structural arrangement for the compound. On the basis of the NMR data, in particular, the problem space could be reduced to one molecular model that was best supported by the data collected from searching the experimental space.

After the data were collected and the think-aloud protocols were analyzed in comparison to the hypothesized model, it was clearly evident that the subjects in this

study did not follow this initial model as prescribed in the research proposal. While the subjects did attempt to complete the Subgoals, they did not necessarily do it in order of the Subgoals, nor did they follow the expanded procedural models found in the research proposal for this study. Major revisions and simplifications of the initial model were required to explain how these experts solved the problems in this study. A further analysis of how the modified SDDS model was used as a theoretical framework for analysis of the data and the revised model of expert problem-solving are discussed in Chapter IV of this dissertation.

CHAPTER II

A LITERATURE REVIEW OF RESEARCH IN PROBLEM-SOLVING

Introduction

Qualitative organic analysis, as discussed in Appendix E, is an important subdivision of organic chemistry by which a chemist can determine the structure of a newly synthesized compound or the structure of an unknown compound. With the advent of Fourier Transform spectrometers and computer databases of spectra, the identity of some organic compounds can be determined by allowing the computer to match absorption peaks with compounds in the database. This has led at least one chemist to question the necessity of qualitative analysis in the curriculum (Zubrick, 1992). He found that many of his students were able to identify unknowns with little more than the proper use of a Fourier Transform Infrared Spectrometer (FTIR). If technology can do the job for us, then why teach the theory and structure of the domain? As Zieger (1993) points out in a rebuttal article to Zubrick, the purpose of teaching the domain is greater than just identifying the unknowns at hand. The IR spectra libraries in an FTIR computer contain only a few thousand spectra, which are only a minuscule fraction of the compounds in existence. Furthermore, they are primarily limited to monofunctional compounds. If students are to receive an education that will help them solve real-world problems, they need to understand how to approach qualitative organic analysis problems, including how the interpretation of data from spectrometers can be used to infer chemical structure. The development of new compounds and the sheer magnitude of compounds in existence requires that qualitative analysis be an important part of the organic chemistry curriculum that will not be replaced by the use of a computer library to match absorp-

tion peaks in spectra. A technician who routinely needs to identify the existence of a compound in a sample may use a computer database to ease job demands, but an organic chemist must know how to solve the problems of organic structure determination. Therefore, qualitative organic analysis problem-solving education is still a necessity. It was hoped that this research would be a first step toward the improvement of teaching in this domain by the development of a model of desired performance.

Definition of a Problem

What is a problem? How this term is defined has an impact upon what constitutes legitimate problem-solving research. The types of problems used in problem-solving research have varied widely. Some studies have examined problem-solving that is algorithmic in nature (Gabel & Samuel, 1986; Gabel, Sherwood, & Enochs, 1984; Yarroch, 1985). On the other end of the spectrum, some research has involved problem-solving in which students have to revise their models of a phenomenon in order to solve the problem successfully (Hafner & Stewart, 1995).

The definition of a problem has varied in the literature. One general definition of a problem that has been widely used is given by Hayes (1980): "Whenever there is a gap between where you are now and where you want to be, and you don't know how to find a way to cross the gap, you have a problem" (p. i). This is a general definition, but one that greatly limits what would be defined as a "problem" and hence as "problem-solving." The implication of this definition is that a problem only exists if the person does not know how to solve a given problem or problems of its type. Since the person would have to discover how to solve the problem, its solution would be a new learning experience for the problem-solver. The genetics problems posed by Hafner and Stewart (1995) to high school students would be of this type. However, by this definition, most—

if not all—of the problem-solving research in chemistry (Gabel & Bunce, 1994) and physics (Maloney, 1994) has failed to be problem-solving research. Bodner (1991) states that often what is characterized as a problem is in actuality an exercise. This creates a dichotomy. What is a problem for a novice may be only an exercise for an expert. In reality, there could be no such thing as an expert if this definition of a problem were applied, since an expert is defined as a person who possesses the necessary declarative and procedural knowledge to solve problems within a domain. This expertise is gained by years of problem-solving within the domain after formal education has ceased (Ericsson & Smith, 1991). If a person has expertise within a domain, such as qualitative organic analysis, he or she knows how to solve problems within that domain. The expert may encounter situations that are unfamiliar to him or her and may have to solve problems that push the limits of his or her expertise; nevertheless, he or she possesses the knowledge and skills necessary to solve such problems.

The definitions and characteristics of a problem and problem-solving given by Smith (1991) was used for the purposes of this research. Smith (1991, p. 8) states:

A problem is any task that requires analysis and reasoning toward a goal (or “solution”). This analysis and reasoning must be based on an understanding of the domain from which the task is drawn. A problem cannot be solved by recall, recognition, or reproduction. Whether or not a task is defined as a problem is not determined by how difficult or by how perplexing it is for the intended solver. “Problem solving” therefore, becomes the process by which a system generates an acceptable solution to such a problem.

This definition accurately describes the problem-solving that experts engage in when solving qualitative organic analysis problems. The problems selected for this research project were of sufficient difficulty for the subjects that they were required to analyze and reason within the domain rather than solving the problems by recall or recognition. The analysis of spectral data as a means to determine the structure of a

compound provided tasks of sufficient difficulty to be regarded as problem-solving and henceforth were fruitful for investigation. The problems, therefore, were formulated to cause the experts selected for this research to utilize their declarative and strategic knowledge in order to develop a model of desired performance. Furthermore, these problems should be solvable by novices within the domain if future research is to be conducted with novices as the subjects. The specific problems used will be discussed in the methodology section of this paper.

Problem-Solving Research in Chemistry

The majority of research in problem-solving in chemistry has been limited to the domain typically found in the high school or freshman undergraduate chemistry curriculum. In a review of research on chemistry problem-solving, Gabel and Bunce (1994) also found that much of this research has focused on problem-solving that involves mathematical reasoning skills used in algorithmic ways. Often, the research pertaining to chemistry problem-solving cited by Gabel and Bunce (1994) has focused on student understanding of specific concepts in chemistry as a basis for problem-solving, rather than on problem-solving itself. Student conceptions about topics such as states of matter and conservation of mass (Osborne & Cosgrove, 1983; Stavy, 1990); the particulate nature of matter (Novick & Nussbaum, 1978; Novick & Nussbaum, 1981; Gabel, Samuel, & Hunn, 1987); mass, volume, and density (Shepherd & Renner, 1982); and the mole concept (Novick & Menis, 1976) have been researched, to name a few. Much of the research into student conceptions has been conducted from a conceptual change theory of learning (Posner, Strike, Hewson, & Gertzog, 1982; Strike & Posner, 1992). According to this theory, the curriculum should be presented in such a way as to produce direct conflict with students' alternative conceptions. The scientific way of ex-

plaining phenomena can then be presented. If a student perceives the conflict and it produces dissatisfaction with his or her beliefs, and if the new concept is seen as intelligible, plausible, and fruitful, then conceptual change may occur. An attempt to understand students' beliefs about scientific concepts so that the curriculum may be designed to produce conceptual change is a major reason why research into student conceptions has been conducted. The consequence of most of this research into students' concepts, therefore, is impacted in the conceptual change literature rather than in the problem-solving literature. As Gabel and Bunce (1994) point out, conceptual knowledge is necessary to solve problems in chemistry. That is the reason for its inclusion in a review of research in chemistry problem-solving. Nevertheless, the emphasis in chemistry problem-solving research has been conducted in relatively simple domains from a conceptual change perspective rather than being conducted in rich problem-solving environments, such as qualitative analysis, from a problem-solving perspective.

Problem-Solving Research in Organic Chemistry

The only extensive research into problem-solving within the domain of organic chemistry has been conducted by Bowen (1990) and Bowen and Bodner (1991). Bowen investigated the representational systems and problem-solving processes used by graduate students as they solved organic synthesis problems. He defined a representational system to be "a cognitive structure constructed by the solver based on his organization and breadth of domain-related knowledge" (1990, p. 352). He concluded that graduate students use at least seven representational systems in the solving of tasks related to proposing and evaluating organic synthesis problems. These systems were labeled Verbal, Pictorial, Methodological, Principles-Oriented, Literary, Laboratory-Oriented, and Economic. Verbal and Pictorial representational systems were used 100 percent of the time

by these students. Clearly, this would have to be the case since communication is verbal and the use of drawings to represent a compound's structure is firmly entrenched in the chemist's culture. The subjects had to use the verbal and pictorial representational systems just to communicate their ideas.

The other five representational systems were used as means to determine the best course of action in proposing a mechanism for the synthesis. These representational systems, from this author's perspective, are synonymous with strategies used by the problem-solver. For example, the Methodological system consisted of the subjects using various reactions as algorithms to solve subgoals (partial reactions in the overall synthesis) of the synthesis. The Principles-Oriented system was often used when the Methodological approach failed to produce the desired results. This system makes use of thermodynamic or kinetic arguments to predict the products of a reaction. The Literary approach was used when students used the chemical literature to find a similar type reaction or to confirm a step proposed by the subject. The Laboratory-oriented system was utilized by students when they mentioned specific knowledge about reactants, solvents, and reaction conditions the students had experienced in the laboratory as these conditions pertained to the problem at hand. A student might use this system to evaluate the effectiveness of a proposed solution. The Economics system was also used primarily as a means of evaluation. This system consists of evaluating the practicality of the synthesis based on time and expense involved to perform the synthesis.

From his research Bowen (1990) found that the graduate students used the Methodological approach to problem-solving 53.8 percent of the time. This was the predominant strategy used by the students. He found that most graduate students approached the problems by trying to recall reaction types that could be used to synthesize particular functional groups within the target molecule. They viewed synthesis largely as a pro-

cess of linking together several reactions that would ultimately result in the desired compound. The Principles-Oriented system was used 33 percent of the time, followed by the Literary, Laboratory-Oriented, and Economics systems being used 5.4, 6.8, and 1.0 percent of the time, respectively. These final representational systems were used primarily when the Methodological approach failed to produce the desired results or as a means of checking the efficacy of a proposed mechanism.

Bowen and Bodner (1991) used an information-processing model of problem-solving proposed by Bourne, Dominowski, and Loftus (1979) to interpret the problem-solving processes used by the graduate students solving organic synthesis tasks. According to this model, problem-solving is a non-linear process involving the three stages of preparation, production, and evaluation. Preparation is the process by which the subject attempts to interpret the problem and formulate a representation of the problem. In the production stage the problem-solver attempts to formulate a solution to the problem by utilizing declarative and strategic knowledge upon the representation developed in the preparation stage. Evaluation is the stage in which the problem-solver evaluates the proposed solution for both completeness and correctness. While these three stages may appear to be sequential, they may not be in most problem-solving processes. A subject may not make a complete initial representation, but may have to refine the representation as he or she attempts to solve the problem. Clearly, if the solution is deemed incorrect during the evaluation stage, the problem-solver will have to modify either the representation or the solution, or both.

From Bowen's analysis of the subjects' think-aloud protocols, he found that in each stage of the problem-solving process the subjects used qualitatively different decision-making processes. First, he concluded that each subject made strategic decisions. Strategic decisions are those decisions that have a major impact upon the direction that

the subject follows. These strategic decisions consisted of the choice of representational systems the subject used. The problem-solver decided what type of representational system to employ in the different stages of problem-solving. Once the strategic decision was made, Bowen found, the subjects made tactical decisions. Tactical decisions are a subset of a representational system and consist of the heuristics and algorithms used by the subjects within that system. Bowen analyzed the data to find which strategic decisions (representational systems) were predominantly used in each of the stages of preparation, production, and evaluation. A finer-grained analysis yielded specific tactical decisions (heuristics and algorithms) used in each stage of the problem-solving process.

The research by Bowen is the only extensive research in the science education literature that deals with expert problem-solving within the domain of organic chemistry. To help situate this research proposal in the science education literature, a review of problem-solving research in the domain of physics is discussed. How subjects solve problems in physics, specifically mechanics, was one of the first domains to be studied and is one of the most thoroughly researched areas in the problem-solving tradition of science education.

Problem-Solving Research in Physics

Much of the research into problem-solving in physics has dealt with the differences between how experts and novices solve physics problems. This research is important from Reif's (1983a) perspective because effective teaching methods should "be systematically designed on the basis of a theoretical understanding of underlying thought processes" (p. 15). Models of desired performance based upon analysis of expert problem-solving and models of novice performance in problem-solving provides insight into the state of student understanding before instruction and the desired state of under-

standing after instruction. This allows for teaching to be designed to aid in the transformation of students from an initial novice state to a state which is more expert-like. This instruction would be founded and developed upon research and theoretical models rather than anecdotal beliefs of teaching and learning.

What does the problem-solving research in physics have to say about the development of such models in chemistry problem-solving? Reif (1983b) addresses a general analysis of research into effective problem-solving. Such research will break the problem-solving process into stages which address the following subproblems: 1) How does a subject initially represent a problem which allows for effective search for its solution? 2) How does a subject synthesize a solution to the problem using his or her declarative and strategic knowledge? 3) How does a subject analyze a solution for reasonableness and correctness, so that suitable improvements can be made in the proposed solution? These three stages are similar to those described by Bourne et al. (1979).

One of the important findings from physics problem-solving research pertains to the differences in the types of initial representations that novices and experts develop for a problem. Their representations are based upon how their knowledge is organized. Chi, Feltovich, and Glaser (1981) attempted to determine the differences in how experts and novices organize their physics knowledge. In their research, subjects were presented 24 physics problems dealing with mechanics and kinematics and were asked to sort the problems into groups based upon similarities of solutions. They were then asked to repeat the sorting. Chi, et al. (1981) found that the experts took considerably more time to make the initial sorting than the novices did. This is suggestive of a deeper analysis by the experts. The second sorting pattern was very similar to the initial sorting, demonstrating that the grouping was based on some type of representation rather than being a random sorting. When the groups were analyzed, Chi, et al. (1981) found a

significant difference in the way the subjects sorted the problems. Experts organized their knowledge, and hence made initial representations of the problems, based upon the underlying physics principle needed to solve the problem. The novices, however, grouped the problems based upon the surface features of the problem. Surface features are defined by Chi, et al. (1981) as either specific objects referred to in the problem: the literal physics terms, such as friction, mentioned in the problem; or the physical arrangement of the objects described in the problem. These results were largely confirmed when the researchers conducted a second experiment in which they deliberately selected problems for sorting that had nearly identical surface features but utilized very different physics principles to solve correctly. The results indicate that the knowledge representations of novices and experts in physics are qualitatively different. How subjects utilized this representation when solving problems in physics was researched in the following study.

Larkin (1979) had two experts and one novice solve physics problems which required using an application of Newton's laws of motion. Even though the novice was as successful as the experts at finding the correct solution to the problem, Larkin found significant differences in the ways in which the experts made an initial representation of the problem. Larkin found that the novice tended to move directly from a study of the physical situation described in the problem to the equation or equations needed to produce an answer to the problem. The experts, on the other hand, performed an additional analysis. After reading the problem, the experts formulated a qualitative analysis of the problem based on the physics principles needed to solve the problem. It was not until the problems were redescribed that the experts utilized the necessary mathematical equations needed to solve the problem. Larkin (1979) and Larkin, McDermott, Simon, and Simon, (1980) postulate that the qualitative redescription performed by the experts de-

termines the appropriateness of their approach, reduces the chance of error, and serves as a means to provide a concise and easy way to remember the description of the problem's details. Similar research by Larkin and Reif (1979) yielded the same type of results. Experts organize their knowledge into coherent methods rather than individual principles or equations, and they approach problem-solving by successive refining of their initial representations. Table 1 delineates models of novice and expert problem-solving processes when solving physics problems. This table is taken from Larkin and Reif (1979, p. 195).

Table 1

Larkin and Reif's Models of Novice and Expert Problem-Solving Processes

The novice's processes

- Construct original description.
- Construct mathematical description.
 - Identify and apply relevant principles.
 - (For example, force laws, Newton's equation of motion.)
 - Combine equations to eliminate undesired quantities.

The expert's processes

- Construct original description.
 - Construct low-detail "physical" description.
 - Select method (for example, force or energy method).
 - Select key aspect(s) of problem.
 - Apply main principle (e.g., $F=ma$).
 - Construct description showing forces parallel to acceleration or velocity.
 - Check that no anomalies exist.
 - Apply subsidiary principles (for example, force laws).
 - Check that no quantities seem problematic.
 - Construct mathematical description.
 - Apply main principle (e.g., $F=ma$) to generate equations.
 - Apply subsidiary principle (for example, force laws) to eliminate undesired quantities.
 - Combine and solve equations.
-

Larkin (1979) also found evidence that the experts stored physical principles in memory as “chunks.” A chunk is collection of coherent interrelated units that can be stored in short-term memory. Simon (1974) postulates that a chunk may consist of a word, a phrase, or a concept. Furthermore, the number of chunks that can be stored in short term memory is approximately five, depending upon the size of the material stored in the chunk. The novice, on the other hand, seemed to have principles individually stored in memory. This chunking by experts allowed them to solve problems in bursts. They would take considerable time in deciding what to do, but once they accessed a chunk, they rapidly applied a number of principles which were easy to access because they were in the same chunk which was already recalled into short-term memory. The novice, however, needed considerably more time to make each decision in the process because each of the principles was held individually in memory. Thus, the novice required more time to recall pertinent information and make connections between this information.

To test these conclusions Larkin (1979) explicitly taught a group of students to make a qualitative representation of the problem and appropriate ways to chunk information based upon underlying physics principles. Even though these students received no opportunity to practice these skills, they showed a greater ability to solve problems than students who did not receive this instruction. This research supports Reif's (1983a) contention that modeling what experts do when solving problems can be an effective means to improve instruction and learning since it provides a model of desired performance. Using a model of novice and expert problem-solving, Reif, Larkin, and Brackett (1976) also proposed a simple model of learning and instruction. They then used these models to test the effects of implementation of the models in teaching students problem-solving skill in physics. They found significant improvement in those students who

received the special instruction when compared to students who received traditional instruction. Furthermore, they found evidence that students were able to transfer this skill to problems outside the domain of physics, specifically, inventory turnover in the domain of accounting. Reif, et al. (1976) were successful in developing models of underlying thought processes within the domain of mechanics, and were able to demonstrate increased problem-solving skill by students when these models were explicitly used in instruction. While domain-general problem-solving heuristics may be transferable from one domain to another, most of the declarative knowledge and strategies are domain-specific. This makes the results of much of this other research non-transferable to the domain of qualitative organic analysis. It is believed that this research into problem-solving in qualitative analysis will be a first step in developing models of problem-solving in the domain which may be used to enhance instruction in the undergraduate organic chemistry course.

Approaches to Research in Expertise

How does one account for the superior performance of experts as they address tasks within their area of expertise? The answer depends upon whether the underlying cause of the expertise is believed to be largely an inherited or acquired trait of the expert. Table 2 is taken from Ericsson and Smith (1991, p. 4).

This table lists the research approaches that have been utilized to account for superior performance as a result of inherited versus acquired characteristics of the subject. Furthermore, the outstanding performance can be attributed to general characteristics of the individual or to more specific characteristics of the individual, and the table is partitioned accordingly.

Table 2

Different Approaches to Accounting for Outstanding Performance

Attribution	Construct	Research approach
<i>Primarily inherited</i>		
General abilities	Intelligence, personality	Correlation with personality, general intelligence
Specific abilities	E.g., music ability, body build, artistic ability	Correlation with measures of specific ability
<i>Primarily acquired</i>		
General learning and experience	General knowledge and cognitive strategies	Investigation of common processing strategies
Domain-specific training and practice	Domain- or task-specific knowledge	Analysis of task performance, i.e., the expertise approach

Expertise in qualitative analysis is a skill that is primarily acquired by domain-specific training and practice. Through years of education and practice, organic chemists develop sophisticated knowledge structures and strategies which allow them to infer the structures of organic compounds from a variety of data sources.

The Expertise Approach to Research in Problem-Solving

How was a model of desired performance developed as experts solved problems within the domain of qualitative organic analysis? Ericsson and Smith (1991) provide a framework for research using the expertise approach. According to their framework, there are three fundamental steps in the expertise approach. First, one must capture

superior performance. That is, researchers must develop tasks which will allow for expert performance in the domain. Second, an analysis of expert performance must be conducted prior to the actual research. This consists of an analysis of expected performance by the subjects. This is comparable to the development of a model of performance based upon a logical analysis of the tasks required to solve the problems (Larkin & Reif, 1979). Once the theoretical model is developed, then data—such as verbal protocols—can be collected and analyzed. Finally, after the research is conducted, one must account for the expert performance. Analysis of data obtained during the research allows for the modification and refinement of the model developed before the research. The result is a model of expert, or desired, performance that is supported by theoretical models and experimental observations. Each of these three steps will be elaborated upon in the following sections.

Capturing Superior Performance

In selecting tasks which are designed to elicit superior performance by experts, it is imperative that the tasks reflect the stable characteristics of the expert problem-solver (Ericsson & Smith, 1991). Stable characteristics are those characteristics of the expert that allow him or her to demonstrate how he or she performs in an outstanding fashion. These are the characteristics that the expertise approach to research is designed to account for. Consequently, the tasks selected should not show significant changes in performance due to the subjects' gaining experience or practice as they solve the series of problems. If this were the case, then the tasks selected would not allow for optimal performance by the expert problem-solvers. This would provide data which could not be analyzed to reveal the mediating processes that lead to superior performance. On the other hand, the tasks selected must not be solvable by mere recall, recognition, or repro-

duction (Smith, 1991). If this were the case, the tasks selected would not be “problems” for the experts and would provide meaningless data.

A second important factor in the selection of tasks is a consideration of the amount of data to be collected. There should be a sufficient number of tasks to provide enough data to allow for a detailed account of the outstanding performance. The data in this research largely consists of think-aloud protocols given by the subjects as they solve the problems. Think-aloud protocols will be discussed further in the next section. If the data are not sufficiently large, then the conclusions drawn from the analysis will be suspect. On the other hand, the experts who volunteer for this research study will likely only be able to donate one day of what may be their most precious commodity—time. Anticipating this to be the case, the tasks cannot be so long as to cause a great deal of fatigue in the subjects. Fatigue could cause them to perform less than optimally. Consequently, this would fail to reveal the characteristics of the individuals that lead to desired performance.

Ideally, the tasks selected for this research will be representative of problems that allow the experts to utilize all of their knowledge and strategies in problem-solving. In simple domains this might be possible. In a semantically rich domain, such as qualitative organic analysis, this would not be possible. The number of functional groups and possible arrangements of atoms in a compound make the problem space so large that it is not possible to design a limited number of tasks that elicit all of the expert's knowledge and strategies. Furthermore, the number of tests the experts could perform on the unknown compound is extremely large. Fortunately, the major chemical and spectrometric tests discussed earlier in this proposal are the predominant means of qualitative analysis which limit that aspect of the problem space. Consequently, the tasks selected for this research need to be varied in terms of the types of functional groups,

arrangements of atoms, and testing mechanisms used by the experts to elicit a representative sample of the knowledge and strategies used by the subjects. This should provide sufficient data to build an initial model of expertise in the domain.

Analysis of Expert Performance

The analysis of desired performance consists of two stages. First, a preliminary model of expected performance should be described based upon the literature available. This was done in the research proposal for this dissertation. Second, data must be collected and analyzed using a methodology from cognitive science. The primary data source for this research was the think-aloud protocol.

Verbal protocols and the analysis of the cognitive processes used by subjects as they solve problems are based upon the information-processing theory of human cognition (Newell & Simon, 1972). When subjects are given a task to perform, they undergo a series of processing steps until they finally arrive at an answer to the problem. The use of verbal protocols from subjects as they think aloud serves as a source of data that reveals, in part, information that may be used to infer the cognitive structures that are used by subjects during these processing steps (Ericsson & Simon, 1980). This model of how subjects respond to think-aloud commands assumes that the processing of information involves three types of memories in which information may be stored: 1) sensory stores of short duration, 2) short-term memory with limited capacity and intermediate duration, and 3) long-term memory with extremely large capacity, but relatively slow access time. When subjects are involved in solving a task, they are stimulated by sensory input and information is placed in short-term memory. Information in long-term memory may be retrieved and placed in short-term memory as the problem-solving process proceeds. According to this model, information that is in short-term

memory is reliably accessible to the subject and may be reported by the subjects. Consequently, if the subjects are talking concurrently with being engaged in a task, the protocol may be regarded as a subset of the cognitive processes used by the subject. Thinking aloud should not alter the cognitive processes the subjects use since they are only reporting that which is in their short-term memories. If they have to be retrospective or introspective about why a task was performed in a certain way, this would necessitate a probe of long-term memory and a reconstruction of events. This may or may not be an accurate reflection of their thought processes, and is not a desired form of protocol.

One impact of concurrent verbalizations is that the subjects may perform the task analysis at a slower rate than would be expected without think-aloud verbalizations. This is due to the extra cognitive load. However, the increased time for completion of the task should not alter the information processing of the subject and should yield reliable data for the researcher to infer cognitive structures.

Criticisms of using verbal reports as data have been given by Nisbett and Wilson (1977). However, Ericsson and Simon (1980) argued that the studies cited by Nisbett and Wilson were retrospective protocols in which subjects were forced to reconstruct their thought processes. They further demonstrated that their criticisms should not apply to think-aloud protocols that are given as subjects perform tasks in real time.

It was the working assumption of this research project that the theoretical model for the use of verbal reports as data, as proposed by Ericsson and Simon (1980), is a valid model. Furthermore, it is assumed that the verbal protocols as collected in this study are a subset of the thought processes used by the subjects through which a valid representation of their thought processes could be inferred.

Accounting for Superior Performance

The final stage of the expertise approach involves accounting for how experts demonstrate their expertise in the domain. What conditions and cognitive structures allowed experts to perform optimally? Using the model developed from this research should allow for claims of this type.

An Initial Model of Problem-Solving in Qualitative Analysis

No research has been conducted on how people solve problems in qualitative organic analysis. Articles pertaining to qualitative organic analysis that are found in the chemical education literature generally focus either on compounds to be analyzed by students that the authors believe provide special insight into one or more aspects of the domain (Jefford, McCreadie, Muller, & Pfyffer, 1973; Dorn, Kingston, Simpers, 1976) or upon ways to interpret data provided by spectrometers (Gurst, 1981; Venanzi, 1982; Brown, 1985; Ingham & Henson, 1984; McQuarrie, 1988; Turek, 1984; McMin, 1984; Jeffreys, 1979; Bright & Chen, 1983). One article focused on the integration of writing in a course in qualitative analysis (Hermann, 1994). Consequently, it was from textbooks, rather than research articles, that an initial model of problem-solving was developed.

The rational analysis model, however, proved to be less than satisfactory in accounting for these experts' performance. The proposed model involved a rather linear model through a maze of procedures that, based upon the protocol evidence, the subjects did not follow. Rather, the subjects seemed to glean information from a particular experiment that caused them to jump from Subgoal to Subgoal or to jump from one part of a Subgoal to a removed part of that particular Subgoal. Consequently, the final model that accounts for expert performance is much more simplistic procedurally than the rational analysis model from the research proposal. The differences are sufficient

that the expanded version of original model is not included in the final draft of this dissertation. However, the general hypothesized model is included since the subjects did work within the basic Subgoals which were hypothesized.

One framework by which to analyze this process is described by Reif (1983b). In Reif's framework, the problem-solving process is broken down into three stages: 1) How does a subject form an initial representation of the problem? 2) How does the subject formulate a solution to the problem? 3) How does the subject evaluate the proposed solution to the problem? The initial representation in qualitative analysis was hypothesized to be that of determining a molecular formula for the compound, as described in Subgoal A of the model. (See Figure 2.)

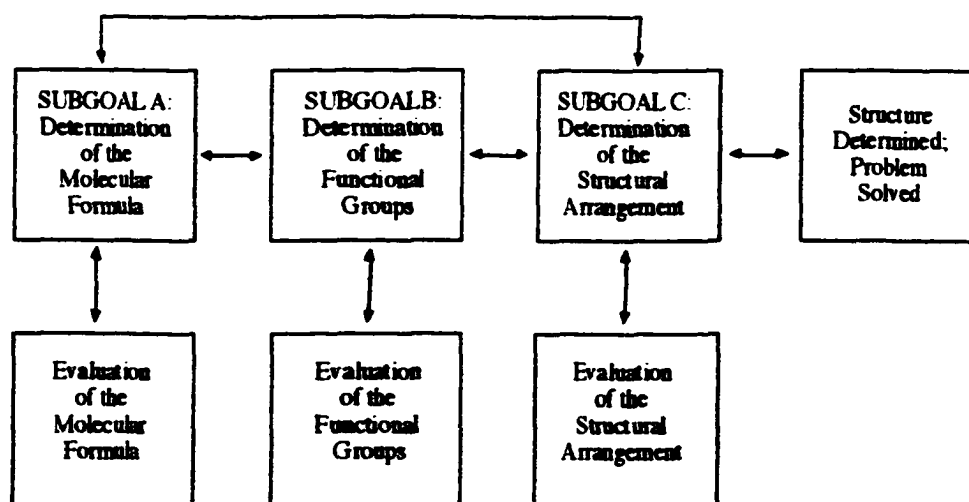


Figure 2. The Hypothesized General Model of Problem-Solving in Qualitative Organic Analysis.

Once this was determined, the hypothesized functional groups and structure must be in agreement with this determined molecular formula. In reality, this is not only the initial representation, but the first step in the formulation of the solution as well. It was

hypothesized that the solution process would continue with subgoals B and C of the model, the determination of functional groups and of the structural arrangement, respectively. The evaluation phase in this model would not necessarily occur only at the end of the process. The evaluation phases of the model summarize the evaluation process, which consists of finding supporting data for the proposed compound from other data collection sources. The process would not be linear, but recursive, since this evaluation may occur as each new piece of data was used to infer something about the structure of the compound. Furthermore, it was believed that the subject might search for information relative to functional groups or structure before the molecular formula was determined. In this model one phase does not have to be entirely completed before movement into another phase of the problem-solving process.

In Chapter IV of this dissertation, this general model will be modified to reflect the strategies used by the experts who participated in this research project.

CHAPTER III

METHODOLOGY

Introduction

The research design for this project was that of a qualitative case study of eight experts solving problems in the domain of qualitative organic chemistry. These experts were called upon to think aloud as they solved selected problems designed to elicit expert performance in the domain. A modified version of the computer software Identification of Organic Compounds[®] (IOC) was employed as the research tool. The IOC[®] software was believed to be a viable representation of the tools used by organic chemists, and the use of this program saved considerable time as the experts solved simulated problems instead of actually performing wet chemistry and spectrometric experiments. Using the computer software allowed the subjects to solve eleven problems without fatigue, due to the problem-solving process, becoming a significant detractor in their performance. Ultimately, in the time they could allot for this study, it allowed them to solve more problems than if they actually had to conduct the experiments. Additionally, computer software was chosen as a research tool because the results of this study had the potential to provide direction to the improvement of the software, thereby having the potential to enhance the quality of education in the domain. It was hoped that this research would have a positive impact in the teaching of qualitative organic analysis by providing a model of desired performance in the domain.

Rationale for Task Selection

What makes one organic compound different from another organic compound revolves around two factors: the functional groups present, and the skeletal arrange-

ment of carbon atoms and functional groups in the compounds. The differences in functional groups and arrangement affect the data that are collected as subjects conduct experiments. The spectral data from an IR spectrometer, mass spectrometer, and NMR spectrometers appear significantly different if, for example, the compound is an aromatic amine as opposed to an aliphatic ketone. The differences in these spectra allow the chemist to infer the presence or absence of functional groups. The wet chemistry tests for different functional groups will also differ; therefore, the chemist must possess the necessary declarative knowledge to choose the proper test and to interpret the test's significance. Likewise, different skeletal arrangements in isomers can also cause significant differences in ^1H NMR and ^{13}C NMR spectra. Subtle or significant differences may also appear in the infrared and mass spectra of isomers.

The solving of qualitative organic analysis problems, according to my hypothesis, can be interpreted as an interaction of subjects searching both a space of molecular models and a space of experiments (Klahr & Dunbar, 1988; Hafner & Stewart, 1995). The first search of the experimental space yields ideas about the molecular structure of the compound. The second search of an experimental space of possible wet chemistry tests and spectrometers yields data to decrease the problem space by providing evidence which can alter the chemist's model of the compound. That is, the chemist performs tests that help to eliminate possible groups of compounds while gathering evidence to solve three subgoals: 1) They search for a particular simple molecular formula, 2) they search for the existence of specific functional groups within the compound, and 3) they search for the particular atomic arrangement of the compound. The model in this research is recursive, since new evidence may cause the chemist to cycle backwards to evaluate previous models pertaining to the formula, functional groups, and structural arrangement.

The theoretical model of problem-solving in qualitative analysis as developed in this project was based upon a rational analysis of the domain and guided the selection of compounds and tests the subjects could use in their problem-solving. To elicit responses demonstrating different forms of declarative knowledge from the subjects, a variety of compounds with differing functional groups were selected for solution. Additionally, some of the compounds were selected because of subtle difficulties in the determination of the skeletal arrangement, so that a significant range of interpretation was utilized in the problem-solving tasks.

Two warm-up problems and seventeen additional problems were originally selected for the subjects to solve in this research. Once the first practice problem was solved, the subjects in this study felt comfortable with the IOC[®] and the think-aloud procedure and did not express the need to work the second practice problem (P2). Furthermore, it became clear that the time of 3-4 hours the expert subjects were able to donate to this project would not allow for completion of the entire problem set. The first two subjects were only able to solve through P12 in the time they donated to the project, so the researcher chose to limit the selection of problems to the ones solved by the first two subjects. This allowed the problem set to be uniform from subject to subject. Consequently, only the first ten compounds (P3-P12) were solved in addition to the practice problem, P1. The name of each compound and a generalization of each type of functional group and distinctive structural arrangement is given in Table 3. The compounds' numbers in bold are the problems actually solved by the subjects in this study. Henceforth, the problems in bold will be referred to by the numbers designated in Table 3 in the rest of this dissertation.

Table 3

Compounds Selected for Use as a Result of the Rational Analysis

Compound	Functional Groups/Structure	Sources of data
1) 3-pentanol	alcohol	IOC [®] , Tomasi
2) Benzoic acid	carboxylic acid, aromatic	IOC [®] , Tomasi
3) 2-methoxy-benzaldehyde	aldehyde, ether, aromatic	IOC [®] , Tomasi
4) hexanedioic acid	carboxylic acid, saturated aliphatic, symmetry	IOC [®] , Tomasi
5) 2-isopropyl-5-methyl cyclohexanol	alcohol, saturated ring	IOC [®] , Aldrich [®]
6) 4-chloro-3-nitrobenzoic acid	carboxylic acid, aromatic, nitro-, halogen	IOC [®] , Aldrich [®]
7) 2-methyl-3-butyn-2-ol	alcohol, triple bond	IOC [®] , Aldrich [®]
8) (E)-3-phenyl-2-propenal	aldehyde, aromatic, double bond, cis-trans-isomerism	IOC [®] , Tomasi
9) dipropyl amine	secondary amine, symmetry	IOC [®] , Tomasi
10) ethyl cyanoacetate	ester, nitrile	IOC [®] , Aldrich [®]
11) 3,7-dimethyl-6-octenal	aldehyde, double bond	IOC [®] , Aldrich [®]
12) Quinoline	heteroaromatic, multiple rings	IOC [®] , Aldrich [®]
13) camphor	ketone, bicyclic ring	IOC [®] , Aldrich [®]
14) o-benzoyl benzamide	amide, ketone, aromatic	IOC [®] , Sadtler [®]
15) 4-bromoacetophenone	ketone, aromatic, halogen	IOC [®] , Aldrich [®]
* = limited available data		
*16) 3-phenyl-2-propen-1-ol	alcohol, double bond, aromatic	IOC [®] , Tomasi
*17) 5-methyl-2-isopropyl phenol	phenol	IOC [®] , Tomasi
*18) 2-heptanone	ketone, saturated aliphatic	IOC [®] , Tomasi
*19) 3-methyl-1-butyl acetate	ester, saturated aliphatic	IOC [®] , Tomasi

These compounds were selected, first, because of their availability in the IOC[®] software. IOC[®] already contains the results of the chemical tests for all of the compounds in the program, and it was decided for the sake of convenience to utilize a subset of these compounds, since suitable compounds could be found in the software. Second, since searching the experimental space to achieve Subgoal B yields data that greatly differ based upon the functional group or groups that are present, it was decided that a wide variety of functional groups should be present in the compounds selected. Sixteen types of functional groups were present in these compounds: alcohols, aldehydes, aromatic rings, amides, amines, carboxylic acids, esters, ethers, heteroaromatic rings, halogens, nitriles, nitro- compounds, ketones, phenols, and double and triple bonds. While these are not representative of all of the types of functional groups that could be used, they did represent the major classifications of compounds that constitute a significant majority of the organic compounds in existence. While only compounds 1 and 3 through 12 were attempted by the subjects due to time constraints, most of the functional groups were still part of the analysis. Of the functional groups present in Table 3, only an amide and bicyclic ring functional groups were not part of the problem-solving environment the subjects actually attempted. Furthermore, these compounds contained many of the necessary elements and functional groups to cause the subjects to utilize various types of declarative knowledge from the qualitative organic analysis domain. For example, pertaining to the interpretation of mass spectral data, the two halogenated compounds produced large $M + 2$ peaks in the mass spectral data, whereas the other compounds produced small $M + 2$ peaks. Furthermore, some of the compounds contained nitrogen, which could have elicited the use of the nitrogen rule to estimate the number of nitrogen atoms present in the compound. Both of these examples of declarative knowledge were useful in accomplishing Subgoal A of the proposal.

The compounds selected also allowed for experts to utilize the different pathways in Subgoal B. There are compounds with degrees of unsaturation greater than, less than, and equal to four. The variety of functional groups also forced the subjects to use their knowledge in interpreting most of the regions of the infrared spectrum. Menthol (2-isopropyl-5-methyl cyclohexanol) was selected because it would ultimately force the subjects to propose a ring structure when they could not directly account for the degrees of unsaturation. Finally, the variety of functional groups in the compounds used in this research allowed the subjects to perform a variety of classification tests to confirm their functional group models.

Besides functional groups, the next major consideration in the selection of compounds for inclusion in this study was their structural arrangement. There are an extremely large number of ways that atomic fragments in organic compounds can be arranged. However, there are a limited number of types of structures. The twelve problems solved in this study contained cis-trans isomerism, saturated rings, multiple rings, symmetry, multiple substitution patterns on aromatic rings, and significantly long saturated aliphatic structures. Since NMR spectroscopy is the primary tool in determining structural arrangement, these compounds caused the subjects to consider symmetry, chemical shift, and coupling that varied from simple to difficult interpretation.

Not all types of compounds with differing functional groups and structural arrangements were selected for the subjects to solve. These, however, were selected on the basis of their availability in the IOC® software and upon their ability to elicit the use of various knowledge and strategies by the subjects as they solve problems in the domain. Based upon my rational analysis of qualitative organic analysis, these compounds were highly representative of the most common types of organic compounds that would allow the subjects to utilize components of the model originally proposed, if that was

their problem-solving strategy.

Originally, the last four problems in Table 3 were going to have limited data available for the subjects to force them to make use of those techniques that are most readily available in the undergraduate chemistry context. Time did not allow for the solving of these problems. However, the expansion and use of technology in the undergraduate program is growing. Students as sophomores may very well have access to ^{13}C NMRs and Mass Spectrometers. Consequently, the fact that the subjects did not attempt these particular problems did not affect the research detrimentally.

In summary, the compounds selected for this research varied in functional groups and structure. This assortment was designed to elicit various strategies and algorithms used in the problem-solving process of qualitative organic analysis. As shown in Table 3, compounds 1 and 2 were selected as warm-up problems for the subjects so that they would gain familiarity with the IOC[®] software and with the process of thinking aloud. Because of time pressure demands on the subjects, they solved only problems 1 and 3-12. However, because many of the problems had redundancies in functional groups and structure, this was an adequate number of problems to elicit their problem-solving knowledge in the domain. For example, three compounds had the alcohol functional group, and four had the ketone functional group. Nevertheless, each compound had the potential to provide unique insights into the problem-solving process.

The data for the compounds listed in Table 3 came from a variety of sources. All of the compounds selected for this research were found in the IOC[®] program. Consequently, data pertaining to combustion analysis, fusion tests, solubility, classification tests, and derivatives were found in that database. Additionally, some IR and ^1H NMR data were also found in the IOC[®] program. Other data, including missing IR and ^1H NMR spectra and ^{13}C NMR and MS data, were obtained from other sources. These IR and NMR

spectral sources included Dr. Richard Tomasi, Aldrich Chemical Company, and the Sadtler Division of Bio-Rad Laboratories. Mass Spectral data was obtained from the *Registry of Mass Spectral Data*, Vols. 1 & 2. Permission to use their spectra was obtained from these sources. With the exception of the mass spectral data, the particular sources of data for each compound is listed in the third column of Table 3.

Data Gathering

A total of eight doctoral-level organic chemists participated as subjects in this research project. Data from the first subject was collected in August of 1998, and the final subject participated in June of 1999. Of the eight subjects, two (S2, S7) worked as chemists in industry, while the other six subjects worked in academia. Data were collected in sessions at Western Michigan University in Kalamazoo, Michigan, at Harding University in Searcy, Arkansas, or on site at the subjects' places of employment. Two of the subjects were female (S4, S6). All of the subjects were American and received their graduate degrees from institutions of higher education in the United States of America. All subjects read and signed an informed consent form (Appendix A) before participation in this research project. Each subject agreed to volunteer without receiving financial compensation. However, the researcher did provide dinner for each subject after the sessions were over. All of the subjects who participated were recruited via e-mail correspondence and telephone conversation. Contacts with these subjects were made by references from chemists and science educators known by the researcher.

Participants were asked to think aloud as they solved problems using the modified version of the IOC[®] simulated environment for qualitative analysis in organic chemistry. The IOC[®] program simulated the results of wet chemistry and spectrometric techniques upon the request of the subject. This permitted each subject to explore the ex-

perimental space at his or her discretion, as well as allowing for individual interpretation of the data.

As the subjects solved problems, their verbalizations were tape-recorded for later transcription. Subjects were provided with pencil and paper and a calculator. The writings of each subject were also collected for analysis. To coordinate the verbalizations with the writings and the computer images being viewed by the subjects, each session was also videotaped. IOC[®] does not have a function allowing for a trace of the search through the experimental space. Consequently, the videotaping allowed the researcher to trace the movements of the subjects in the experimental space.

In addition to pencil, paper, and a calculator, several references were available to the participants. It was not assumed that the subjects would have derivatives or IR and NMR correlations memorized. Consequently, Rappoport (1984) was available as a reference to derivatives and their melting points. Charts found in Silverstein & Webster (1998) and Shriner, et al. (1998) were available as general references and for reference to the correlation charts in mass spectrometry, infrared spectrometry, and nuclear magnetic resonance spectrometry. Additionally, the IOC[®] program has a "help" feature which allowed the subject to inquire as to the particular purpose of a test and the characteristic results of the test. It was decided that subjects should be allowed to access this function, because the volume of declarative knowledge pertaining to the domain is significantly large that it was doubtful that they would have all of the tests and possible outcomes in long-term memory. In fact, several of the subjects did utilize the references and the help function in the program.

The tape-recording, writings, and videotape of each session are confidential. The names of the subjects are not included with any of this data. Rather, each subject is referred to by a number, both in the data and in this dissertation. When a subject is

referred to singly, the letter "S" precedes the number. For example, S1 refers to the first subject in the study. If subjects are grouped together, the numbers of each subject are included in parentheses. For example, S (4, 5, 8) refers to subjects four, five, and eight. The names of the participants are on a master list, separate from the data. This list will be destroyed once the final analysis of the data has been completed and the dissertation has been successfully defended.

In similar fashion, each problem solved by the subjects is referred to by a number, both in the data and in this dissertation. When a problem is referred to singly, the letter "P" precedes the number. For example, P3 refers to the third problem listed in Table 3. If multiple problems are referred to in a single context, the numbers of each problem is included in parentheses. For example, P (3, 8, 11) refers to problems three, eight, and eleven, the three problems that contain an aldehyde functional group.

In order to standardize the instructions and procedures of the research, a checklist was made and followed. This checklist is Appendix B. In each session, after the tape- and video-recorders were set up and the computer program was booted, the researcher read the informed consent form to the participant and the subject signed the informed consent form. Instructions about the use of IOC® and think-aloud problem-solving was read to each participant. The researcher then demonstrated the use of the software. Each function in the program was explained, but the researcher avoided suggesting to the subject how to proceed with the program. After this explanation, the subject was called upon to practice using the program and thinking aloud by solving P1 listed in Table 3. During the initial practice problem the researcher attempted to answer all questions about the software and the nature of the experimental test results.

After the initial practice problem, all of the subjects felt comfortable with the software and the think-aloud procedure. Therefore, the second practice problem was

skipped, and the subjects worked on P3 next. During the problem-solving sessions the researcher minimized his verbalizations. However, several participants at various times failed to verbalize during a portion of the think-aloud session, which prompted interactions such as "Can you say what you're thinking?" from the researcher. Other prompts that were used were taken from Larkin and Rainard (1984, p. 250), including phrases like "Please tell me what you are writing," "Mmm," and "Okay." These were designed to minimize the researcher's interaction with the problem-solver while keeping the subject verbalizing.

As a subject wrote on the scratch paper provided to him or her, the researcher made occasional notes pertaining to when the subject added material to the scratch work. This assisted in coordinating the scratch work with the verbalizations and experimental space search used to construct the frames.

When a subject finished solving a problem, the researcher sometimes asked a few clarifying questions. This called for retrospection on the part of the subject, but the clarifications did prove effective in helping the researcher to understand the rationale for some moves made by the subject in his or her model and experimental space searches.

Data Analysis

In this research project three types of data were collected: the video-tapes, the audio-tapes, and the writings of the subjects. The audio-tapes of the verbal protocols were transcribed verbatim. College students were hired to perform this task. Only one of these students was familiar with the chemical terminology, so when the researcher viewed the video-tapes, they were used to verify and correct — if needed — the transcriptions. Furthermore, the video-tapes were used to correlate the verbalizations with the computer images viewed by the subject and the writings made by the subject at the

time of verbalization. This correlated data was printed in three side-by-side columns and analyzed in an artificial unit called a frame. A frame consisted of that portion of each of these three types of data collected for each chemical or spectrometric test conducted by the subject. Consequently, each problem solved by a subject yielded data consisting of a number of frames as the subject searched the experimental space for data to modify their molecular models. The frames were used to infer the knowledge and strategies used by these experts as they conducted searches between a space of molecular models and a space of experiments. It was this interrelated search of these spaces which was used to account for how the experts modify their models. The system of frames as a unit of analysis has been utilized in other problem-solving research. For example, a frame in genetics (Collins, 1986; Hafner & Stewart, 1995) consisted of the data pertaining to a single genetic cross, and in phylogenetic tree construction (Brewer, 1996) a frame consisted of the data pertaining to a feature of the phylogenetic matrix or tree that the participant referred to as the basis for taking some action.

Whenever subjects in this study made writings about the problems they were solving, the frame is presented as two columns in this dissertation: The first column is the quote, and the second column is the writings. The writings are recorded next to the part of the quote in which they occurred. If the subject did not write anything during a particular quote, then only the quote is presented as a single block of data. All quotes from the raw data in this dissertation will be referenced to the tapes from which they came. Since all of the subjects were both video- and audio-taped, the raw data can be found from two sources. Each quote will be footnoted for the particular tape from which it came. These tapes are stored in a locked file in Dr. William Cobern's office for the confidentiality of the participants. (S1-V2, T3) is an example of the notation used to cite the raw data in this dissertation. The "S1" refers to the first subject. The "V2" stands for

the second video-tape of this subject, and the "T3" refers to the third audio-tape of Subject 1.

To address the first research question, the protocols were analyzed for the chemical and spectrometric tests chosen by the subjects as they searched the experimental space of the problems. Descriptive statistics were performed to determine the percent of the cases a particular type of test, as outlined in Appendix E, was used by each subject individually and by the subjects collectively. The goal was to determine if there are any tests which are either not utilized or are strongly utilized by the subjects in problem-solving. Particularly, the goal was to determine if chemists still utilize the traditional wet chemistry tests or if determination of structure by spectrophotometric means was the only type of experiment chosen by these experts. This insight may allow for recommendations about what should be included in the qualitative organic analysis curriculum at the undergraduate level.

To address the second research question, the encoded protocols were also analyzed for evidence of the declarative knowledge that subjects used in searching the model space while formulating their initial models and while using data from the experimental space to modify their current models. In particular, the protocols were examined for the critical knowledge used by the subjects to formulate and modify their models. What knowledge did they bring to the problem-solving environment that allowed them to formulate initial models? What knowledge did they utilize that prompted specific searches of the experimental space? What knowledge did they utilize from their experimental space searches that prompted them to modify their existing molecular models? The frames were examined for evidence of this knowledge that the subjects used as they searched both the model and experimental spaces.

In addressing the third research question, the protocols were also analyzed for

evidence of the strategic knowledge utilized by the subjects as they searched the model and experimental spaces. This is very much related to the second question of this study, but it differs in that the frames were inspected for the various heuristics and algorithms used by the subjects. In particular, the protocols were examined for evidence of the critical factors which prompted experimental space searches and the nature of the interaction between searching a space of models and a space of experiments.

Fourth, the protocols were analyzed for evidence of the criteria used by the subjects in accepting, rejecting, and refining their hypotheses about the final structure of the compound. That is, as addressed by the fourth research question, on what basis did the subjects evaluate their "final" proposed model and decide that it was indeed the structure of the unknown compound? After there was evidence in the protocols that the subjects had arrived at a solution to the problem, the subsequent frames were analyzed for the particular tests chosen by the subjects and the knowledge utilized by the subjects as they conducted experimental space searches to confirm in their minds the validity of the proposed molecular model.

Finally, the data obtained from analyzing the frames was applied to the theoretical model developed prior to data collection. This model was then modified to account for differences in the apparent strategies used by the subjects and those developed in advance of the research. As stated previously, the subjects in this study did not follow the expanded model of Subgoals A, B, and C. Consequently, the model proposed in this study after the analysis of the data is an expanded version of the general model in Figure 2 and accounts for the basic strategies used by the subjects in this study.

CHAPTER IV

ANALYSIS

Introduction

A total of eight doctoral level organic chemists participated as subjects in this research project. Data from the first subject was collected in August of 1998, and the final subject participated in June of 1999. Of the eight subjects, two (S2, S7) worked as chemists in industry, while the other six subjects worked in academia. Data were collected in sessions at Western Michigan University in Kalamazoo, Michigan, at Harding University in Searcy, Arkansas, or on site at the subjects' places of employment. Two of the subjects were female (S4, S6). All of the subjects were American and received their graduate degrees from institutions of higher education in the United States of America. Each subject agreed to volunteer without receiving financial compensation. However, the researcher did provide dinner for each subject after the sessions were over. All of the subjects who participated were recruited via e-mail correspondence and telephone conversation.

Originally, two practice problems and 17 other problems were selected for the subjects to solve. However, after the first two subjects completed their sessions it was clear that not all of these problems could be solved in the time volunteered by the subjects who participated in the study. Since the first two subjects were only able to solve the first practice problem and the first ten of the regular problems in the 3-5 hour time allotment, it was decided by the researcher that this would constitute the final problem set to be used in the study. This provided an equivalent data set for each subject to be used in analysis for this project. The second practice problem was eliminated because

each subject felt comfortable with the Identification of Organic Compounds[®] software and with the think-aloud procedure used in this research. The compounds which were used for problem-solving purposes in this research are listed in Table 4 below.

Table 4

Problems Solved by Subjects

	Compound	
Number	IUPAC Name	Alternate name
P1-practice	3-pentanol	Diethyl Carbinol
P3	2-methoxy-benzaldehyde	o-methoxy-benzaldehyde
P4	hexanedioic acid	adipic acid
P5	5-methyl-2-(1-methyl ethyl)-cyclohexanol	menthol
P6	4-Chloro-3-nitro-benzoic acid	—
P7	2-methyl-3-butyn-2-ol	2-hydroxy-2-methyl-3-butyne
P8	3-phenyl-2-propenal	cinnamaldehyde
P9	n-dipropylamine	N-Propyl -1- propamine
P10	ethyl cyanoacetate	ethyl cyanoethanoate
P11	3,7-dimethyl-6-octenal	citronellal
P12	quinoline	benzo[b]pyridine

Henceforth, these compounds will be referred to by the numbers designated in this table in the rest of this text.

Each of the eight subjects attempted to solve all of the problems in Table 4. A problem was determined to be solved when the subject either correctly elucidated the structure by spectroscopic means or determined its identity by the use of matching the melting points of derivatives with those found in the literature (Rappoport, 1984). In some cases the subjects used both techniques. If the subject did not arrive at the exact structure or identity of the compound, that problem was designated as unsolved. This was true even if the incorrect answers were subtly close to the correct answer. For example, if the chlorine and the nitro group were switched in P6, this constituted an incorrect answer even though all of the functional groups were correctly identified.

Table 5 provides the results of how the subjects performed in this problem-solving tasks. The percentage of the problems correctly solved by each subject is provided, along with a description of the overarching approach (spectroscopic means, derivatives, or both) which each subject used to solve each individual problem. Also, the percentage solved correctly is broken down according to problems and the approaches used by the subjects. One of the issues related to the teaching of qualitative analysis is whether or not the traditional wet chemistry techniques, including derivative formations, should be included in the curriculum in light of the power of spectroscopic techniques (Zubrick, 1992). The results of this research indicate that these techniques remain valuable. While the use of spectroscopic techniques was the primary means of solving the problems, the formation of derivatives to identify compounds was significantly utilized by these subjects. This was especially true on more complicated structures such as those in problems P5, P6, and P11. These compounds had structures that were difficult to elucidate perfectly with the spectroscopic data given to the subjects. Consequently, they formed derivatives to isolate the identity of the compounds when they needed to.

Table 5

Results by Subjects

	P1	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	%
S1	S	B	X	X	X	S	S	S	X	B	B	64
S2	S	X	S	S	X	S	S	S	S	S	X	73
S3	S	B	B	B	B	S	B	S	S	D	B	100
S4	B	B	S	X	B	X	B	S	X	D	S	73
S5	B	B	B	B	B	X	B	B	B	D	B	91
S6	X	X	X	X	X	S	B	B	X	D	D	46
S7	S	X	S	X	X	X	S	S	X	X	X	36
S8	S	S	S	S	X	S	S	S	S	X	S	82
%	88	63	75	50	38	63	100	100	50	75	75	71
%D	0	0	0	0	0	0	0	0	0	50	13	
%S	63	13	50	25	0	63	50	75	38	13	25	
%B	25	50	25	25	38	0	50	25	13	13	38	

X = did not solve correctly

D = solved by derivative only

S = solved by spectroscopic means only

B = solved by derivative and spectroscopic means.

From Table 5 it can be seen that the experts had varying degrees of success in correctly solving the problems, ranging from 100% to 36% correct. There are several

explanations why the experts were less than 100% efficient. First, as stated before, the criteria for solving the problem correctly was very strictly defined as 100% accuracy in the structure of the compound. Many problems were missed because of subtle differences in the subject's solution and the actual structure. Second, the data from instruments provided for the subjects was not necessarily as sophisticated as the data the subjects were accustomed to utilizing. All of the proton NMR data were from a 60-MHz instrument, and all of the mass spectral data were from a Electron Ionization (EI) mass spectrophotometer. In the case of the proton NMR, the available spectra may not have provided the degree of resolution the experts were used to. Likewise, the EI mass spectrum did not always contain the molecular ion peak. S2 stated that he had "electro-spray mass spectrum" to work on at his company, adding, "you see the parent [ion] in this case." Furthermore, he stated that in his normal procedure he would "do some other type of mass spectral work to make sure that you have that [parent peak]...". From that perspective, even though the subjects were solving the problems with fundamentally the same instrumentation, the differences that existed did seem to have some impact on their ability to successfully solve the problems in some instances. The data set for this research were chosen because it provided a realistic representation of the data an undergraduate student might be able to collect in solving qualitative analysis problems in organic chemistry lab. Even though it may have negatively impacted the percentage of the problems solved correctly by these experts, the problem sets and data need to be appropriate for undergraduate students who may participate in future research.

The Subjects

A brief description of the problem-solving setting and the demeanor of each subject may be appropriate for discussion. No two subjects approached the problems exactly the same way and each brought differing attitudes to the tasks.

Subject 1 (S1) was extremely conscientious about the assignment. He took the assignment very seriously and was willing to donate the most time. The problem-solving session, in fact, took place on three different days. He generated the most think-aloud protocol data. S1 is an academic in the latter part of his career. He correctly solved seven of the eleven problems. In his defense regarding the problems he missed, there were a few of the problems in which the spectral data in the computer program had weaknesses. In the scanning process there were subtle, yet important errors in the chemical shift in NMR data and in the wave numbers of the infrared data. For example, on P10 the computer program showed a major absorption at 1750 cm^{-1} , when the hard copy of the infrared spectrum showed the absorption at 1730 cm^{-1} . This subtle difference in wave number was significant enough to confuse the issue in the mind of S1 as to the way the carbonyl group was manifested in the compound. This type of inconsistency occurred on several of the spectra in the IOC[®] program. It was S1 who discovered most of these errors and it had an adverse effect on his problem-solving success. After these problems were discovered, the researcher made available hard copies of each spectrum for the problem-solver to utilize. The researcher presented it on all of the spectra with problems and offered it on other problems if the subject requested it.

Subject 2 (S2) was a younger man working in the pharmaceutical industry. He was also very conscientious and volunteered to solve problems on two different days. As a subject, his biggest problem was that he mumbled his thoughts inaudibly on many occasions. The researcher continually had to prompt the subject to "tell me what you're thinking" and "speak louder please." Consequently, much of his information processing was not captured on tape. Of all the subjects, his think-aloud protocol was the sparsest.

Subject 3 (S3) was the most successful of the subjects, solving each problem correctly. S3 was an academic in the middle to latter part of his career. He was very enthusiastic and enjoyed the challenge of solving the problems. His intuition was very

keen, but he was also very thorough with his problem-solving processes.

Subject 4 (S4) was a younger female academic. S4 commented that she used to enjoy solving problems on MacSQUALOR® in graduate school. She was also very enthusiastic about her participation in the project.

Subject 5 (S5) was also a male college professor in the middle to latter part of his career. He was very consistent in his problem-solving approach, in that he consistently solved the problems and then used a derivative to confirm his answer.

Subject 6 (S6) was a female college professor in the middle of her career. Of all of the subjects, she was the least conscientious. She would work rather hastily to solve the problem, arriving quickly at an answer that was often wrong. After missing the first five problems, she settled down and solved five of the remaining six correctly. After solving P9, she said, "Either I know it or I don't know it. ...there's no point just waffling about it. If I can't figure it out, then I can't figure it out." Early on, in her sessions she seemed to be in a hurry to arrive at an answer; but appeared to be a little embarrassed at missing the first five problems and she seemed to work harder to arrive at a reasonable answer after that, rather than just making an educated guess. S6 solved the second lowest percentage of problems correctly, at 46 percent.

Subject 7 (S7) was also a young, industrial chemist. He volunteered to be a subject after he got off work in the latter part of the work week. He clearly became fatigued during the session, and it greatly hindered his performance. Neither S2 nor S7 was very familiar with the wet chemistry techniques available to them in the IOC® software. Consequently, when S7 could not solve the problem spectroscopically, he was unable to make effective use of the wet chemistry tests available to him. S7 was the least effective problem-solver, getting only 36 percent of the problems correct.

Subject 8 (S8) was an academic in the middle of his career. While he was famil-

lar with the wet chemistry techniques, he attempted to solve all of the problems with spectroscopy first. He stated, "I really believe in emphasizing spectroscopy and everything that's involved with it." S8 was also very diligent in his problem-solving; all of the problems he missed were due to subtle differences in structure.

Since this research hinges on expertise in problem-solving, the six most successful problem-solvers S(1, 2, 3, 4, 5, 8) are the focus in the subsequent analysis of the results from this research.

Identification of Organic Compounds[®] Software

When MacSQUALOR[®] was originally chosen for this research project, it was hoped that it would provide a reasonable simulated experimental environment for solving qualitative organic analysis problems. The switch to Identification of Organic Compounds[®] (IOC[®]) was made by the president and owner of Trinity software. He wanted to re-enter the PC software business, and he was developing the IOC[®] program for that purpose. Since only the format and not the content of the two programs was different, it was not believed that it would affect the research adversely. In fact, one advantage of the IOC[®] was that, once the problem-solver "performed" an experiment, it would record the data in a simulated laboratory notebook. The subject could then refer to the notebook at any time during the problem-solving session.

As stated earlier, Trinity software added both the ¹³C NMR and mass spectral data to the problems selected for this research project. This was done during a approximately 5-month period of time from when hard copies were sent to Trinity and Trinity returned the IOC[®] software to this researcher.

Three problems were encountered when using the IOC[®] program. The first problem was probably the fault of this researcher and not the program itself. For some reason, the program did not keep a copy of the experimental searches used by S4. The

researcher had to reconstruct the computer movements by watching the video-tape of the session.

The second problem was related to the design of the software. The spectral data, when selected by the subject, constituted only a fraction of the computer screen in size. Consequently, the resolution of peaks in the spectra was minimal. The program does have a pointer function that allows the subject to point at a peak and the program will display for the subject the wave number of that particular peak in the Infrared spectrum, for example. Nevertheless, the lack of resolution did provide problems for the subjects when they attempted to scrutinize the spectral data. Similarly, the scanning process may have created some resolution that didn't really exist. In P3, 2-methoxybenzaldehyde the methyl peak in the proton NMR is a singlet. However, a slight notch in the peak makes it appear as if it may be a doublet. S3 noticed it at the end of the problem and looked back at the NMR to say, "This guy here, this methyl looks like a doublet, and it shouldn't be a doublet. But it sure looks like it. There must be some problem in reproduction." Figure 3 below shows the IOC[®] copy of the NMR in question.

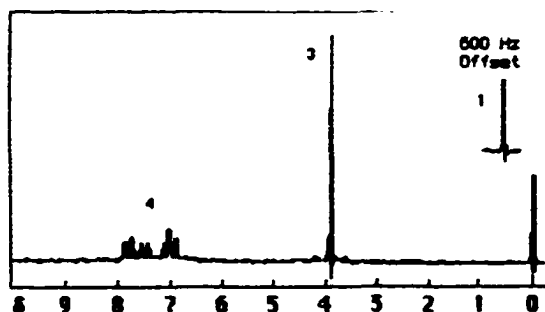


Figure 3. P3, 2-methoxybenzaldehyde Proton NMR from IOC[®].

Another example of poor resolution in an NMR spectrum was with P5, menthol. While the proton NMR is rather messy due to the large number of aliphatic carbons in

the compound, the IOC[®] program shows several of the peaks as indistinguishable bumps.

Figure 4 is the NMR spectrum from the software:

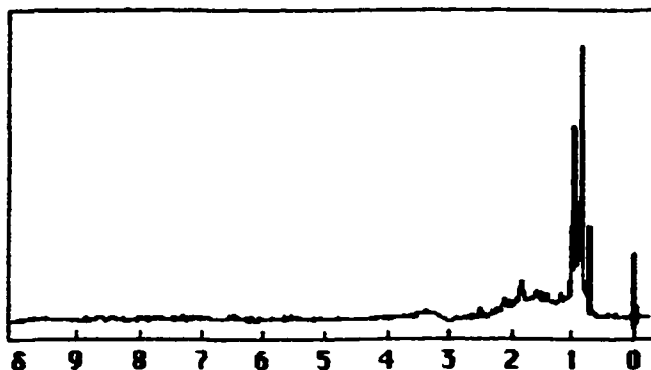


Figure 4. P5, Menthol Proton NMR from IOC[®].

The hard copy of the proton NMR from Aldrich shows in a much clearer fashion several of the aliphatic peaks:

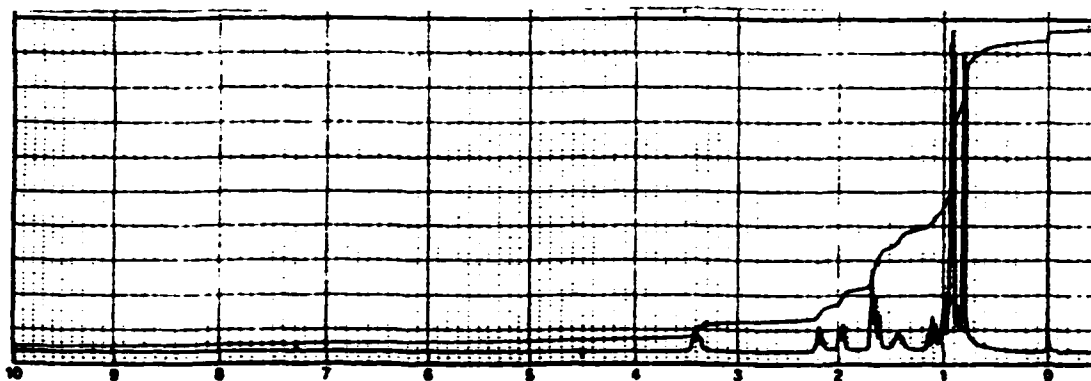


Figure 5. P5, Menthol Proton NMR from Aldrich[®].

The third problem related to errors in some of the spectral data. In the process of scanning the spectra data into the software, some erroneous depictions of chemical shift occurred. For example, one of the spectra that had a mistake in the IOC[®] software was the proton NMR for P8, cinnamaldehyde. In Figure 6, you can see that the IOC[®] inte-

gration, while on the surface appears proper, in reality is incorrect. Furthermore, the chemical shift of the doublet of doublets is incorrect.

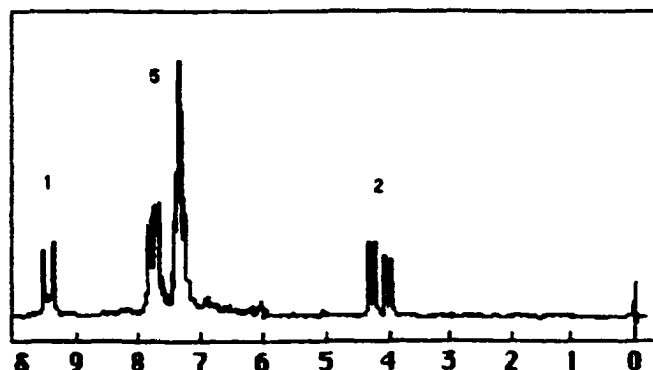


Figure 6. P8, Cinnamaldehyde Proton NMR from IOC®.

Figure 7 shows the hard copy of the proton NMR spectrum for cinnamaldehyde:

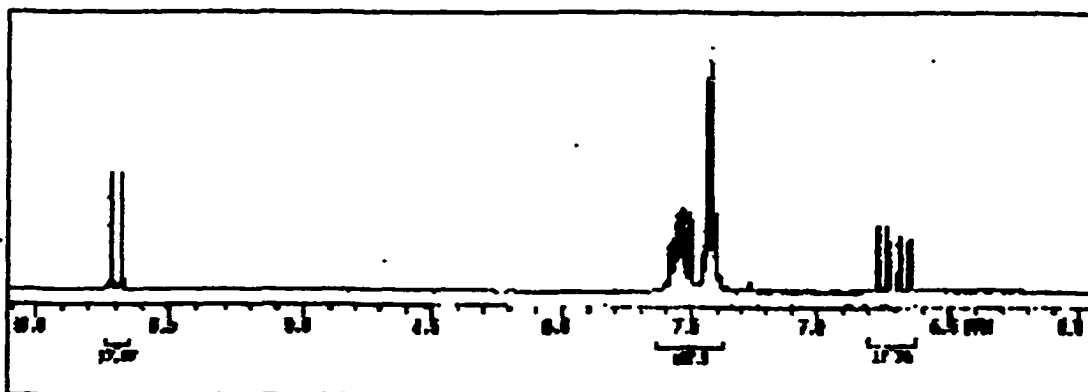


Figure 7. P8, Cinnamaldehyde Proton NMR from Tomasi.

Instead of the doublet of doublets chemical shift being at approximately 4 δ , as it is in the software, the actual shift is at 6.7 δ . Furthermore, the proton alpha to the phenyl ring actually appears as part of the ring integration. The integration should be 1,6,1, rather than the 1,5,2 integration found in the IOC® program. For a novice, this might not create a problem. In fact, the 1,5,2 integration of the spectrum in the IOC® program

may actually seem more reasonable to a novice; but the experts possessed the declarative knowledge to realize the error in the program.

The errors in the spectra created some difficulty for the first subject in particular, although other subjects noticed some of the mistakes as well. However, the researcher gave the subjects hard copies of each spectra to view when there was a clear error in the spectrum, and the researcher allowed them to view other hard copies of spectra to allow for better resolution when the hard copies were available. This did not interfere with the problem-solving of the subjects, and the video-tape allowed the researcher to capture the use of the spectra for the purposes of constructing the frames.

Clearly, these are areas that need to be resolved before IOC[®] can become an effective tool to be integrated into the curriculum as a realistic computer-based problem-solving environment. Each spectrum in the simulation should be closely inspected, and correction should be made if there are discrepancies between a simulation and the actual spectrum of a compound. The programming format could be changed also to allow for increased viewing size and better resolution when spectral data are viewed.

One of the most positive aspects of the software as a problem-solving environment is the way in which data are reported to the subject. All data are presented as observations, not interpretations. Figure 8 is a sample laboratory report printout from the IOC[®]. This is a realistic means for presentation of the data. The subject should be able to determine the significance of solubility in sodium bicarbonate or the appearance of a silvery surface during a Tollen's test. IOC[®] presents such data in a manner consistent with laboratory experiments. Students utilizing this software to deepen their understanding of qualitative organic analysis would either have to possess the declarative knowledge needed to interpret the results or have to search references for that information. The "help" function in the program does allow for such a search, but the user must

Identification of Organic Compounds — Laboratory Report**S1****Assigned Unknown #11 (3, 7-Dimethyl-6-octenal)****Remaining Points: 200 Remaining Quantity: 3.5 mL****Analysis Started: January 14, 1999****Not Identified Yet****• Physical Properties Jan. 14 (10:05 a.m.)****Yellow Liquid****bp 200-209°C****%C = 77.87; %H = 11.76****• Solubility Tests Jan. 14 (10:07 a.m.)****In water . . . insoluble****In 5% hydrochloric acid . . . insoluble****In 5% sodium hydroxide . . . insoluble****In conc. sulfuric acid . . . soluble****• Infrared Spectrum Jan. 14 (10:17 a.m.)****• NMR Spectrum Jan. 14 (10:21 a.m.)****• Mass Spectrum Jan. 14 (10:28 a.m.)****• 2, 4-DNP Test Jan. 14 (10:32 a.m.)****When the unknown is treated with an acidified ethanolic solution of 2,4-dinitrophenylhydrazine a yellow precipitate is formed.****• Bromine in CCl₄ Test Jan. 14 (10:34 a.m.)****A solution of bromine in carbon tetrachloride is added to the unknown which is also dissolved in carbon tetrachloride. More than 35 drops of the test solution are decolorized.****• Tollen's Test Jan. 14 (10:55 a.m.)****Fresh reagent is prepared by adding 1 drop of NaOH to a silver nitrate solution. Then enough ammonia is added to dissolve the precipitate. When the unknown is added, a bright, silvery mirror forms on the inside of the test tube.****• Potassium Permanganate Test Jan. 14 (10:58 a.m.)****The unknown is dissolved in ethanol and water and a test solution of aqueous potassium permanganate is added. The purple color is discharged and a brown precipitate appears.****• Semicarbazone Derivative Jan. 14 (11:05 a.m.)****A crystalline derivative is formed. Recrystallization yielded a White Solid, mp 77-81°C.****• 2, 4-DNP Derivative Jan. 14 (11:05 a.m.)****A crystalline derivative is formed. Recrystallization yielded a Yellow Solid, mp 75-78°C.**

Figure 8. Sample IOC® Laboratory Notebook.

initiate the search. The answers are not automatically provided.

While the subjects in this study were not allowed to utilize the compound data base found in the software, the data base did seem rather small. A student utilizing the data base might be able to “guess” the compound relatively easily from the list of possibilities since the selection in the program is limited. If IOC[®] were to be used in the undergraduate setting to teach problem-solving, it might be desirable to limit access to this database. Alternatively, Trinity would have to increase significantly the number of compounds found in the database.

Overall, the ability of IOC[®] to elicit expert performance was hindered by the lack of resolution in the spectra and by the errors contained in a number of the spectra. This researcher was able to make use of hard copies of the spectra to compensate for these problems. However, the software package should be thoroughly checked and corrected to increase its potential to be a viable problem-solving tool in the domain of qualitative organic analysis.

Research Question 1

The development of technology has created a shift from traditional wet chemistry techniques to instrumental techniques of solving problems in chemistry. This is true in many branches of chemistry, including qualitative organic analysis. Zubrick (1992) argued that the teaching of the wet chemistry procedures in qualitative analysis as obsolete for this reason. This challenge led to the first research question in this study. Would the experts utilize wet chemistry techniques or spectroscopic means or both to solve the problems? That is, what combinations of chemical tests and spectrometry would be used by experts in searching the experimental space, allowing them to be effective problem-solvers of qualitative organic analysis problems? This was the preliminary ques-

tion: Would the experts use traditional approaches, utilizing both wet and spectroscopic tests as described in Shriner, et. al. (1998), or would they rely on spectroscopic means only as described in Silverstein & Webster (1998) and Feinstein (1995)?

Table 6 provides an overview of the percentage of the problems in which a particular subject utilized a technique found in the IOC[®] program. These raw data show that the subjects utilized the spectroscopic techniques more often in their problem-solving than they did the wet chemistry procedures. Proton NMR was the most utilized instrument. The only time it was not utilized was by S1 in the solving of P12. In that problem, the subject was able to deduce the presence of nitrogen by solubility tests and calculate the molecular formula of C₉H₇N. This greatly limited the model space, and he hypothesized the structure of quinoline based upon the formula. He then confirmed

Table 6

Percent Utilization of the Experimental Space in IOC[®] by Subject

	Solubility	Fusion	IR	H-NMR	C-13 NMR	Mass Spec.	Classi- fication	Deriva- tives
S1	91	73	73	91	73	82	64	55
S2	9	9	64	100	91	91	91	9
S3	91	64	100	100	100	36	36	64
S4	82	27	100	100	100	64	9	55
S5	100	27	91	100	64	55	82	100
S6	9	73	91	100	9	18	82	91
S7	45	0	100	100	100	100	55	9
S8	27	55	100	100	100	82	18	0
Avg.	57	41	90	99	80	66	55	48

the identity with a derivative. If not for this problem, the proton NMR would have been used in every problem by every subject. This is not surprising since the proton NMR is a powerful tool for structure elucidation. The proton NMR provides the greatest information about the arrangement of the components that make up the compound.

The wet chemistry tests were not utilized nearly as often as the spectroscopic techniques. The fusion tests were performed the least, being used in 40.9 % of the problems, whereas the classification tests and the solubility tests were the wet chemistry test that were used the most at 55.7 % and 56.8 %, respectively.

Subjects S2 and S7, the two industrial chemists, were not familiar with most of these techniques. During the initial explanation of the IOC[®] program, the researcher engaged in this conversation with S7:

R: If you pull on experiments here [on the computer], click on experiments so you can see what's here. You can test solubilities, sodium fusion tests if you need those, classification tests, and

S7: Functionalities?

R: Yes.

S7: Some of those I'm not familiar with.

At the completion of the first practice problem, P1, he stated:

S7: You know, I am not sure that if you're asking me what would I do if I were in a lab in this day and age, I am not sure I would do many of these [points to classification tests].

R: Right. Basically, if you can't get it from the spectral data, you...

S7: probably aren't going to get it. I mean I would start, if I went through here [classification test inventory], it would, I would probably start doing things outside what I would normally do. But a few of these I am familiar with, such as bromine water. I understand some of that - potassium permanganate. Got those, but uh, I don't want to start...

Later he was asked as a follow-up question:

R: ...Did they do that [spectroscopy only] at [name of his undergraduate chemistry program], or did they do all the wet chemistry stuff and...?

S7: Yeah, we would have. But I think back on graduate school and what we would have done.

R: Right, and graduate school is where you..?

S7: Yeah, we had whole classes where this [spectral data] is all we had...

R: Right.

S7: the whole class, and so that is where I tend to migrate first. (S7-V1, T1)

From this dialogue, S7 indicated that his training at the Graduate School level did not utilize the wet chemistry techniques in the solving of qualitative analysis problems. He made it clear that the utilization of these tests were not part of his normal problem-solving strategies. During P6 this subject had difficulty resolving some functional group issues. He conducted a 2,4 - DNP test, solubility, and a neutralization equivalent. He then started searching the classification test options and stated: S7: "I guess, I was starting to give you the things I wouldn't normally do in the lab." (S7-V1, T1) Clearly, S7 did not possess the declarative knowledge pertaining to most wet chemistry tests used in qualitative analysis. He utilized them only when he was stumped by the spectral data. When he did use the wet chemistry he was most often conducting a random search of the experimental space available.

S2, also an industrial chemist, utilized wet chemistry sparingly as well. He did use it more often than S7, but his use of these tests was also generally based upon exploration rather than purposeful testing. A prime example of this was during the working of P6. During that problem he conducted seven different classification tests and attempted to make six derivatives. He consulted the "help" function that explained the chemistry of these tests six times and searched the index of appropriate tests five times.

About midway through the problem-solving process, he stated: I'm just kind of randomly looking for simple tests that I know, and I am not finding anything." (S2-V2, T3) At the conclusion of the problem, he stated, " In order to know what's in there you have to, in this case, you have to do all these tests, which I obviously did not know." (S2-V2, T3)

At the conclusion of P6 [4-chloro-3-nitro-benzoic acid], S2 went on to detail why he does not normally need to know all of the wet chemistry tests in his job.

S2: When I put down my compounds, well in the laboratory, I have a big advantage because I know what I have put into the flask, which is enormously helpful. And I'm trying to figure out what has happened [to the reactants]. I usually do not, have not, identified a lot of the aromatic compounds like this, substituted nitro-, chloro-, and so forth. So the only way to figure out what [it is] is on the wing, is by going through all the various qualitative organic tests. (S2-V2, T3)

Of the subjects from academia, S8 used the wet chemistry tests the least. He never took a derivative and only utilized classification tests on two of the problems. At the start of P5 he stated, " I really believe in emphasizing spectroscopy and everything that's involved with it." (S8-V1, T1) When he had difficulty and failed to solve P6, he said, "Maybe I should have looked at the elemental analysis and things. I didn't look at that. I was merely trying to do it from spectra." (S8-V1, T2) It was obvious he believed spectroscopy to be the most appropriate means of problem-solving in qualitative organic analysis. Nevertheless, he did utilize some of the wet chemistry tests when he was unable to resolve all of the issues raised by the spectra.

In contrast S5, took a derivative on every problem, either to confirm a proposed structure or, as in P11, to determine the structure. With the exception of S8, the subjects from academia generally made use of traditional techniques in qualitative analysis. That is, while they made extensive use of the spectrometric data, they also included the wet

chemistry as an integral part of their problem-solving strategies. Solubility was used extensively to provide indication, after the initial elemental analysis, of how a heteroatom would manifest itself as either an acidic, basic, or neutral functional group. It was used an average of 75 percent of the time by the remaining five academicians (S1, S3, S4, S5, S6). S6 did not utilize solubility very much (9%), but this subject was the least effective problem-solver of the group. If S6 is excluded from the average, the percent rises to 91 percent usage. S3 at the beginning of P1 provided insight into the reason he started with solubility in almost every problem.

"I'm going to do solubility test. Soluble in water, insoluble in these guys [5% HCl, 5% NaHCO₃, etc.] , soluble, okay. So I'm going to guess that it's probably some sort of neutral aldehyde, ketone, or alcohol and I'm going to try an infrared [to determine] which of those it is." (S3-V1, T1)

Sodium fusion, classification tests, and derivatives were used by these five academicians to a lesser but significant extent. See Table 6. When S3 ran into a roadblock on P6, he turned to sodium fusion tests. He had correctly deduced that the compound was an aromatic carboxylic acid using solubility, infrared, and NMR data; but he had also decided that there must be another heteroatom element present besides oxygen because he could not resolve discrepancies in the percent composition. S3 stated,

"I'm thinking that maybe I'm making a false assumption when I assume that, that it has no other element in it, [that] it's got to be oxygen. Um... I'm going to try for some odd element at this point." (S3-V1, T2)

He went on to discover that both chlorine and nitrogen were also components of the compound, and he eventually solved the problem correctly. This was one of his longest problems to solve, and the events did seem to impact his strategy on future problems. Before this, he had not utilized the fusion test option. After P6 he used sodium fusion on every problem, very early in the problem-solving process, along with solubility. At the start of P7, right after testing solubility, he said, "I'm going to start

getting smarter; we're going to do the sodium fusion test." (S3-V1, T2) This change is a reflection of two things. One is the subject's ability to make adaptations in problem-solving strategy when called upon. The second, indicates the problem with a computer based environment as a research tool. It is unclear if the subject would have started doing sodium fusion tests if he had actually been doing the analysis in the laboratory. The ease at which subjects can "conduct" a test in the computer environment may have caused S3, in this case, to adopt an altered strategy based upon the problems he encountered in P6. All of the subjects were admonished to use the same tactics they would actually use if they were physically performing the experiments. However, from this data it is not really possible to determine whether or not the inclusion of fusion tests would have been his strategy in an actual experimental environment.

Classification tests were also used by these five academicians in slightly over half of the problems. They were generally used for two purposes. The first purpose was to confirm the presence of a functional group when their other data were inconclusive to them. S3, during the solving of P3, took an infrared spectrum. The evidence in the spectrum could not allow him to distinguish between a ketone or an aldehyde functional group with complete confidence. Consequently, he performed a Tollen's test to provide the additional evidence to make the distinction.

S3: Try an infrared again. Ah, and this time it's not an alcohol, it uh...peak at 1690, which looks like an aldehyde or ketone that's conjugated with a ring. And there's a ring right here that looks like it might be an aldehyde, an aldehyde CH. Uh, perhaps that will be my guess right now. . . . Anyway, let's go back up here and try . . . classification test. I want to do, uh, Tollen's test. And uh, so we got a silver mirror, so it is probably, so it is an aldehyde. (S3-V1, T1)

A second way in which the classification tests were used was to distinguish whether a functional group was primary, secondary, or tertiary. S1 performed a chromic acid test during the solving of P5.

S1: I'm going to see if I can get some evidence as to whether this is a primary, secondary, or tertiary alcohol before I look at the NMR spectrum, or the mass spectrum. The chromic acid test. . . . [Reading] 'Several drops of chromic acid reagent are added to a solution of the unknown and reagent grade acetone. After about three seconds, a green precipitate appears.' Probably a primary alcohol, could be secondary, however. Um . . . probably primary. Maybe secondary. (S1-V3, T4)

From the protocols, it is quite evident that there was a difference in the combinations of tests utilized by the chemists in industry and academia. Neither of the industrial chemists made use of the wet chemistry unless they reached impasses with the spectral data. When they did utilize traditional tests, they were often searching an experimental space with which they were unfamiliar. S8 was the only professor to avoid the wet chemistry, and that was by design. He felt that spectroscopy is the contemporary way to solve the problems, so he did not use many of the traditional techniques. It should be noted that while their first choice was to use the spectral data, the industrial chemists did make use of the wet chemistry when needed. The spectral data provided - in this study, at least - did not allow subjects to solve all of the problems using those experiments only. The industrial chemists did, on a number of problems, have conflicts in their models. When this arose, they decided that the wet chemistry would provide more functional and structural information than reassessing the spectral data repeatedly. Even though they may not have opted for the wet chemistry test as a first option, the wet chemistry did assist them in the problem-solving process.

It would appear that the combination of spectroscopy with wet chemistry experiments was an integral part of the problem-solving model used by the other five chemists. No doubt, the curriculum they teach in the various undergraduate organic chemistry programs contain many of these traditional tests (Shriner, et al, 1998; Morrison & Boyd, 1992; Solomons, 1996; Streitweiser, et al, 1992).

Research Question 2

Declarative and Strategic Knowledge

The experts in this study were able to successfully solve qualitative analysis problems by utilizing domain specific declarative knowledge.

While the declarative knowledge of the subjects in this study was considerable, there was a significant difference in the declarative knowledge possessed by the academic chemists and the industrial chemists. Unlike the academics, the industrial chemists, S2 and S7, did not possess much declarative knowledge about the traditional wet chemistry techniques of qualitative analysis. While S8 may have possessed the necessary declarative knowledge of these particular techniques, he opted not to utilize them with any frequency. The remaining subjects demonstrated significant declarative knowledge about most of the techniques, both wet chemistry and spectroscopic. However, in all cases, the subjects indicated different degrees of confidence in a particular instrument or test when compared to the rest of the tests. In other words, there were certain instruments that they utilized but were not completely comfortable or able to interpret to the degree they would have liked. For example, S1 stated, "I'm not as good a mass spectroscopist as I ought to be." (S1-V4, T6) Even though they may not have felt as comfortable with some of the data, they still exhibited significant declarative knowledge pertaining to the model-building aspects of the data. In this section of the dissertation, examples from the protocols will be examined, showing evidence of declarative and strategic knowledge pertaining to each type of experiment in the IOC®. It will not be possible to capture examples of all the types of declarative and strategic knowledge utilized by the subjects. These examples will by no means be exhaustive, but will be representative. The intention here is to provide a glimpse into the types and degree of declarative and strategic knowledge these particular subjects possessed and applied to

solving the problems in this study. The traditional wet chemistry experiments will be discussed first, followed by the instrumental methods.

Physical Properties

While all of the subjects may have been able to make inferences about an unknown based upon the phase change temperatures and the color of the unknown only S1 verbalized extensively about the significance of the physical properties. The other seven subjects usually did not make much commentary, other than to make note of the physical properties verbally or on paper. S1, however, made numerous statements about physical properties and made these inferences about P3 at the start of the problem:

All right, I've got a colorless liquid, boiling point 240 to 246 degrees. Tells me, um, probably have quite a bit of intermolecular associations going on and a compound that probably [is] not very susceptible to oxidation.... (S1-V1, T1)

S1 knew that significant polarity and hydrogen bonding cause "intermolecular associations" that result in high boiling point temperatures. Retrospectively, he said that he concluded the compound was not very susceptible to oxidation because it was colorless. Certain classes of compounds, like amines, auto-oxidize and are typically yellow to brown. Extensive conjugation can also produce colored compounds. He did not refer to this here, but on P1, another colorless compound, he also stated,

Since it's a colorless liquid would imply that it is not compound susceptible to light deterioration, taking on colored contaminants due to exposure.... Since it's a colorless liquid, this tells me that it does not have a great deal of conjugation in the molecule. Maybe, totally unconjugated. It does not have a characteristic chromophore. (S1-V1, T1)

Based upon color, S1 was able to draw inferences about the functional groups of the molecule that were not present in both cases. Similarly, the presence of color evoked knowledge about the compound that initially limited the problem space. On P12, S1

said, "I have a brown liquid, which tells me that it once again may be an amine." (S1-V5, T10)

The other subjects probably also possessed this knowledge, but they usually did not make much commentary about the physical properties. Rather these subjects just made note of it for future reference in the problem-solving process, when they sometimes compared the melting point or boiling point temperatures of the unknown to those of compounds found in a reference (Rappoport, 1984).

Fusion Tests

Based upon verbal protocols and frequency of utilization (See Table 6 - Research Question 1) the subjects' knowledge of the sodium fusion tests was more limited than any other type of experiment. As expected, the industrial chemists, S2 and S7, were not familiar with these experimental procedures. S7 never used the fusion tests, and S2 utilized them only once on P6. Sometime late in the problem-solving process on P6, S2 said he was "just kind of randomly looking for simple tests that I know and I'm not finding anything." (S2-V2, T3) When he did perform the tests, he had to read extensively from the sodium fusion help function to understand the results. Later, on P10, he commented, "I don't want to have to use that crazy sodium fusion test again." (S2-V2, T4) Clearly, neither of these subjects was familiar with these procedures.

Even the chemists who took the more traditional qualitative analysis approach of wet chemistry combined with spectroscopy did not seem to be able to recall information pertaining to these tests without extensive thought or reading of the help function in the program. S3, first used the fusion tests on P6. After performing the test, he read aloud the all of the results and finally commented,

I'm not up on all this kind of chemistry, so I'm going to have to think about this a little bit....Heated and acidified with sulfuric acid and an

intense blue color resulted. I don't know what that means. The part that was treated with lead acetate means that there was no sulfur, but I'm not sure what the deep blue color means. I'm going to find out about sodium fusion. (S3-V1, T2)

S3 then read from Shriner et al. (1998) for information of the interpretation of the sodium fusion tests. Apparently, the sodium fusion test is not a procedure used regularly in his work. He had partial recall of the significance of the results but needed to refresh his memory on the complete interpretation.

S4 first commented upon the sodium fusion test in P3 and, based upon these comments, appeared to be familiar with interpreting the test:

Could be a nitro group or something fun like that. Let's see that would mean, well I like the sodium fusion test for that. Let's see here. Okay, so there is no fluorine, and I think silver nitrate. Okay, so there is really nothing there other than carbon, hydrogen, and oxygen. (S4-V1, T1)

In the previous example, S4 was able to interpret the data easily since the observations reported by the computer were "no observable change." The next time she performed the sodium fusion tests was in P7. Here it is less clear how confident she was in interpreting the results. In fact, she checked the fusion help function to make sure of her interpretation.

There's got to be something other than just carbons in this compound. I'm going to look at sodium fusion tests. I know that it's not chlorine or bromine. Okay, there is no nitrogen either, based upon those, if I remember my fusion stuff correctly. (S4-V1, T2)

S (1, 5, 6) appeared to be more familiar with the sodium fusion tests, with S1 and S6 using this procedure the most. On P4, based upon the Beilstein test, S6 inferred that a halogen might be present in the compound. She could not resolve that with the other data she collected and turned to the sodium fusion tests.

I just don't think I'm seeing evidence there for it to be a chlorine. Guess I could look at the sodium fusion. Silver nitrate, white precipitate, sug-

gests chlorine. For silver chloride is white, whereas silver bromide is kind of tan colored. So now if that's the case.... (S6-V1, T1)

Likewise, S1 frequently used the fusion tests in his problem-solving. On the very first problem, P1, had determined an empirical formula, and the solubility tests had been inconclusive about possible functional groups so he turned to the fusion tests.

So I really didn't learn anything from that [solubility]. I expected all of those. And so, sodium fusion tests. I'll just anticipate here. I like to be predictive whenever I can. This is going to tell me that it doesn't have any halogens or sulfur or nitrogen. Maybe it will tell me something. (S1-V1, T1)

Most subjects didn't know anything about the tests, or they had to refresh their memories to interpret the results properly. From this evidence it can be concluded that the use of sodium fusion tests was not an initial strategy that the subjects used when solving problems. Only S1 and S6 used the sodium fusion tests frequently in this study. These two subjects were the same subjects who approached the problems by determining the empirical formula initially as part of the Subgoal A strategy. From this combination of evidence, it appears that S1 and S6 were the most traditional in their approach to the qualitative analysis, making extensive use of classical wet chemistry techniques and calculating an empirical formula before extensive probing of Subgoals B and C.

Solubility

Four of the subjects, S (1, 3, 4, 5) made extensive use of solubility, particularly as an initial or secondary move to gain insight into functional groups (See Table 6). Using this data, these subjects were able to glean significant information about the compounds, and their next searches tended to be guided by positive test results about a particular functionality. Protocol examples are provided here from each of these four subjects to give an overview of the declarative knowledge these subjects demonstrated

regarding the solubility tests. S1 on the first problem clearly demonstrated this knowledge.

Okay, solubility. I like solubility for supplemental information. Very, very, quickly. So, I'm going to look at solubility. Slightly water soluble. Insoluble in hydrochloric acid which you would expect for just about anything with that chemical composition. Likewise, the sodium bicarbonate doesn't tell me much because I'm not expecting it to be a carboxylic acid. I would expect it to be insoluble in sodium bicarbonate regardless. At least I can't think of anything that $C_5H_{12}O$ would be, likely be, soluble in sodium bicarbonate. And likewise, sodium hydroxide, that doesn't tell me anything. Because I can't imagine it would be a weak base with that molecular formula. And I do expect it to be soluble in concentrated sulfuric acid because it's an oxygen-containing compound. It's a weak brönsted base. So, I really didn't learn anything. I expected all of those. (S1-V1, T1)

Even though he claimed that the results did not tell him anything, in actuality the results confirmed hypotheses he had formulated based upon the empirical formula of $C_5H_{12}O$, which he had calculated with the assumption that oxygen was the heteroatom present in the compound. S1 expected that the compound would be insoluble in hydrochloric acid, because only significant bases like amines are soluble in an acidic solution based upon the Brönsted-Lowry acid-base theory. With only one oxygen in the formula, the compound could not be a carboxylic acid, which he anticipated by the lack of solubility in sodium bicarbonate. Finally, he acknowledged the solubility of the compound in sulfuric acid as characteristic of monofunctional oxygen-containing compounds of its size. Thus, while he may not have gained new model-building information from the solubility tests in this case, his knowledge about solubility theory allowed him to confirm the reasonableness of the empirical formula and the possible functional groups in the unknown.

In another example, S3 on P4 immediately inferred the presence of a strongly acidic functional group based upon the compound's solubility in sodium bicarbonate.

I'm going to do the solubility test again. Soluble in hot water. Soluble in sodium bicarb. Soluble in sodium hydroxide. So it looks like a carboxylic acid. (S3-V1, T1)

Similarly, S4 on P4 made similar, but expanded, inferences about the compound when she chose solubility at the start of the problem.

Okay, just because I like solubility. Soluble in hot water, soluble in bicarb, and hydroxide which means it's weakly acidic. I'm sorry, strongly acidic. Quite possibly a carboxylic acid. Maybe a phenol, depending upon what else is on the ring. (S4-V1, T1)

S4 knew that, besides carboxylic acids, phenols can also be strongly acidic if there are strong electron-drawing substituents on the benzene ring, making the phenol proton easier to react.

As a final example, S5 tested the solubility of P5, which proved to be insoluble in the hydrochloric acid, sodium bicarbonate, and sodium hydroxide solutions, but soluble in sulfuric acid. From that he was able to infer basic functionalities. "Solubility test. Slightly soluble in water, but neutral. So may be a mono-functional neutral compound". (S5-V1, T1) Menthol, P5, a mono-functional alcohol, fits this solubility profile, which is characteristic of alcohols, aldehydes, ketones, and esters with only one functional group. Clearly, S5 was thoroughly familiar with the solubilities of the various classes of organic compounds.

The remaining four subjects, S (2, 6, 7, 8) did not make nearly as much use of solubility. S2 and S6 utilized solubility only once each. When S2 used it, he made no verbalizations that would indicate that he was or was not able to infer useful information from the solubility profile. S6, however, utilized it on P12 after noting, "Brown liquid, could be an amine." The solubility of the compound in hydrochloric acid led her to conclude that it was "definitely an amine." (S6-V2, T2) Based upon this, it would appear that she possessed at least some declarative knowledge comparable to the four

subjects who used solubility regularly, even though solubility was not part of her normal problem-solving strategy. Neither S7 nor S8 chose to use solubility much, but when they did they possessed sufficient declarative knowledge to interpret the observations correctly. On P4, S7 hypothesized a symmetrical ketone based upon NMR and mass spectral data and then opted to perform the solubility tests.

Let's look at solubility tests and see what it says. Okay water soluble, water soluble in hot water. Five percent HCl is insoluble, so that probably knocks out an amine of any sort. Amines would protonate and form a salt, and it would be soluble. Sodium bicarbonate, soluble in that. That means it may be some acidic functional group. (S7-V1, T1)

S7 switched his hypothesis to a carboxylic acid and proceeded to search the infrared spectrum for confirmation of this new finding.

Likewise, S8 also demonstrated proper knowledge of solubility when he reluctantly chose to use it on P6.

I'm going to look under the IR and maybe I can get a little wet chemistry. I reckon he [the programmer] is going to make you do something like solubility. It's insoluble in water, hydrochloric. Soluble in sodium bicarbonate, soluble in sodium hydroxide, and concentrated sulfuric acid. Okay. So it ought to be a carboxylic acid. (S8-V1, T2)

From this evidence each subject, with the exception of S2, demonstrated the declarative knowledge pertaining to solubility tests. Only S (1, 3, 4, 5) chose to make solubility a regular part of their problem-solving process, but S (6, 7, 8) did on occasion make use of this knowledge, when the situation dictated to them the need to use solubility.

Classification Tests

Twenty one different classification tests are programmed into the IOC[®] software. Table 7 shows the functional group information that can be gained by each

Table 7
Use of the Classification Tests by Subject

Test	Functional Group	S1	S2	S3	S4	S5	S6	S7	S8	Total
Beilstein	halogen	2	1			1	2			6
Combustion	aromaticity	1								1
2,4-DNP	carbonyl	4		1		4	1	3		13
Tollen's	aldehyde	1	3	3			1		2	10
Chromic acid	aldehydes 1 ^o ,2 ^o alcohols	4	1		1	4	2			12
Iodoform	methyl ketones (methyl) alcohols	3						1		4
Bromine/CCl ₄	unsaturation	4	1					4	2	11
Bromine/water	phenols		1			1				2
Ferric Chloride	phenols	1								1
Hinsberg	amines		2	1		2	1			6
Nitrous Acid	amines		1							1
KMnO ₄	unsaturation	1						2		3
Acetyl Chloride	alcohols amines									
		2	3							5
Lucas	alcohols	3	1		1		2			7
Ferric hydroxamate	esters	2				1	3			6
Ferrous hydroxide	nitro		1							1
Silver nitrate	halogens	3	1							4
Silver nitrate/ nitric acid	carboxylic acid	1								1
Basic hydrolysis	esters	1	2							3
Basis hydrolysis/ test for NH ₃	amides, nitriles									0
pH of Ethanol/ water	acid/base		4							4
Totals		33	22	5	2	13	12	10	4	

test as it pertains to these problems and the frequency of use for each of these tests by subject. While the numbers may be small for each classification test, this is logical. A subject would not utilize the 2,4-DNP test unless he or she believed a carbonyl functional group to be present and wanted to distinguish between an aldehyde and a ketone. With evidence from the infrared, for example, indicating that no carbonyl group was present, a subject would not have any reason to utilize the 2,4-DNP test. Consequently, particular classification tests were utilized for specific situations as other evidence dictated the need. Classification tests were almost always utilized for confirmation purposes or to determine if a functional group was primary secondary, or tertiary in its structural arrangement. When utilized in this manner, a classification test also provide information from Subgoal C.

S1 made the most extensive use of searching the classification tests experimental space. While he did not have the highest percentage of usage across the problems (Table 6), numerically he did use them significantly more than the other subjects. S1 was readily willing to follow the traditional qualitative analysis strategy of using classification tests. This use of classification tests is consistent with the initial Subgoal A strategy he used on most problems. On each of the four problems in which he did not use a classification test, he reached a solution with relative ease and did not feel the need to probe this aspect of the experimental space.

The most common way in which classification tests were used was to confirm the presence of a functional group. On P5, S1 had calculated that the empirical formula was $C_{10}H_{20}O$, with one degree of unsaturation. Furthermore, from the solubility tests he concluded that the compound was neutral and mono-functional.

That means we have one degree of unsaturation. So it can't be aromatic. The site of unsaturation will either have to be a carbon-carbon or a carbon-oxygen, so let's do an experiment here, and look for bromine in

carbon tet. [Performs Bromine/ CCl_4 test]. Solution of bromine and carbon tet was added to the unknown to which it dissolved in carbon tet. The red bromine color persists after three drops are added. So that tells me that we're not looking at a carbon-carbon double bond. We're looking most likely at a carbon-oxygen double bond. So putting things back into a somewhat a mental perspective, we have a neutral compound [based upon solubility] that probably at this point is either an aldehyde or a ketone. It does not contain carbon-carbon double bonds and I'm really resisting the temptation to go immediately to the spectra, but I'm going to. I'm going to look at the 2,4-DNP. [Performs 2,4-DNP test] The unknown was treated with an acidified ethanolic solution with 2,4-DNP. No visible precipitate is observed. Okay, have it your way. That tells me that my site of unsaturation is probably a ring instead of an aldehyde or ketone. Let's look at the spectrum. (S1-V3, T4)

S1 systematically used the classification tests to eliminate functional groups and confirm which neutral functional group was present. The bromine in carbon tetrachloride test results eliminate a carbon-carbon site of unsaturation. He then performed the 2,4-DNP to distinguish between an aldehyde and a ketone, the two remaining functional groups consistent with his empirical formula. When neither of those tests was positive, he postulated that the compound must consist of a ring to account for the unsaturation. S1 then viewed the infrared spectrum to confirm the results of the classification tests and determined the oxygen to be present as an aliphatic alcohol. He then proceeded to utilize the classification tests in the secondary way they were utilized: to determine whether the functional group was primary, secondary, or tertiary.

I'm going to see if I can get some evidence as to whether this is a primary, secondary, or tertiary alcohol before I look at the mass, before I look at the NMR spectrum, or the mass spectrum. The chromic acid test. [Performs chromic acid test] Several drops of the chromic acid reagent are added to a solution of the unknown and reagent grade acetone. After about three seconds a green precipitate appears. Probably a primary alcohol, could be secondary, however. Probably primary. May be secondary. (S1-V3, T4)

This example from S1's protocol is representative of his knowledge pertaining

to the classification tests. He used them readily, and possessed the knowledge to make effective use of the experimental results.

S (3, 4, 5, 6, 8) used the classification tests on a more limited basis than S1. While they seemed to possess the basic declarative knowledge of the tests they chose to use, it was not central to their problem-solving strategies. Rather, the classification tests provided supplemental and confirmatory evidence when needed. Nevertheless, these subjects did seem to possess the necessary declarative knowledge about the tests they used. This passage from S6 on P3 illustrates this point. In this problem she looked at the infrared and proton NMR spectra and concluded,

Looks like I have an aldehyde...I'm not sure of what I have. I'm just going to bully on to my tollen's test. [Performs Tollen's test] I do have a silvery mirror, so that tells me I have an aldehyde. (S6-V1, T1)

At this point she started to inventory possible classification tests she could use, with the expected results of each test.

S6: I expect positive chromic acid test from the aldehyde. I expect a positive 2,4-DNP. I don't think that's going to tell me any more. I don't think I have an ester, so I don't think basic hydrolysis or some of these other things are going to help me much. Um, unless I have, well no. It's not likely that I have a halogen, because that should have been noted in the elemental analysis.

R: The elemental analysis only gives you the carbon and the hydrogen. It doesn't give you anything else.

S6: Okay, then I do want to do a Beilstein test....[Performs Beilstein test] A yellow and blue flame is observed, and I don't believe that is positive since positive is green. (S6-V1, T1)

In the first passage of this protocol, S6 was inventorying three different classification tests she could possibly use. In each case, she exhibited declarative knowledge about the test by correctly matching the expected results of each test with the aldehyde structure in the compound. Since none of the tests would shed new light on the com-

pound, she opts not to perform any of these tests. When she later realized that the compound could have a halogen, she performed the Beilstein test and interpreted that no halogen was present.

Other examples from S (3, 4, 5, 8) could be provided to illustrate similar understanding of the classification tests. However, like S6, they used the classification tests sparingly.

S2 performed the second most classification tests, but he did not initially possess significant knowledge about the tests. He revealed his basic strategy for the classification tests on P6 when he was “randomly looking for simple tests” (S2-V2, T3) because the spectral data he collected was inconclusive. On this problem he performed seven different classification tests without any apparent systematic strategy. Furthermore, he frequently had to make use of the classification “help” function to be able to interpret the tests. The one classification test S2 made frequent use of was the pH of the compound in an ethanol water mixture. He used this four times to determine the acidity of the sample. Since he did not use solubility to determine whether the unknown was an acid or a base, it seems reasonable that he would make use of the pH. While S2 ranked second in the frequency of use of the classification tests, his protocols indicate that he did not possess much declarative knowledge of these tests.

Likewise, S7, the other industrial chemist, did not know much about the classification tests. He expressed this at the end of the practice problem, P1, when he stated,

I am not sure that if you're asking me what I would do if I were in the lab in this day and age. I am not sure I would do many of these [points to classification tests].... If I went through here [classification tests] I would probably start doing things outside what I normally would. But a few of these I'm familiar with, such as bromine water. I understand some of that. Potassium permanganate. Got those. I don't want to start [using those]. (S7-V1, T1)

His understanding of the classification tests apparently was limited to the tests

listed here, along with the 2,4-DNP. He did not need to use the "help" function on any of these three tests: bromine in carbon tetrachloride, potassium permanganate, and the 2,4-DNP. As a result, he used only these tests except for the one time he explored the experimental space by using an iodoform test.

Summarizing, S1 was the only subject who made extensive use of the classification tests. As revealed by the protocols, he had extensive knowledge of these tests. The other academic chemists, S (3, 4, 5, 6, 8) also seemed to understand this chemistry well, but they made much less extensive use of this wet chemistry in their problem-solving. S7 and S2, the industrial chemists, made limited productive use of the classification tests and did not utilize this aspect of the experimental space extensively, except when searching for the resolution of problems from the spectral data. When the classification tests were used, it was primarily for the confirmation of functional groups; but on occasion they were used to determine whether a particular functional group was primary, secondary, or tertiary.

Derivatives

S (2, 7, 8) did not form derivatives, consistent with their small usage of wet chemistry techniques. S2 performed four derivatives on one problem, and S7 formed one derivative; but in both cases the subjects were randomly searching for tests to provide information and did not possess the necessary declarative knowledge to interpret the results to their advantage without help. They certainly did not make derivatives an integral part of their problem-solving process. S8 never took a derivative.

The remaining academic chemists, S (1, 3, 4, 5, 6) formed derivatives on 73 percent of the problems. Formation of a derivative was an integral part of their problem-solving process. When they did not form a derivative, it was because they felt that their proposed model fit the data to the point that there was little doubt in their minds that the

solution was correct. Otherwise, these subjects performed derivatives for two purposes. The first strategic use of derivatives was to explore the experimental space. Subjects often employed this strategy when they were having problems elucidating the structure from the NMR spectral data. If they had reached an impasse in which they could not propose a specific model, they would form a derivative and utilize Rappoport (1984) to match the melting point temperatures of the derivatives to samples in the tables which approximated the melting point or boiling point temperature of the unknown. This strategy allowed them either to find a match for their unknown or at least to limit the problem space to a handful of compounds. From this limited problem space they were able to resolve the conflicting experimental data and solve the problem.

Derivatives were used to explore the experimental space early in the problem-solving process. S5 was the subject who most often made use of this exploration strategy. For example, on P8, immediately after determining that a carbonyl group was in the infrared spectrum, he performed a 2,4-DNP classification test and derivative. He made no apparent use of the information, other than to write down the melting point of the derivative. Even at the end of the problem he did not compare the derivative with table values in Rappoport (1984). In similar fashion, on P11, he performed a 2,4-DNP of the unknown immediately after discovering a carbonyl in the infrared spectrum. This time, however, he did utilize Rappoport (1984) and the derivative data to determine the unknown at the end of the problem.

In order for a derivative to be characterized as an exploration of the experimental space, the derivative had to be performed before the subject had proposed a specific structure. The subject may have been able to infer pieces of the structure from a search of Subgoal B in this exploration phase, but once a complete model of the compound was formulated, the subject left this exploration phase and the derivative was classified a confirmation derivative.

The second strategic use of derivatives was for confirmation purposes. Subjects using this strategy proposed a complete model of the unknown and then used the derivative experimental space to provide additional evidence that the solution was correct. In order to be classified as part of a search of the experimental space for confirmation purposes, the test must have been selected after the subject had proposed a complete structure of the unknown.

Table 8 contains the data pertaining to these two strategies of the use of derivatives. "C" is for the confirmation strategy, and "E" is for the exploration strategy. These letters are followed by a number indicating how many derivatives were formed. On some problems, the subjects utilized both strategies, and these are simultaneously listed in the table cell. If the cell is left blank, it is because the subject did not form a derivative.

Analysis of this data shows that when no derivatives were formed the subjects successfully solved the problems 65 percent of the time. These numbers may be skewed somewhat because S7, the least successful problem-solver, did not perform derivatives. If he is not included, the success rate rises slightly to 72 percent. When derivatives were formed solely for exploration purposes, the percent solved correctly is 40 percent. When the confirmation strategy was utilized, the subjects were 100 percent efficient, and when a combination of exploration and confirmation was used, the subjects were 80 percent correct in their solution.

Several generalizations can be made about the use of derivatives. First, the use of derivatives to confirm a proposed molecular structure is a sound strategy. Forming the derivative allows the subject to catch any small errors that might have been made in the structure proposal. Furthermore, it allows one to distinguish between subtle structural differences that might not be easily deducible from the spectral data. This was

Table 8

Strategic Uses of Derivatives by Subject and Problem											
	P1	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
S1		C1	E1	E1	E4					E2	C1
S2					E4						
S3		C1	C1	E1C1	C1		C2			C2	E2
S4	C2	C1			C1		C1			C1	E1
S5	E1	E1	C1	E1C2	E1C1	E1	E1	C3	E2	E1	C1
S6		E1C1	E1	E3	E4	E3	C1	C1	E2	E1C1	E3
S7					E1						
S8											

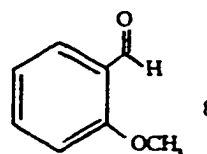
C = Confirmation Strategy

E = Exploration Strategy

= Number of derivatives formed

done on P3 by both S1 and S4. Both subjects had determined that the compound was a methoxybenzaldehyde, but both were uncertain if the structure was ortho- or meta- in its configuration. The following comments from the protocol of S4 illustrate the reasoning she applied:

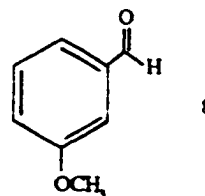
It's either ortho or meta. In other words, 2- or 3-. It really doesn't match the information [physical properties] for 3-. So I'm guessing it's 2-, and I don't see two in here [Rappoport].... Derivatives. I'll do something here. Do what I always tell my students to do. That's one option.



This is the second option. Let's see here, six, eight [carbon].

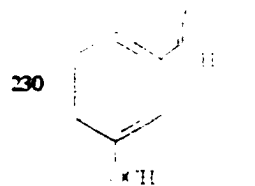
Unfortunately, since the two groups I have aren't different, both of them are going to have eight peaks in the carbon spectrum, which they do. And...also can't remember how to tell substitution pattern from the IR. I used to be able to do that. I will not be able to tell from the mass spec.... [Performs the semicarbazone derivative]. . . .

Boiling point ten degrees off [for 3-methoxybenzaldehyde].



semicarbazone
209-217
(dec)

bp 240-246C



I really wish they had the other compound in here. That would help. I know it's not para-. The NMR rules that out. Actually the carbon [spectrum] rules that out as well because there would be fewer peaks....The data, I don't think [it's] close enough for it to be 3. It has to be 2-methoxybenzaldehyde. That's going to be my final guess. (S4-V1, T1)

Even though she did not find the ortho-methoxybenzaldehyde in Rappoport (1984), she was able to eliminate the only structural competitor by performing the derivative, thereby negatively confirming the proposed structure.

While the confirmatory strategy was highly successful, it was used in only 22

(25 percent) of the problems overall and in 40 percent of the problems by the academic chemists. Classical qualitative analysis dictates the formation of a derivative to confirm the identity (Rappoport, 1984). However, these experts clearly did not elect to do this on a majority of the problems.

A second generalization that can be made from Table 8 is that it is unnecessary to perform a derivative to determine the structure. The industrial chemists S (2, 7) and S8 never performed a derivative (for the purposes described here), yet S2 and S8 were successful problem solvers.

Finally, it would seem that using derivatives to explore the experimental space was the least effective strategy among these chemists. It may be that the use of derivatives for this purpose draws the subject into a pattern of thought about the compound that does not allow him to synthesize all of the data properly. S5 commented on this very concept in P4:

S5: So [I'll use] information tables [Rappoport]. Cheat that way. Carboxylic acid.

R: Now why would you consider that cheating?

S5: Oh, because it biases me. I mean that sort of locks me in, you know, if I've made a mistake, and I've written something down here that, that's wrong. Then I go to this place then I may forget that this is unreliable because this is unreliable. (S5-V1, T1)

It may also be that the use of derivatives to explore the experimental space was not a very efficient because this strategy was used on problems that were by nature more difficult for the subjects to solve by spectral structure elucidation. The derivative information was insufficient to guide them to the correct answer if they couldn't find a match in a reference (Rappoport, 1984). Consequently, the solution of the problem was not enhanced when this strategy was utilized.

Infrared Spectroscopy

The infrared spectrum was used by these experts to determine the presence of functional groups. Furthermore, they relied on their extensive declarative knowledge pertaining to the spectra in terms of functional groups containing OH, NH, and C=O bonding. Whenever infrared spectra were viewed, every subject—on first inspection—was able to identify the alcohol OH stretch peak on P (1, 5, 7), the carboxylic acid OH stretch and C=O stretch on P4, and the amine NH stretch on P9. On other problems with carbonyls, P(3, 6, 8, 10, 11), the subjects always recognized the C=O stretch but did not necessarily pinpoint how the carbonyl was manifested in the compound. On 60 percent of these problems, the subjects precisely identified whether the carbonyl was part of an aldehyde, ketone, carboxylic acid, or ester functional group. In the remaining 40 percent, the subjects were less willing to take a definite stand on the functional group or made no further comment other than stating that a carbonyl was present. Both of these can be illustrated by S8 on P6 and P10, respectively. On P6, he said,

Absorption at, uh, 1700. Carbonyl group probably. And I have absorption here at 2550 and 2650. I don't know. Could be an aldehyde, but that seems to be a little out of position and doesn't look quite right. Big question mark on that. Nothing else to go after on this. (S8-V1, T2)

The broad OH stretching band, near 3000 cm^{-1} , that is typical of carboxylic acids was not evident in the infrared spectrum of Unknown 6, 4-chloro-3-nitro-benzoic acid. Furthermore, he recognized the two absorptions at 2550 and 2650 cm^{-1} which are characteristic of an aldehydic CH stretch. Although out of the expected range of 2830 – 2695 cm^{-1} (Silverstein & Webster, 1998) the presence of these peaks was sufficient to cause S8 to hypothesize skeptically that the unknown was an aldehyde instead of a carboxylic acid. He immediately performed a proton NMR spectrum next, and from the chemical shift was able to determine that the compound was a carboxylic acid.

An excerpt from P10 provides a more common example of how the subjects interpreted the infrared spectrum when they failed to identify correctly how the carbonyl group was manifested in the compound: "We have a carbonyl group greater than 1700." (S8-V2, T3) They were apparently not attempting to narrow the functional group possibilities down by the infrared alone but were satisfied just to identify the carbonyl presence. Failing to pinpoint the functional group in these circumstances does not indicate a lack of declarative knowledge. Rather, it may be an indicator of the subject's understanding that the absorption of the carbonyl in the infrared spectrum can be shifted by the presence of other atoms or by conjugation, and that there can be overlap in wavenumber for the different types of carbonyl containing functional groups if such a shift occurs. Table 9 shows the "typical" wavenumbers of absorption from the C=O stretch for the functional groups found in the problems of this research (Silverstein & Webster, 1998). The typical absorptions in column 2 are for aliphatic compounds without conjugation for the carbonyl, and column 3 lists the absorptions for the conjugated carbonyl groups.

Table 9

Absorption of Carbonyl Stretch in the Infrared Spectrum by Functional Group

Column 1	Column 2	Column 3
Functional Group	Unconjugated (cm^{-1})	Conjugated (cm^{-1})
ketone	1715	1685-1666
ester	1750-1735	1730-1715
aldehyde	1740-1720	1710-1685
carboxylic acid	1760	1710-1680
amide	1695-1650	1695-1650

For example, on P6, S1, upon viewing the infrared spectrum, speculated between a carboxylic acid and an amide:

Nujol spectrum. Boy, that does not look like a good carboxylic acid. Whoa. Scratch my head. Looks like an amide possibly.

1710 [cm^{-1}], 1686 [cm^{-1}]. IR, that bothers me. 1710, 1686. That can be a carboxylic acid. That depends somewhat on how the spectrum was taken. (S1-V3, T5)

IR 1710, 1686, 1663

While he did not verbalize his thinking, S1 also placed the pointer from the IOC® on the 1663 cm^{-1} as an absorption as indicated by the record of his writings. Figure 9 shows the infrared spectrum from P6. The absorptions referred to by S1, labeled on the spectrum refer to parts of the same absorption. The P6 infrared did lack the characteristic broad absorptions of a carboxylic acid. Furthermore, the most intense part of the peak at 1686 cm^{-1} was in the range for a conjugated carboxylic acid and an amide.

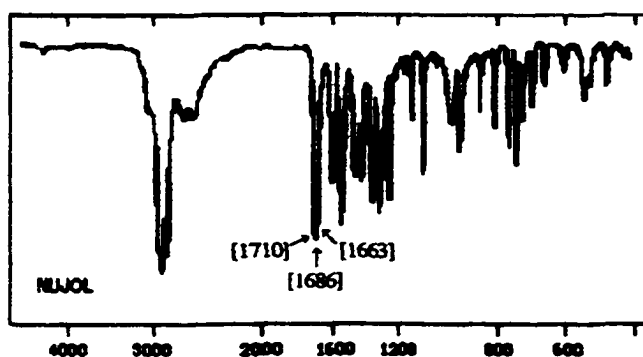


Figure 9. P6, 4-Chloro-3-Nitro-Benzoic Acid Infrared Spectrum.

Clearly, S1 demonstrated significant declarative knowledge by not making a definitive assessment of the carbonyl absorption. The absorption overlap made it difficult to be definitive on how the carbonyl was manifested. S1 then proceeded to search other aspects of the experimental space to confirm the carboxylic acid functional group.

One of the major uses of the infrared spectrum is to determine if a compound is aliphatic, aromatic, or both in structure (Shriner, et al, 1998). Only in about one third of the problems did these subjects comment on this while viewing the infrared. They were able to distinguish clearly whether the compound was aliphatic or aromatic, but since this may be one of the most obvious distinctions that can be determined by the infrared, they did not verbalize about it often. It was clear from the protocols, however, that they did not have any problem making this distinction.

While these subjects interpreted the infrared for the major OH, C=O and NH absorptions, they did not scrutinize the spectra as thoroughly for other absorptions in this problem set. None of the subjects, upon first inspection, recognized the C-O stretch of an ether in the $1150\text{--}1085\text{ cm}^{-1}$ range on P3, the halogen or nitro absorptions on P6, or the small alkyne stretch on P7. It is reasonable that the subjects may have overlooked the alkyne stretch on P7 because the absorption at 2122 cm^{-1} was a very small absorbance peak. See Figure 10 for the infrared spectrum of P7, 2-methyl-3-butyne-2-ol.

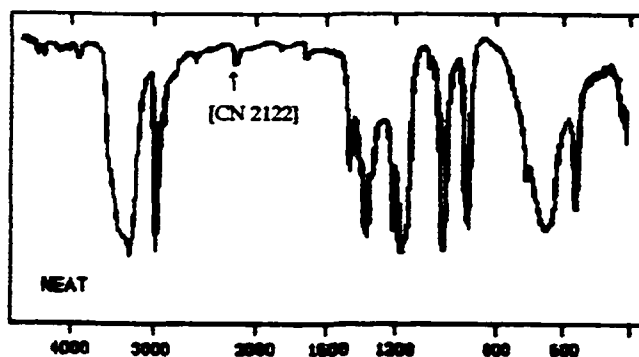


Figure 10. P7, 2-Methyl-3-Butyn-2-ol Infrared Spectrum.

However, only half of the subjects, S (1, 3, 4, 8), commented on the nitrile stretch on P10 when its absorption peak at 2260 cm^{-1} was clearly visible. From this evidence, it appears that these subjects utilized the infrared for coarse observation of functional groups which are readily visible and readily distinctive but did not scrutinize the spectra for less readily characterizable absorptions.

Of all the subjects, only S3 utilized the infrared to determine the ring pattern on the aromatic compounds P (3, 6, 8). On P3 he commented while viewing the infrared spectrum,

Try the infrared again. Ah, and this time it's not an alcohol. Its peak's at 1690, which looks like an aldehyde or a ketone that's conjugated with a ring. And there's that thing right there that looks like it might be an aldehyde. An aldehyde CH stretch. Perhaps that will be my guess right now. Uh, there's a peak there at 760. 760 looks like a substituted benzene ring. I don't remember what those patterns are exactly, but it's not monosubstituted. Looks like it may be ortho-, if I can remember those correctly. (S3-V1, T1)

While S3 expressed concern about the substitution pattern absorptions, he clearly knew that the benzene ring was not monosubstituted and was correct in his assessment of the ortho- configuration based upon the peak at 760 cm^{-1} . His protocol on P3 also provides an additional example of how the subjects exhibited considerable knowledge of the carbonyl absorptions. He hypothesized that the peak at 1690 cm^{-1} indicated either a conjugated aldehyde or a conjugated ketone. S3 made no comments on P6 pertaining to the aromatic substitution pattern, but on P8 he commented, "750, looks like a monosubstituted benzene ring." (S3-V1, T2) While he did not verbalize about the peak near 680 cm^{-1} , the combination of these peaks would indeed indicate a monosubstituted aromatic ring. While none of the other subjects seemed to inspect the infrared for these patterns, S4 on P3 did comment that she could not "remember how to tell substi-

tution pattern [on the ring] from the IR,” adding “I used to be able to do that.” (S4-V1, T1)

In summary, the subjects in this study utilized the infrared primarily for determination of those functional groups that have very distinctive and highly recognizable absorptions. They did not scrutinize the infrared to glean all of the information that could possibly be gleaned from the spectra, nor did they seem to have this type of information in their working memory. Apparently, these subjects, while competent in interpreting the fundamentals of infrared spectra, did not demonstrate great expertise regarding the more subtle information found in the spectra. They did not utilize this instrumental tool alone to determine the functional groups. Rather, they used the infrared either to hypothesize or to confirm basic, easy-to-find functional groups.

Mass Spectroscopy

The mass spectrum was the least used instrumental method in this study. The industrial chemists, S (2, 7), and S (1, 8) utilized mass spectroscopy more than the other academics. When the mass spectrum was used, it was used to determine the molar mass of the compound or major fragments found in the spectrum. This was often done as a check of a proposed molecular formula (See page 150), but S7 searched the mass spectrum experimental space as his initial strategy on all of the problems. On P4 he stated, “Mass spec. Gives an idea of what weight range we are looking at.” (S7-V1, T1) Likewise, on P5 he stated, “Look at the mass spec. and see if anything jumps out.” (S7-V1, T1) When used initially, the mass spectrum helped to determine the molar mass of the unknown, to provide evidence of key fragments which might be present in the compound, and to determine if halogens were present.

The protocol from S1 illustrates how the mass spectrum was used to establish the molar mass of the compound. On P3 he had determined the empirical formula based

upon the percent composition and the assumption that oxygen was the only heteroatom. He used the mass spectrum to determine if the molecular formula was the empirical formula or some multiple of the empirical formula.

So I come down and look at the mass spectrum. Okay. Uh, it's a 137, which means that since it's odd it has to be the $M + 1$ peak. Or you would think that it is. But that's the 136. It's a little unusual for the molecular ion to be the base peak, but I'm going to go with the data and say that we've got a molecular weight of 136,

MW = 136

whereas C_4H_4O [the empirical formula] is 48 plus 16 plus 4. 68.

$$\begin{array}{r} 48 \\ 16 \\ 4 \\ \hline 68 \end{array}$$

And 68 is one half of 136. So that tells me that was a good move. The molecular weight is $C_8H_8O_2$, and that is more consistent with a boiling point of 240 to 246 degrees. (S1-V1, T1)



S7 demonstrated the process of searching the mass spectrum for characteristic fragments in addition to the molar mass. On P5 he incorrectly correlated the parent peak with the molecular ion peak and missed the small peak at 156, which was the actual molecular ion peak. Nevertheless, through this discourse he attempted to utilize the mass spectrum in the three ways described above.

Look at the mass spec and see if anything jumps out. Looks like we're looking a mass of 138? Parent. A base peak of 71, which is a loss of 67. It's uh, nothing really jumps out at a loss of 67. Uh, there is another peak here pretty close,

mass = 138

parent = 71 = 67 loss

which is 123. That is going to be a loss of 15. So that is a methyl group. [Peak at] 95. That is [a loss of] 43. that number sounds familiar. 43, a common loss. I can't recall off hand what that would be. Hmm. Also got, let's see, 81. No, uh, looks like no halogens based upon isotopes, common isotope effects, not effects, but natural isotopes. (S7-V1, T1)

123 = 15 (CH₃)

95 = 43

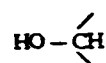
81
no halogens

According to the protocol evidence, S7 was only able to determine with certainty the loss of a methyl group. While a loss of 43 was familiar to him, he did not recall what type of fragment that might be. Silverstein and Webster (1998, p. 88) list several fragments which would have a mass of 43, so it is not surprising that S7 would not have these possibilities memorized. As with the infrared spectrum, these subjects did not seem to have in their long-term memory complicated fragment losses. They seemed to focus on the fundamental losses, such as methyl groups, ethyl groups, phenyl groups, and water. For example, S2 on gave a rudimentary assessment of the mass spectrum on P5.

Look at the mass spectrum. Looking at this, it is probably the parent, then it's hard to get [the cursor] on it. I'm getting 156, That's probably the parent. And this thing is 138. That's a loss of 18. So that's just simply dehydration, that again indicates that it is an alcohol of some type. (S2-V1, T1)

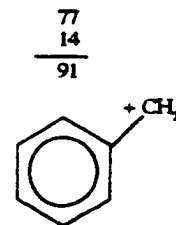
156

138



Likewise, on P6, S6 looked to find a fundamental fragment in the mass spectrum.

Okay, 77 plus. Let's see. What's tropylium do? That's 77 and 14 [equals] 91. So that's not what the base peak is. That doesn't help me. I'm just not right on top of that. (S6-V1, T1)



In this case, S6 was expecting to see the base peak at 91, the characteristic tropylium fragment from an alkyl substituted benzene ring. However, when she discovered the base peak was actually at 89, she was unsure of its significance.

S1 made the most extensive use of fragment analysis on P5, menthol. During this problem he analyzed the mass spectrum twice. During the first analysis, he determined the molecular ion peak and looked for fundamental fragments.

I'm going to take a look at the mass spectrum. And there is, there is a molecular ion apparently at 156. 156 minus 138, that's a difference of 18. And so, the difference between this peak and this one here tells me it's dehydrated, uh, which one would expect for an alcohol. Let's see what this one does. This is 95. 156 minus 95 is 51. That doesn't really grab me. Look at the base peak here. A base peak of 71. 71 is five carbons and eleven hydrogens. Okay this is 95 minus 81 is 14. 55 minus 41 is 14. 71 minus 55 is 16. 136 minus 123 is 15. It's tending to lose methyls or CH₂'s. It's tending to lose methyls or methylenes. (S1-V3, T4)

mass spec

$$\begin{array}{r} \text{mol ion} = 156 \\ - 138 \\ \hline 18 \end{array}$$

$$\begin{array}{r} 156 \\ - 95 \\ \hline 51 \end{array} \quad [\text{sic}]$$

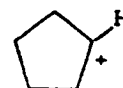
$$\begin{array}{r} 71 \\ - 60 \\ \hline 11 \end{array} \quad \text{C}_5\text{H}_{11}$$

S1 did not attempt to identify what each peak might represent, but rather looked at the size of the fragments between peaks, the methyl and methylene groups. Later he

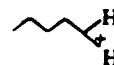
attempted to re-analyze the spectrum, after he had concluded that the one degree of unsaturation in the compound was due to a ring.

I have ten-carbon atom, primary alcohol that contains a ring. Tends to lose methyl groups or methylenes in the mass spec. Let me go back to the mass spec and see if I can make a second guess to the size of that ring... Well, I'm going to play it off that right there. Play off of 71. I did that a few minutes ago and that gave me C_5H_{11} . I would like to think C_5H_{11} . Uh, back to the mass spec. C_5H_{11} for the base peak. Um, two, four, six, eight nine [counting hydrogens in structure] problem. Of course, weird things happen in the mass spec.

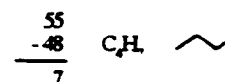
mass spec C_5H_{11} .
M = 71, base peak



Two, three, four, five. Two, four, six, eight, nine... three, four, five, six, seven, eight, nine, ten, eleven I think I'm on the right track.

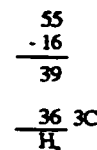


Fifty-five, lets try that. That's C_4H_9 , no, it can't be, oh so. That must contain the...

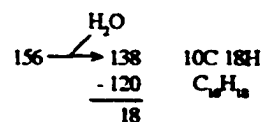


R: Keep talking.

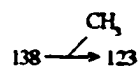
Subject 1: Well, I'm trying to, I'm trying to locate uh, from the mass spectrum I'm trying to get some idea as to where the OH is. It has, it uh, it evidently has a Um, a norm, a pentyl, but that does not have to be normal.



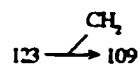
It could be, except it's a primary alcohol. Oh boy, let's look at this. 138 all right. 38, 138 means that it has lost water. So 156, 138, it lost water and it looks, oh, maybe it still has ten carbons. Well that's interesting. 120 minus 18 so its uh, its $C_{10}H_{18}$. So it has lost, it has lost water, gone from 158 to 138... its still $C_{10}H_{18}$. Now what does it tend to do after that?



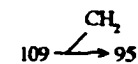
138 minus 123 is 15. So it loses a methyl. 138 to 123, it loses a methyl..



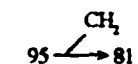
123 to 109... it leaves us a CH_2 .



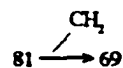
109 to 95, it loses a CH_2 .



95 to 81, it loses a CH_2 .



81 to, that's interesting... 69 is just 12. But there's some other stuff in there.



Let's see what that is. 67, we're fixing to do that... 67. That's a CH_2 . 55, 67 to 55 with another 12 again, there it, there it is its losing another methylene. Well its losing CH_2 's like crazy. Its just, just, just, just, just, just chopping it down (noises) methyl. (Sigh.) Normal decanol is a good, is a good possibility. So I'm going to uh, I'm going to look up the melting point just, I, I, I'm sort of a hunch here. I feel like I may be wasting my time, but I think it's probably worth the effort to look up the 3,5-dinitro benzoate of normal, of 1- decanol. (S1-V3, T4)



Even though S1 spent considerable time analyzing the mass spectrum, he was unable to infer much more than the loss of water, methyl groups and methylene groups. He proposed 1-decanol as a possible compound, but he retracted that when he reconsidered that the compound must be a ring.

All three of these examples are indicative of the utilization of the mass spectrum in the early problem-solving process. These subjects were able to analyze for the basic peaks, but did not in these cases infer greater details of the compound's structure. As discussed in the Research Question 4 Section of this dissertation (p. 131), the subjects did utilize the mass spectrum to confirm that the molar mass was correct and that the fragments were significantly consistent with a proposed structure. When used as an evaluative tool rather than a structure elucidation tool, the mass spectrum seemed to be more fruitful for these subjects.

The mass spectrum can also be used to determine if halogens are present in the compound. On the problems the subjects worked, only P6 contained a halogen. In this case the halogen was chlorine. Figure 11 is the mass spectrum of 4-chloro-3-nitro-benzoic acid. The ^{37}Cl isotope is present in nature in a quantity that is approximately one-third that of the ^{35}Cl isotope. This causes pairs of peaks, separated by a mass of two, that have these relative intensities in the mass spectrum. S5 did not use the mass spectrum on this problem.

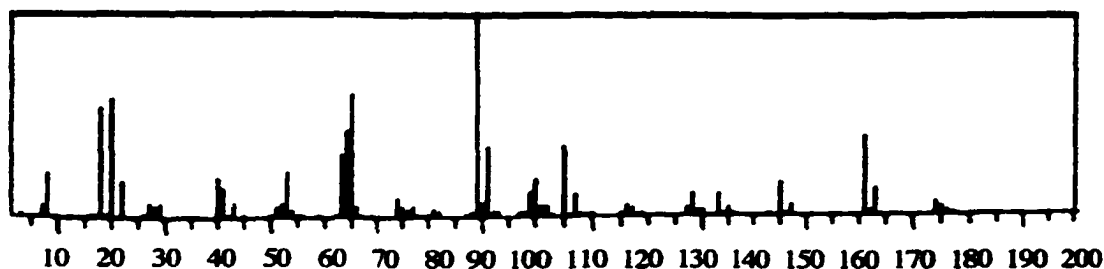


Figure 11. P6, 4-Chloro-3-Nitro-Benzoic Acid Mass Spectrum.

Of S(1, 2, 8) none were able to infer that chlorine was present based upon their analysis of the mass spectrum. Based upon his protocols, S1 was looking for evidence of chlorine but did not conclude that chlorine was present. S2 seemed to be interested only in the molecular ion peak when he first inspected the mass spectrum. Upon second inspection of the spectrum, he stated, "I don't see doubling of some peaks in the mass spectrum. Probably there's no chlorine there." (S2-V1, T2) S8 never commented on chlorine in the mass spectrum. When the mass spectrum is viewed, it is easy to see how they may have overlooked the chlorine peak pairs. Nevertheless, it is surprising that they were unable to infer the presence of the chlorine since the characteristic peaks were present.

The remaining subjects S(3, 4, 6, 7) did correctly conclude that chlorine was present when they inspected the mass spectrum of P6. When S3 performed the mass spectrum, he already suspected that chlorine was present and was actively looking for the chlorine peaks.

Okay, well what I'm looking for, I guess, the primary thing I'm looking for is, I'm looking for peaks that have a 1 to 3 ratio, which would indicate the presence of chlorine to confirm what I interpreted from the elemental analysis. And there it looks like a peak at 161 and 163. And another peak at, a set of peaks at 91, or looks like 89 and 91. That will fit the pattern, so I'm going to say this guy has got chlorine in him. (S3-V1-T1)

Use of the Nitrogen Rule

The nitrogen rule is an algorithm which can be applied to the mass spectrum. According to Silverstein & Webster (1998), the nitrogen rule states that if the molecular ion peak in the mass spectrum has an odd mass, then the compound must have an odd number of nitrogens within the compound. If the mass of the molecular ion peak is

even, then either no nitrogen is present or there is an even number of nitrogens in the compound.

In the research proposal for this dissertation it was hypothesized that subjects might use the mass spectrophotometer as part of Subgoal A in an effort to determine the particular heteroatoms present in the compound. It was believed that this would particularly be the case if the molecular ion peak was an odd number, indicating the presence of nitrogen. Of the problems solved in this research project, only four compounds contained nitrogen. P6, P9, P10, and P12 all contained only one nitrogen atom in their molecules. Consequently, the molecular ion peak — if present in the spectra of these compounds — could elicit the use of the nitrogen rule from the subjects. In most cases, the subjects made few verbalizations pertaining to the nitrogen rule specifically. However, if the subject, after viewing the mass spectrum, was able to draw the conclusion that there was one nitrogen, or that an odd number of nitrogens was present in the compound, it is reasonable to assume that the nitrogen rule had been evoked. In approximately one-third of these problems, the subjects did not choose to use the mass spectrometer as part of their experimental space search. In P9, for example, the problem was relatively simple to solve if the subject recognized the symmetry in the NMR data. The subjects did not see the need to perform a mass spectrum in that case.

Table 10 contains the data pertaining to the use of the nitrogen rule. A blank left in the table indicates that a subject did not use the mass spectrophotometer for that particular problem. Subjects utilized the nitrogen rule 7 out of 20 times (35%) in problems containing nitrogen. The subjects' use of the nitrogen rule did not have a significant correlation to success. Subjects were just as likely to solve a problem correctly if they did not use the nitrogen rule. While the nitrogen rule can indicate the number of nitrogens present in the compound, it does not ultimately impact Subgoals B and C.

Table 10
The Use of the Nitrogen Rule for Compounds Containing Nitrogen

	P6	P9	P10	P12
S1	✓		✓	(—)
S2	✓	(—)	(—)	✓
S3	(—)			
S4	(—)			(—)
S5			(✓)	
S6	—			
S7	—	(✓)	✓	—
S8	—	(—)	(—)	(—)

() in Bold indicates correct problem solution.

— Did not use the Nitrogen Rule.

✓ Did use the Nitrogen Rule.

The nitrogen present can be manifested in a number of ways, such as amines, amides, cyano-, and nitro- functional groups. Consequently, just knowing that nitrogen is present does not reveal how the nitrogen is manifested in the compound, nor does it indicate how the compound is structurally arranged. S1, at the conclusion of P6, confessed that he never considered the possibility of a nitro- functional group in the compound: “I didn’t think nitro. Didn’t think it.” (S1-V4, T7) Even though he was able to determine one nitrogen atom in the compound, his interpretations of the other data did not allow him to solve this problem correctly .

Carbon-13 NMR

Only S6 failed to make extensive use of the carbon-13 NMR spectra. The only problem in which she used carbon-13 NMR spectroscopy was P3. At that time, she commented, "I'm less familiar with that [carbon-13 NMR], so that's not as helpful for me. I don't know it as well." (S6-V1, T1) While she may not have felt comfortable with interpreting chemical shift in the C-13 NMR, it is surprising that she did not utilize it to determine the number of non-equivalent carbon atoms in the compound. S6 did use the Subgoal A initial strategy on nine of the problems and may have felt comfortable enough with the calculated empirical formula that she did not see the need to determine the number of carbon atoms in the C-13 NMR. However, since the molecular formula was a multiple of the empirical formula on P (3, 4), this lack of a correct molecular formula may have contributed to her inability to solve these particular problems correctly. Both of these problems were early in the problem-solving process, when she was in an apparent hurry to work the problems. Her rushing through the problems seems to have been the major contributor to her lack of success early in the session. Nevertheless, when she viewed the C-13 spectrum on this problem, she did not even count number of non-equivalent carbons, which could have helped her with the molecular formula. She did make some observations on the chemical shift, but these were general and did not seem to guide her thinking afterwards.

The rest of the subjects made extensive use of the C-13 NMR spectra. Of the remaining subjects, S5 used it in only six of the eleven problems. S5 generally solved the problems, in part, by formation of a derivative instead of structural elucidation by spectroscopy alone. Consequently, he rarely utilized the C-13 NMR because he had gathered enough structural information from the other data to perform derivatives to identify the compound. Likewise, when S1 did not use the C-13 NMR data, it was because he had already solved the problems without the C-13 spectra.

Except for S2 on P3, the remaining subjects, S (2, 3, 4, 7, 8), utilized the C-13 NMR data on every problem. The information gained most often from the C-13 NMR by these subjects was the number of non-equivalent carbon atoms. The subjects made verbal references to the number of carbon atoms on all of the problems in which the C-13 NMR was used, with the exception of S2 on P1 and P9, and S6 on P3. This information was used both early in the problem-solving process and as an evaluative experimental space search to confirm the reasonableness of the solution. The evaluative approach is discussed in the Research Question 4 section of this dissertation (p. 134). The C-13 NMR was used to determine the number of carbon atoms after the proposed solution on twelve of the problems, and it was used earlier in the problem-solving process on 57 problems. While most of the subjects favored using the C-13 NMR earlier in the process, S3 utilized it the most for evaluative purposes. On six of the problems, he proposed the solution, then viewed the C-13 NMR to make sure the number of peaks agreed with his structure. He typically did this on problems that he solved fairly easily. On more difficult problems, he would utilize the C-13 NMR spectra as the others did to help limit the problems space.

None of the subjects who used this instrument had any problem interpreting symmetry in the C-13 NMR. Each possessed the declarative knowledge to recognize that a few number of peaks was most likely due to symmetry in the compound. The most subtle compound with symmetry was P7. S7 illustrated well the ability to recognize this symmetry on P7, 2-methyl-3-butyne-2-ol, a compound in which two symmetrical methyl groups results in four non-equivalent carbon atoms in a five-carbon compound. On this problem, he had already determined from the mass spectrum that the molar mass of the compound was 83 or 84.

Carbon spectrum. 4? 4 non-equivalent carbons? Okay. Got a big one at 29.6 [δ], one at 64.1, 73, 86.2... 4, uh let's see. May be some symmetry in

this one, too. It [molar mass] gets up to 80-something. Hmm, may be some symmetries, but I'm not for sure yet. But with a mass of 83-84, it couldn't have more than 6 carbons. 6 [carbons] is [a mass of] 72. Well couldn't have more than 5 and have many heteroatoms. If you have 5 carbons, that would get you to 60. Uh, maybe 24 [left]. That would give you enough room for maybe one oxygen [or] one nitrogen....I don't know. (S7-V1, T2)

S7 recognized that the compound probably had symmetry, but that the symmetry could not have more than two other equivalent carbon atoms, based upon the molar mass of the compound. In fact, he postulated that 5 would be the most likely number of carbon atoms if a heteroatom were to be present. Proton NMR then confirmed that there were two identical methyl groups when a singlet integrated to six protons.

Carbon-13 NMR spectral data can also be used to infer the presence of heteroatoms by the chemical shift of the peaks. Whereas the subjects used the C-13 NMR to identify the number of non-equivalent carbon atoms in 96 percent of the problems wherein the spectra was viewed, these subjects only made verbal inferences about heteroatoms from the chemical shift in the C-13 data 38 percent of the time. For most of these subjects, the C-13 was not used to determine this information. Rather, they relied on the infrared or classification tests to determine the presence of a heteroatom, and the proton NMR to determine the position of heteroatoms to particular carbon atoms. Comments about chemical shift in the C-13 NMR were typically generalized, like the comments made by S3 on P4 when he used the C-13 to evaluate a solution. "If it's adipic acid, it should have three peaks in the carbon-13. And it's got them where they ought to be, so I can do some other test if you would like, but I don't have any doubt in my mind." (S3-V1, T1) The reference "it's got them where they ought to be" indicates that he was looking for the appropriate chemical shift of the carboxylic carbon atoms compared to the aliphatic atoms in the compound.

An exception to the pattern of general comments about chemical shift came

from S7. He made extensive verbalizations regarding the C-13 chemical shift data on every problem but one. An example of this was during P1, as he viewed the C-13 spectrum immediately after the mass spectrum.

I would like to check the carbon spectrum and count the non-equivalent carbons. And it looks like we have 3 non-equivalent carbons. Umm, looks like possibly one heteroatom attached to it. 73.8 ppm equals heteroatom. Possible heteroatom — most likely oxygen since the masses [in the mass spectrum] were odd. The masses [of the fragments in the mass spectrum] were odd, so that indicates no nitrogen. Possibly. (S7-V1, T1)

C = 3 non Eq.

73.8 ppm = heteroatom

odd mass
no nitrogen

Besides counting the number of non-equivalent carbon atoms, he used the chemical shift of the peak at 73.8 in connection with the data from the mass spectrum to infer that oxygen was present. A corollary to the nitrogen rule in the mass spectrum is that even massed compounds break up into fragments with odd masses, and vice versa. He was none the less cautious about this assessment, since the 73.8 ppm range is suitable for both alcohols and amines.

Providing another example of his declarative knowledge and use of chemical shift S7 also made significant assessment of the C-13 on P3.

There are lots of carbons in this one. 1, 2, 3, 4, 5, 6, 7, 8 non-equivalent carbons. Looks like one is possibly non-substituted at 126.9 ppm. Um, possible aromatic compound due to the peaks in the 120-140 range. There does not appear to be alkyl carbons, based on the fact there are no resonances between 0

nonequivalent 8

non-substituted 126.9 ppm

possibly 120 - 140 ppm

and 40, or non-saturated carbons with hydrogen. Uh, possibly one carbon-oxygen bond, or carbon-nitrogen at 50-ish. 52.4. There is resonance at 189. Possibly be a carbonyl associated with an ester or an aldehyde. The possibility of an ester be accounted for by the peak at 52.4 and the peak at 189. Although methyl ester. I'm not sure if it could be a methyl ester or not. (S7-V1, T1)

no -CH

C - O or C - N 52.4 ppm

C = O 189

Figure 12 is the C-13 spectrum of P3, 2-methoxybenzaldehyde. At least 5 different inferences were made by S7 about the nature of this molecule based upon the chemical shift and peak size. The first was that the peak at 126.9 ppm is much smaller than the other peaks in the aromatic region, indicating that it must not be coupled to a hydrogen.

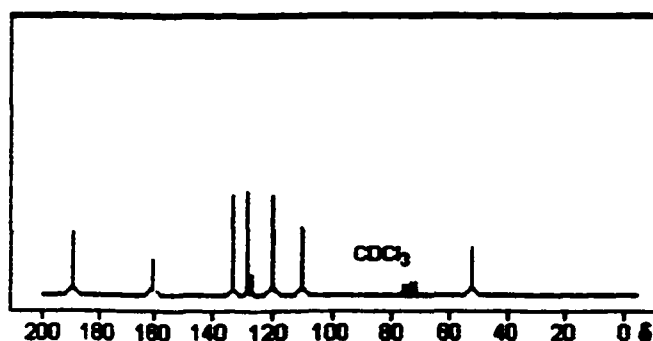


Figure 12. P3, 2-Methoxybenzaldehyde Carbon-13 Spectrum.

His second inference was the aromatic nature of the compound. The third was the lack of aliphatic carbons. The fourth was the presence of the heteroatom. Finally, the fifth was the presence of a carbonyl at 189, which he hypothesized to be either an ester or an aldehyde. Clearly, S7 made much more extensive use of the chemical shift in the C-13 in his problem-solving than the other subjects did. It would appear on the surface that he also possessed the most declarative knowledge about chemical

shift in the C-13. However, that is not definitive, since the others may have chosen to emphasize chemical shift in the proton NMR rather than to focus on chemical shift in the C-13 NMR.

As with infrared and mass spectroscopy, these subjects did not scrutinize the carbon-13 NMR spectra for all of the possible information that could be gleaned. Only S7 made deep inferences about the C-13 spectra. These subjects, on most problems, were content to utilize the C-13 to determine the number of non-equivalent carbon atoms.

Proton NMR

Performing a proton NMR was the experimental procedure used most extensively by the subjects in this research. The only instance in which the proton NMR was not used was by S1 on P12. On that particular problem he was able to arrive at the quinoline identification largely from the empirical formula and the physical properties of the compound and did not need to view the NMR. Otherwise, proton NMR was used by every subject on every problem. Furthermore, each subject demonstrated extensive declarative knowledge pertaining to interpreting the spectra. Strategically, proton NMR was the primary experimental tool to arrive at structure elucidation in Subgoal C. To achieve Subgoal C using the proton NMR, subjects' knowledge focused upon the integration, the chemical shift, and the coupling of the peaks. On simpler problems they had little difficulty piecing the structure together using this tool. However, if the subjects were unable to elucidate the structure via the proton NMR, they had to rely on derivatives to solve the problem. When utilizing complex spectral data such as the NMR for large aliphatic compounds such as menthol (P5) and citronellal (P11), they were able to infer a great deal about the structure. However, they generally were either unable to infer the structure based upon the proton NMR alone or chose the derivative as an easier

means to solve the problem. The inability to interpret the NMR completely may have been, in part, due to the lack of resolution in the NMR spectra, a lack of knowledge, or a heuristic of solving the problems by the means of least resistance. That is, the identification of the compound by derivative match may have been deemed an easier way to solve the problem than extensive reasoning and analysis of the NMR spectra at hand.

While the subjects may not have verbalized directly upon integration, chemical shift, and coupling on every problem, it can be inferred from reading the protocols that they did glean this type of information in nearly every case. It should be noted that on P (1, 3, 4, 7, 8, 9, 10, 11) the IOC[®] proton NMR spectra provided a numerical printout of the integration. Consequently, the subjects had to do little interpretation about the number of hydrogens in the compound in these problems. Figure 13, the proton NMR of P4, provides an example of an NMR with the numerical integration values present.

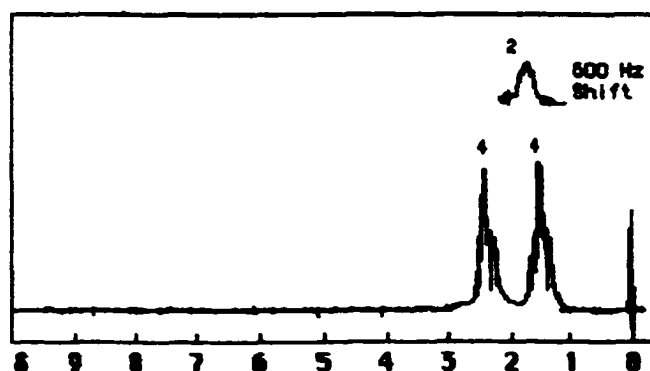


Figure 13. P4, Hexanedioic Acid Proton NMR.

S5 commented on this flaw in the IOC[®] programming on P4, the symmetrical compound hexanedioic acid.

NMR. Has an absorption down around 11 and 12 [δ]. And some aliphatic CH's. I had a question here. It shows [an integration of] 2 and 4

and 4. Is that, is that, uh, unfairly giving me an answer I shouldn't have? Ordinarily, it just gives ratios of that would be 1 to 2 to 2, and I presume that when this says 2 to 4 to 4 that this is implying the number of hydrogens rather than the ratio of hydrogens. (S5-V1, T1)

Apparently, Trinity software did not want students to get bogged down in trying to interpret integration curves on the computer screen and programmed the numerical ratios into the software. While it may be reasonable to include the numerical integrations on a computer simulation, the integration values should be in the lowest numerical ratio, similar to interpreting the integration values from the curves, to make the problem-solving environment as realistic as possible. The presence of these integration values prevented the subjects from demonstrating interpretation of the integration on these problems, but on P(5, 6, 12) the IOC[®] did not provide any integration information. The researcher, however, did provide the subjects with a paper copy of these spectra, which showed the integration curves. This allowed the subjects to demonstrate their declarative knowledge of integration to a greater extent.

As in other sections of this paper, examples of declarative knowledge pertaining to the proton NMR will be presented to represent the knowledge held by the subjects in the study. These examples are not exhaustive, but they do provide samples of the types of interpretations the subjects made.

S3, the most successful problem-solver in this study, was able to recognize patterns and arrive at structural inferences with ease. He commented during one problem, "I usually get more information from a proton NMR than anything else, and that's probably because I've spent more time doing these guys." (S3-V1, T1) In fact, upon viewing the proton NMR on several problems, he almost immediately believed he recognized the spectrum. On other problems, he quickly interpreted the spectra. For example, on P3 he had already deduced that the compound was an aromatic aldehyde from the infrared spectrum when he viewed the proton NMR.

Oh, and we got 4 aromatic peaks, so it looks like it is in fact di-substituted benzene. There's, uh, 3 things here that looks like, uh, looks like a methoxy because of where the methyl is. It's at 4 [δ]. And this guy's offset 600 hertz, so he's an aldehyde. That would be 10 point something [δ]. And, let's see, uh, yeah, that looks like an ortho-methoxybenzaldehyde. (S3-V1, T1)

On this spectrum he focused primarily on the chemical shift. The singlet at 4δ was shifted downfield due to its proximity to the oxygen atom, which he immediately inferred was a methoxy functional group from the benzene ring. The chemical shift of the aldehyde was also routine knowledge for S3. While he correctly concluded that the compound was ortho- substituted, it is not clear if he concluded that from the coupling pattern in the proton NMR, since he had inferred that the pattern was ortho- from the infrared spectrum immediately before viewing the NMR.

S8 made the most thorough verbalizations while interpreting the proton NMR. On the very first problem, P1, he took the NMR (Figure 14) after concluding from the infrared spectrum that the compound was an alcohol, all alkyl, with no C=O or C=C bonds.

Well, assuming all hydrogens are showing, it says there are 12. H-12. Okay. Uh, ratio of 6 hydrogens. That could be two methyls. 4 has to be a grouping. 1 is probably a CH and 1 standing alone is probably, could be the OH signal. [Pause]

H 12

6H 2 Me

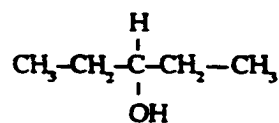
4

1 CH

1 OH

R: Can you talk while you're looking at that? Thinking?

S8: Can I talk while looking at it? Well, I'm trying to decide whether those are equivalent. They appear to be equivalent.



If they are equivalent, they look like they are next to CH₂ groups because they are triplets, okay. And, the one under 4 [protons] looks like, uh, it's a quartet maybe, and that means adjacent to methyl groups. From the IR and that, I would choose that [compound] at this point based on the NMR, okay? (S8-V1, T1)

H 12

6H 2 Me < CH₂^t

4 q -CH₂

1 CH

1 OH

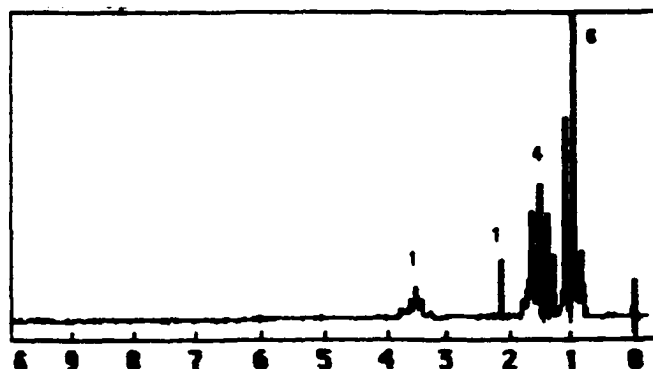


Figure 14. P1, 3-Pentanol Proton NMR.

S8 initially made inventory of the integration and likely corresponding fragments that would be appropriate matches to the integration. He did not postulate a fragment for the peak integrating to four hydrogens, but he did for the other peaks in the spectrum. As he paused to study the spectrum, he clearly saw the ethyl pattern of a triplet and a quartet and proposed the 3-pentanol structure even before he made com-

plete verbal inventory of the structure. Only after drawing the structure did he fully analyze the spectrum verbally to check that the coupling and integration of the peaks explained the compound's symmetry.

The ability to recognize patterns in the proton NMR was evident in this example and others, including P9. Just like S8 in the previous example, S1 took a general inventory of the fragments in the NMR, postulated a structure, and then more fully verbalized about the coupling and chemical shift in the spectrum on P9, dipropyl amine. This heuristic of drawing a possible chemical structure and making sure that the data supported such a structure was commonly used by the subjects in this study. Figure 15 is the IOC[®] proton NMR spectrum of P9.

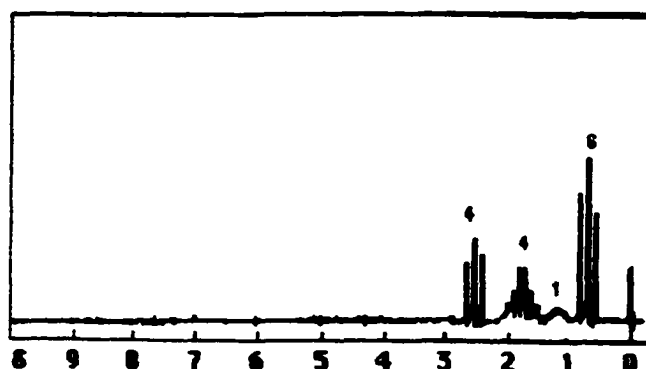


Figure 15. P9, Dipropyl Amine Proton NMR.

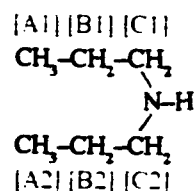
So we are left with $C_6H_{15}N$. And I would like, once again, to know if we are dealing with a molecular formula or an empirical formula, so let's take a look at the NMR. Ah, he tells me 6, 10, 15. Uh, I don't want to look at that thing anymore right now.



So, um... C_6H_{14} , 12, 15, no sights of unsaturation. That's saturated is just what I expected. Therefore, we are dealing with a saturated amine, $C_6H_{15}N$; I have what looks like a pretty good triplet integrating to the 6 protons. I have a pretty good triplet with 4 protons; I have um, one signal here at about 1.2 delta that is very broad at the base. That is the single proton on the nitrogen, which tells me that it is a secondary amine; and now I've got 6, I've got 6 carbons, I've got all 6 of my carbons left. And uh, it's looking like it's a symmetrical; it's looking like it's a symmetrical amine. Maybe something like this.

These two [B1 protons] would split this [A1 protons] into an upfield triplet, which would have the same chemical shift as this upfield triplet [A2]. So the two [A1 & A2] would integrate to 6, so I'm looking at an upfield triplet integrating to 6. I'm looking at a downfield triplet that will integrate to 4 cause the chemical shift here [C1] matches the chemical shift here [C2]. And then these three [A1] plus this two [C1] is five, and since these are nonequivalent, I'm go-

$C_6H_{15}N$
saturated



ing to find a mid-field, messy multiplet that would have five or six spikes to it. 1, 2, 3, 4, 5, 6 [counting spikes in multiplet at 1.8 δ (B1)]. I'm happy again. (S1-V4, T8)

The only definitive structural claim made by S1 in the second paragraph of this protocol was that the broad peak at 1.2 δ was the peak of the secondary amine, NH proton absorption. Nevertheless, he recognized that integrations of 4, 4, and 6 would be typical for a symmetrical dipropyl group and drew the structure. By inventory of the peaks, one by one, in the final protocol paragraph, he made sure that each fragment yielded the appropriate integration, shift, and coupling. The fragments have been labeled by the researcher for clarity of discussion. First, S1 verbalized that the fragments labeled A1 and A2, the triplet integrating to six protons, were two symmetrical methyl groups next to methylene groups. The coupling led to the triplet at 0.8 δ . He then turned his attention to the other triplet at 2.7 δ . These fragments, labeled C1 and C2 in the drawing are also coupled to the methylene groups of B1 and B2 and are shifted downfield because of the proximity of the amine group. Finally, he determined that the multiplet should be a pentet or hextet due to the coupling to A1 and C1. These fragments are not equivalent, so he expected some possible lack of clarity in the multiplet. However, as soon as he counted six peaks in the absorption at 1.8 δ , he correctly declared the problem solved.

These examples provide evidence of the proton NMR related declarative knowledge that these subjects held in long-term memory. This knowledge allowed them to construct a model of the compound and was the primary means of achieving Subgoal C. In many cases it was sufficient to allow complete elucidation of the structure when used in conjunction with other spectrometric tests and wet chemistry results. When it was not

sufficient, a subject either relied on compound identification by derivative formation or was not able to resolve the problem. As described earlier, these subjects tended to scan the spectra of other spectrometric techniques for primary information rather than exhausting a study of the spectra for all of the information possible. That was not the case for the proton NMR. These subjects exhibited the greatest amount of declarative knowledge pertaining to the NMR and scrutinized the spectra the most.

Ultraviolet Spectroscopy

Seven of the eight subjects in this study did not ask about nor comment on the absence of ultraviolet spectral data in the IOC[®]. This type of experimental data was not included because the Silverstein and Webster (1998) did not include it in their most recent text. The information from the ultraviolet spectrometer can be obtained easily from the proton NMR. The lack of questioning by most of the subjects would indicate that this data was not missed by the subjects. It may be reasonable to conclude that they do not regularly use such data in their problem-solving.

Only S2, an industrial chemist, asked about the ultraviolet spectra, and regretted its exclusion from the program. On P1, he viewed the proton NMR and then asked,

S2: There is no UV?

R: No. No UV. Do you use UV a lot?

S2: I particularly use it with unsaturated carbonyl compounds. It's very useful. (S2-V1, T1)

So one out of eight subjects indicated a use for the ultraviolet spectra. Since industrial chemists tended to rely almost exclusively on the spectroscopic techniques, it is not surprising that an industrial chemist asked about the ultraviolet spectra data. However, as a whole, it would seem that the exclusion of UV data did not impact the problem-solving of the subjects in this study.

Strategies for Using Percent Composition

Types of Strategies

At the start of this research project, it was hypothesized that organic chemistry experts would solve qualitative organic analysis problems by the refinement of their molecular models in three stages. Subgoal A was the determination of the empirical or simple molecular formula of the compound. Subgoal B was the determination of functional groups present in the compound. Subgoal C was the synthesis of this information with the data that provide information on molecular arrangement. While this researcher acknowledged that the problem-solving process would be recursive and not linear, he did hypothesize that the subjects would primarily start with Subgoal A to limit the problem space to compounds with one particular formula. Based upon instructional texts (Shriner, et.al., 1998; Feinstein, 1995; Silverstein & Webster, 1998) and personal educational experience, this seemed like the most probable first approach to the problem-solving process.

To achieve Subgoal A, the chemist would most likely utilize the percent composition of carbon and hydrogen in conjunction with analysis or assumption of particular heteroatoms to utilize a mathematical algorithm to calculate the empirical formula. The percent composition is the crucial piece of information for the determination of the empirical formula, and it was believed that the subjects would utilize this information in the initial stages of the problem-solving process. However, this was not the case most of the time. Since each of the eight subjects solved eleven problems, the research presented a total of 88 opportunities to use the percent composition as part of the problem-

solving process. The percent composition was utilized by the subjects in four ways. Most commonly, however, the subjects disregarded percent composition entirely.

Table 11
Frequency of the Strategic Uses of Percent Composition

Initial use in Subgoal A	Reverted to Subgoal A	Check of Solution	General Inference	Not Used
n = 21 (24%)	n = 14 (16%)	n = 13 (15%)	n = 14 (16%)	n = 26 (30%)

In Table 11, it can be seen that the percent composition was utilized initially as part of Subgoal A, 21 times (24 % of the problems). This was a relatively small percentage compared to the original hypothesis. S3, when solving P8, started with this strategy immediately after opening the new unknown. Below, to the right, is a reproduction of the writings he made during this verbal protocol.

Okay, So we have a colorless liquid. Has a boiling point 248. Decomposes. That's cool. Percent carbon 81.79, percent hydrogen 6.10. Add those guys up. 81.79 plus 6.1 is 87, uh 12.1, 12.11 percent something else that I'm going to assume it's oxygen. (S3-V1, T2)

%C 81.79	6.82	9
%H 6.10	6.10	8
%O 12.11	.757	1

The initial use of Subgoal A strategy helped to confine the model space so that the subjects could interpret future data in light of this simple molecular structure. Furthermore, the molecular formula provided insight into degrees of unsaturation and possible functional groups in the compound. The empirical formula C_9H_8O in this case

was most certainly the molecular formula. The six degrees of unsaturation could provide evidence of aromaticity, double or triple bonds, or oxygen manifested as a carbonyl group. When used in this manner, the determination of the empirical formula provided guidance for future experimental moves and subsequent interpretations of the data.

Subjects did utilize the percent composition in three other ways. A second way occurred when they reverted to the use of the percent composition to determine the empirical formula after attempting to solve the problem and reaching some sort of impasse to the solution. In this manner they utilized the pathways of Subgoal A only after some exploration of the experimental space, failing to solve the problem. This exploration may have been thorough or relatively brief. However, it was enough of an exploration of the experimental space to cause the subject to revert to the use of the percent composition to determine the empirical formula. This strategy of reverting to Subgoal A occurred 14 times. S3 followed this approach in P7:

Let's do this, let's go, let's approach this a little more systematically. 71.39 plus 9.59. 19.02. divided by twelve is 5.95. 9.59. 1.12, that kind of guys going to be a 1. This guys going to be a 5. This guys going to be an 8. (S3-V1, T2)

%C	71.39	-	5.95	5
%H	9.59	-	9.59	8
%O	19.02	-	1.12	1

When used in this manner, the "revert to Subgoal A" strategy allowed the subjects to try to arrive at a solution, independent of a formula. The empirical formula could then provide the data necessary to distinguish between conflicting evidence.

The third way the subjects used the percent composition was as a check of their proposed formula. This strategy was not initially proposed since it was assumed that the subjects would obtain the formula first. However, this technique was used 13 times to

make sure that the subject's structure matched the percent composition stated in the problem. During the solving of P9, S2 had arrived at $C_6H_{15}N$ as the molecular formula by utilizing C-13 and proton NMR and mass spectral data. He checked his work later on:

Let's check carbon and hydrogen analysis. I have 6 [carbons]. So 14.006 plus 72.06 plus 15.12. 72.06 [divided by] 101.186. 71.21 [percent], that's going to check, so. 101.186. So I have the correct molecular formula. (S2-V2, T4)

6	12.01	72.06
15	1.008	15.12
1	14.006	$\frac{14.006}{101.186}$

Using the percent composition as a check does not guarantee that the structure of the formula is correct, but it does assist the problem-solver in knowing that the molecular formula is correct. Since the subject arrived at the structure through various experimental searches and model revisions, this confirmation is a means to check their solutions.

The final way in which percent composition was used was as a very generic way to infer whether or not there was a significant number of heteroatoms in the compound. When percent composition was utilized in this manner, quantitative calculations were not used. Rather the subjects used the information as an initial thought before moving on to Subgoals B and C. In their protocols, subjects made reference to the general elemental composition 14 times. S7 generally made these types of inferences at the start of his problem-solving attempts. At the beginning of P4 he stated, "Carbon and hydrogen account for roughly 55.56 percent of this molecule. So we still have some substitutions here." He made no further use of the percent composition in that problem.

Finally, in 26 of the problems, the subjects made no verbal or mathematical reference to the percent composition. They immediately went to Subgoals B and C to

solve the problems. Upon completion of a given problem, they were satisfied enough with their proposed solutions that they did not feel the need to check for agreement with the percent composition. It should be noted that this information is based upon the protocols. It may be that, while the subjects did not verbalize about the percent composition, they may have, in fact, made inferences based upon the composition of a compound. In the information processing model of cognition, verbal protocols provide only a subset of the information being processed by the subjects (Ericsson & Simon, 1980).

Success of Strategies

Table 12 shows, problem by problem, how the subjects made use of the percent composition. The numbers in bold indicate the problems the subjects solved correctly. Table 12 illustrates that the strategy of using the percent composition as a check of a proposed molecular formula resulted in a correct resolution of the formula in 100% of the problems. It seems logical that this would be an effective strategy since the subject has viewed other data to determine the structure, and the check would serve to provide confirmatory evidence of the viability of the solution. Nevertheless, one implication of these results is that checking the proposed formula against the percent composition is a viable means of confirming the molecular formula.

There were two ways to use the percent composition in achieving Subgoal A. When used as an initial strategy, it was successful 57% of the time. When subjects reverted to this strategy, it was successful 79% of the time. Using the composition to determine the empirical formula initially was the approach predominantly of two subjects, S1 and S6. The low success rate may be attributed to S6, who at the beginning of the problem-solving session was not very diligent. S6 missed the first five problems. If these problems are not included, the success rate of the initial usage strategy rises to 75%.

Table 12
Success of Percent Composition Strategies

	P1	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
S1	2	2	2	2	0	2	2	2	2	2	2
S2	4	0	4	4	0	3*	2*	4	3*	4	0
S3	0	1	1	3	3	3	1	2	0	3	3
S4	0	0	0	0	0	0	0	0	0	0	3
S5	1	1	4	3	1	3	3	4	3	1	4
S6	2	2	2	2	2	2	2	0	2	2	0
S7	0	1	1	1	1	1	0	1	0	0	0
S8	0	0	1	4	3	4	4	0	4	3	4

* Percent Composition used to determine molar mass, then formula.

Bold indicates the subject solved the problem correctly.

0 Did not use at all.

1 Used only to infer general inferences.

2 Used at beginning to determine empirical formula (Initial Strategy).

3 Used later, after some degree of problem-solving (Reverting Strategy).

4 Used to check if proposed answer was reasonable (Check Strategy).

S3 and S5 were the two subjects who used the “revert to Subgoal A” strategy the most, although it was also used by S (2, 4, 8). This strategy allowed the subjects to attempt a resolution of a problem using the spectral and wet chemistry data. If they needed to limit the model space because of conflicting evidence, the use of Subgoal A helped them to eliminate a number of erroneous possibilities they may have postulated. At the start of P5, S3 commented on the use of the percent composition:

If I were doing this with my students I'd probably actually calculate the percent oxygen and try to calculate an empirical formula. Uh, and if it gets to be a difficult problem I'll probably do that too. (S3-V1, T1)

In the later stages of P5, S3 had determined that the compound was a ten-carbon aliphatic alcohol, based upon his interpretation of the infrared, proton NMR and C-13 NMR spectral data. The proton NMR for menthol is very complex and difficult to interpret precisely, and he couldn't glean enough information to determine the structure. Based upon these observations and the boiling points of ten-carbon alcohols found in Rappoport (1984), he postulated 2-decanol as the closest possibility. However, he was not satisfied with this conclusion and after deliberation stated:

Okay. Go back and do it the way I would teach my students to do it. Add those percentages.....Convert to moles....Divide those...[C₁₀H₂₀O] . Okay, so this guy has got a ring. ten carbons, twenty hydrogens, it's got 1 degree of unsaturation, but it's not a double bond. It's gotta be a ring. So looking for something like a cyclo alcohol that boils around 210. Well's there's menthol. (S3-V1, T1)

S3 later formed a derivative to confirm the identity of menthol, but the "reverting to Subgoal A" strategy provided the information to limit the model space to an alcohol with a ring structure. This ultimately allowed him to solve the problem correctly.

When the subjects used the percent composition to gain general inferences about the presence of heteroatoms, they were successful on 71% of the problems. All of the incorrect solutions to the problems using this generalized strategy were from S7, the second least effective problem solver. When S (3, 5, 8) made this general inference, they were successful. S5, for example, initially noticed that there was a significant number of heteroatoms in P6 when the percent carbon and hydrogen added to 43.7% of the compound: "lots more than C and H." Later in the problem, the low percentage caused him to speculate about other heteroatoms besides oxygen:

“What if that larger percentage of elemental analysis, the percentage missing 43.7, 52.3 percent other. Two O’s are not going to tell all with an aromatic ring. So try that fusion test.” (S5-V1, T1)

The fusion tests allowed him to determine the presence of nitrogen and chlorine in the compound, and ultimately he solved the problem without calculating an empirical formula.

When the subjects made no apparent reference to the percent composition, they were successful 61% of the time. Each subject, except S5, at some point did not use the percent composition in their protocols.

From this data, two generalizations can be made. First, while determining the empirical formula to limit the problem space is a helpful strategy, these results would indicate that it is not necessary. Second, subjects were able to bypass Subgoal A completely, and still with reasonable success, solve the problems. An empirical formula limits the model space to compounds which contain that specific formula, but it does not help to determine functional groups or to elucidate the actual structure. Consequently, the completion of Subgoal A would not appear to be a necessary component of a model of expertise in qualitative analysis problem-solving.

Algorithms Involving Percent Composition

The most common algorithm used involving the percent composition was the standard calculation of empirical formula. This involves assuming 100 g of sample so that the percentage composition is transformed into gram units. The subject then converts all of the grams into moles, and finally determines the lowest mole ratio of the elements in the compound. This algorithm was used by all of the subjects, except S2, whenever they calculated the empirical formula.

S2 performed a different algorithm utilizing the percent composition on P7, P8,

and P10. Using the percent composition, he set up a ratio to determine the molar mass of the compound:

$$[\% \text{ hydrogen}] = [\text{Molar mass of } x \# \text{ hydrogen}] / [\text{molar mass of compound}]$$

The resulting molar mass was then used to determine the number of carbons in the compound:

$$[\% \text{ carbon}] = [\text{molar mass of } x \# \text{ carbons}] / [\text{molar mass of compound}]$$

Finally, the differences in the molar mass of the compound allowed him to determine the number of heteroatoms (in this case oxygen) by simple subtraction.

In P8, for example, he inspected the proton NMR and determined, based upon the integration, that there were eight protons in the compound. His algorithm, for this problem, taken from the protocols, is worked below. The percent composition is 81.79% carbon and 6.10 percent hydrogen for cinnamaldehyde.

$$0.0610 [\% \text{ hydrogen}] = 8.064 [\text{mass of 8 hydrogen}] / x [\text{molar mass}]$$

$$x = 132.197$$

$$0.8179 [\% \text{ carbon}] = x [\text{mass of } x \# \text{ carbons}] / 132.197 [\text{molar mass}]$$

$$x = 108.12 [/ 12.01] = 9 [\text{carbon atoms}]$$

$$132 [\text{molar mass}] - 108 [\text{mass of C}] - 8 [\text{mass of H}] = 16 [\text{mass of O}]$$

From this algorithm he determined the formula to be C₉H₈O. In P8 he utilized this algorithm as part of the initial Subgoal A strategy. In P7 and P10 he used this algorithm slightly later in the problem solving process, as part of the “revert to Subgoal A” strategy.

Research Question 4

The issue of the evaluation of the solution to a problem is central to problem-solving models (Bourne, et al, 1979; Reif, 1983b). The fourth research question of this study focuses on the types of experimental searches the subjects make after they have proposed a solution to the problem. Would the subjects see the need to conduct additional confirmatory experiments, or would the preponderance of evidence they have already collected lead them to a solution they might not feel the need to confirm?

Traditional qualitative analysis recommends the formation of a derivative to confirm the identity of the unknown (Shriner, et al, 1998). Would these subjects feel the need to form a derivative, or would they rely on the spectroscopic evidence? That is, would the subjects still find a need to confirm the problems in the traditional manner by taking a derivative?

Table 13 suggests that in most problems these subjects did choose to search the experimental space after initially proposing a solution to the problem. In 84% of the problems subjects chose to do some kind of experiment, whether that be a check of the percent composition, a re-inspection of the NMR data, a classification test, or the formation of a derivative. Every type of experiment in the program was selected, at some point, by someone as a means to determine or confirm if a solution was correct. Table 16 consists of the number of different post-proposed solution experimental searches made by each subject on each problem. If the subject chose, for example, to look at the proton NMR data multiple times, it is counted only once in Table 13. However, if a subject chose to perform different classification tests or form several derivatives, these are counted each time, since they constitute different experiments in the same category of experiments.

Table 13

Number of Evaluative Experimental Searches Made After Proposed Solution

	P1	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
S1	3	3	1	3	5	4	0	1	6	2	1
S2	3	1	2	2	9	3	2	3	1	4	3
S3	2	3	2	5	5	2	5	2	2	5	6
S4	4	3	2	1	3	6	4	2	1	7	1
S5	1	2	8	3	3	2	2	5	7	5	2
S6	0	0	1	0	0	1	2	2	0	0	2
S7	0	4	3	0	0	0	3	3	0	0	1
S8	3	0	1	5	4	1	1	1	5	6	4

The only subjects who did not make extensive use of an evaluative search of the experimental space were S6 and S7, the two least effective problem-solvers. This would suggest that the experts who were effective problem-solvers were those who took the time to check for abnormalities between the data and the structure of the compound. They made sure that most, if not all, of the data were in reasonable agreement with their solution.

Figures 16 and 17 show the relationship between the success of the problem solvers and how many times they checked their solution through new experimental searches. Figure 16 is the correlation between success overall by subject and the average number of evaluative experimental searches on all problems. The Pearson product-moment correlation is $r = .918$. This suggests in a quantitative way what a cursory glance of the data suggest: that successful problem solvers check their work to ensure that the solution is in full agreement with the available data.

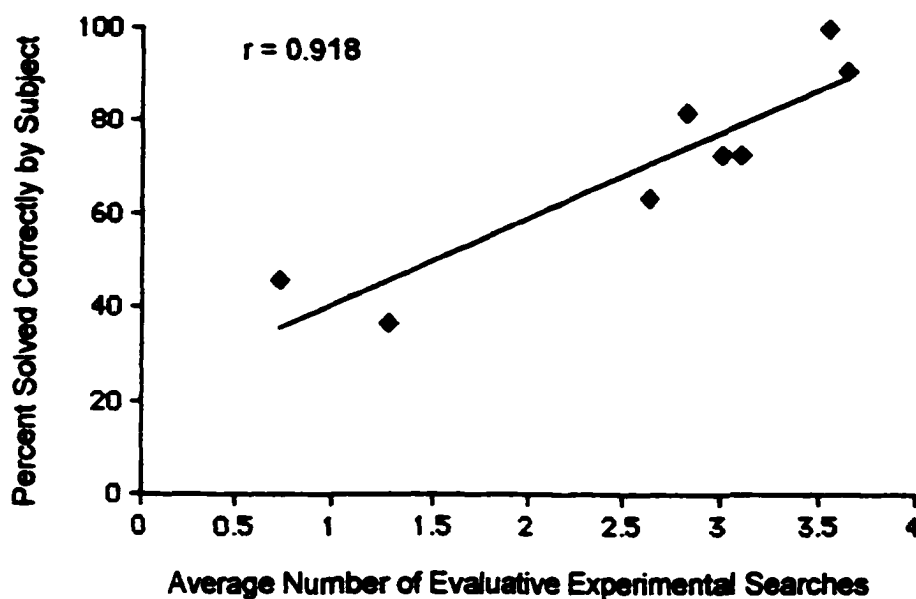


Figure 16. Correlation Between the Percentage of Problems Solved Correctly by Subject Versus the Average Number of Evaluative Experimental Searches on all Problems.

Figure 17 compares the frequency of evaluative experimental searches on only those problems which were solved correctly with the overall problem-solving efficiency of the subjects. This comparison was made since on some problems where there was no correct solution to the problem, subjects seemed to perform a greater number of experimental searches, trying to resolve the problem with no success. Consequently, to avoid skewing the results, it was reasonable to compare the number of fruitful evaluative searches with overall success of the subjects. While the Pearson product-moment correlation in Figure 17 is lower, $r = 0.814$, there is still indication that the use of evaluative searches of the experimental space is an effective strategy for success in solving qualitative organic analysis problems.

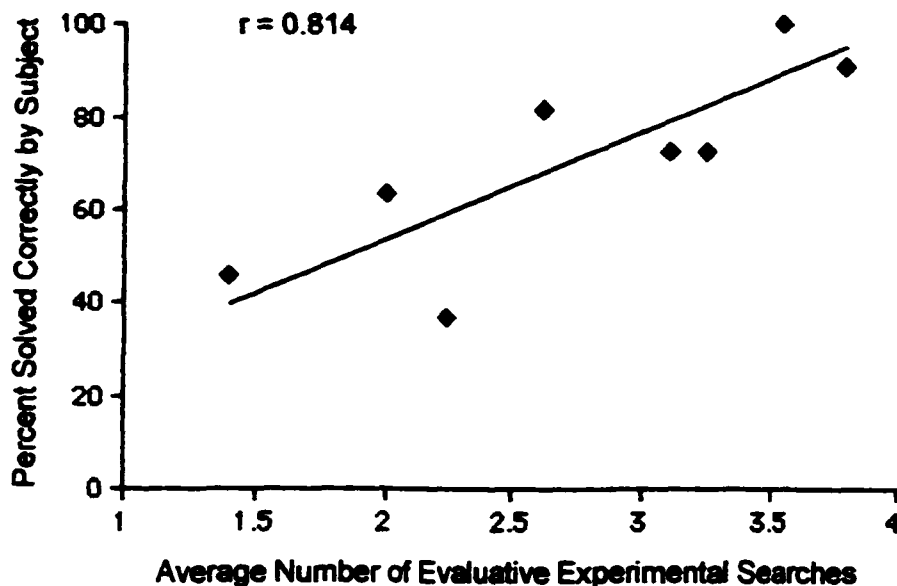


Figure 17. Correlation Between the Percentage of Problems Solved Correctly by Subject Versus the Average Number of Evaluative Experimental Searches on Problems Solved Correctly.

Strategies Involving the Evaluative Experimental Search

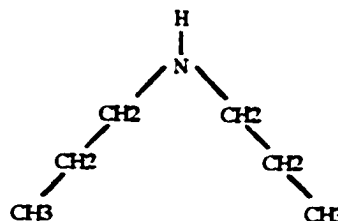
As stated previously, nearly every type of experiment in the IOC[®] was used by subjects when they checked their solutions. The following sections discuss the ways in which each type of instrument or wet chemistry test was used by the subjects. That is, what aspects of the data did the subjects feel was pertinent to checking the proposed solution? Examples of verbal protocols are included here to demonstrate the knowledge utilized by the subjects as they searched the experimental space to verify the structure of a proposed model.

Mass Spectrometry

When used as an evaluative instrument, the mass spectrometer was used primarily as a check of the molar mass of the compound. S8, after interpreting the proton

NMR data on P9, concluded that the structure was dipropyl amine, then proceeded to confirm the mass of the structure with the mass spectrometer.

I think that is what it is. Diisopropyl, dipropyl amine, because 4,4,6 [integration in the proton NMR]. Let's see what to do. Why don't I check the mass spec involved.



That shows you the weight of probably 101. Propyl is 43, 43, and 15 are 101. That's it. (S8-V2, T3)

$$\begin{array}{r} 43 \\ 43 \\ \hline 15 \\ 101 \end{array}$$

Based upon the NMR data, S8 was confident of the dipropyl amine structure; nevertheless he conducted the one additional evaluative search to confirm the molar mass.

The second way the mass spectrometer was used for evaluative purpose, was as a check of fragment losses that would be in agreement with the proposed structure. For example, on P1, S3 proposed 3-pentanol based upon infrared and proton NMR data. He had checked the C-13 NMR for three peaks and finally looked for evidence of an ethyl fragment in the mass spectrum.

And the mass spectrum should have a 29 [fragment loss]. Let's see, 29 [ethyl fragment] plus, 13 [methine fragment] plus 17 [hydroxy fragment] should look like a 59 peak as the base peak. So let's see, and it does. Uh, 59. So I'm going to say this is 3-pentanol. Okay, I'm satisfied. (S3-V1, T1)

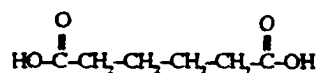
$$\begin{array}{r} 29 \\ 13 \\ \hline 17 \\ 59 \end{array}$$

3-pentanol

Carbon-13 NMR

When used as an evaluative tool, the C-13 NMR spectra served, most often, to confirm the number of carbon atoms in the proposed structure. This was particularly true for compounds with symmetry. P4, a symmetrical six-carbon dicarboxylic acid, was solved by S3 after inspection of the Infrared and proton NMR data. He then chose C-13 NMR to confirm his hypothesis.

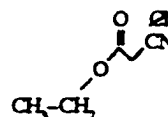
This looks like adipic acid. If it's adipic acid it should have 3 peaks in the carbon-13. And it's got them where they ought to be, so I can go to some other test if you'd like, but I don't have any doubt in my mind. (S3-V1, T1)



S3 not only inspected the C-13 NMR for the expected number of peaks that should be in the symmetrical compound, but apparently also noticed the chemical shift of the carbons. His spoken phrase "Where they ought to be" indicates that he was interpreting the downfield shift of the carbon atoms due to the carboxylic functional group.

While the number of carbon atoms was the most commonly sought data in the C-13 NMR during an evaluative search, on occasion, a subject did search the experimental space specifically for chemical shift. S2 on P10, had hypothesized ethyl cyanoacetate; and the C-13 data confirmed the structure in his mind.

S2: That means that I now have 5 carbons. One, two, three, four, five, and this [115 peak] would account for the carbon in this position [nitrile] and this one [carbonyl] is located here. . . . Yes, the one at 115, is the nitrile carbon, and yes that [ethyl cyanoacetate] must be. (S2-V2, T4)

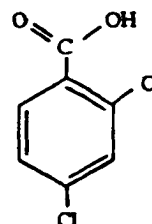


The combination of number of carbon atoms with the chemical shift of key atoms in functional groups was sufficient to confirm the hypothesis in S2's mind.

Proton NMR

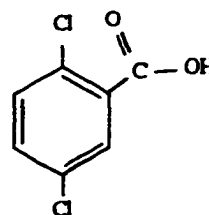
The proton NMR is the most versatile instrument for structure elucidation, and therefore was an extensively used instrument for evaluative experimental space searches. Subjects looked for chemical shift, integration, and coupling to confirm their structures. S3 had hypothesized a chlorobenzoic acid structure on P6. While this was incorrect, he used melting point temperatures in Rappoport (1984) to propose an alternative structure of 2,4 - dichlorobenzoic acid. The NMR data helped to establish that the arrangement of the aromatic ring was indeed a 1-2-4 arrangement.

Looks like it's a 2,4-, and the reason I say 2,4-, if I go back to the proton NMR, then there is the doublet, there's a doublet, then there's a singlet, then there's that guy [carboxylic acid proton]. So I've got two hydrogen's next to one another and one hydrogen off by itself. And it's the one that's most, these guys are all shifted up to the left, most of them are. Except for this guy. (S3-V1, T2)



After he established the coupling of the protons on the benzene ring, he proceeded to postulate the 2,5-dichlorobenzoic acid isomer as an alternative structure.

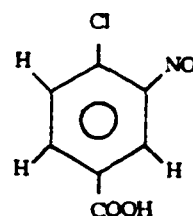
Is this the way I like this? Now that way or I could have this. I could have the chlorine there and a carboxyl here, chlorine there. Hmm. that would be 2,5-dichlorobenzoic acid. (S3-V1, T2)



After drawing the alternative structure, he questioned whether either of these compounds was correct. "Wonder if I have any justification for having two chlorines."

S3 proceeded to check the mass spectrum to see if the molar mass correlated to these structures. When it did not, he conducted a sodium fusion test and discovered that nitrogen was present in the compound. He then hypothesized that the nitrogen was manifested as a nitro- group. Once again, he re-inspected the NMR for agreement of the data.

I still think I've got a benzoic acid. I think I've got a nitro-. I think I've got a nitro-chloro-benzoic acid. Go back to the proton NMR, and those two guys, the singlet and the that guy are the ones that are there. So the singlet is strongly deshielded, one of these guys is strongly deshielded. Something like that, 2-nitro- 4-chloro-benzoic acid [He misnames the compound, but draws it correctly.] Now go back to these guys [Rappoport reference]. This is good for me actually. One of the things I tend to do is get into too big of a hurry about stuff. I thought I saw him in that book. Well, here's 4-chloro-3-nitro-, well that's the one I have drawn. Melting point 182, so that's cool. (S3-V1, T2)



182

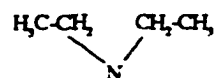
He took a derivative for a final confirmation of the compound.

Derivative anilide, all right. 129 to 131, oh that's all right. So apparently this guy is 4-chloro-3-nitro-benzoic acid. Melting point 182. Okay. I made that one hard, but I ran up two or three blind alleys. (S3-V1, T2)

Each time S3 made a model revision, he checked the proton NMR to make sure that the splitting pattern and chemical shift agreed with the new model.

S7 provided an extensive dialogue on P9 after he postulated triethyl amine as a possible solution. He used both the mass spectrometer and the proton NMR to refine the model into the proper solution.

...triethyl amine is the first thing that popped into my mind, but I don't know that uh, that uh, proton spectrum doesn't fit triethyl amine completely. It fits part of it. It fits the two ethyl part, but then my mass looked awfully low. [Checks mass spectrum]. Can't always, 101 to 72, that's a loss of 29 I believe. That's an ethyl group. Well that is another mass, that's a mass, so I think what I've got is some sort of a CH_2CH_3 , and that takes care of 10 of my 15 [protons].... (S7-V1, T2)

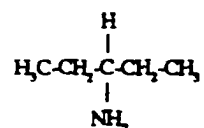


From the peaks at 0.8δ and 1.9δ, S7 concluded based on the coupling that there was ethyl fragments in the compound. The integration of 6 and 4, respectively led him to conclude there are two of these ethyl groups. He still had not accounted for the other peaks at 2.8δ and 1.2δ. He proceeded interpret these peaks, thereby revising his model further.

Got to explain this [triplet at 2.8δ]. I've got four others with that triplet, four others, and they are a triplet. I've got this one little thing to explain [broad peak at 1.2δ], which it looks like it's probably not in the right place for an OH or an NH. It probably is just a multiplet of multiplets, and a lot of small coupling constants in there. 3 carbons, 3 equivalent carbons. (S7-V1, T2)

He was observing that the peak at 1.2δ is not chemically shifted as far down field as an alcohol peak should be. While the peak was in the appropriate range for an alkyl amine absorption, he was not completely comfortable with that conclusion but speculated that the peak may be the result of a methine group in the chain. Finally, as revealed in this protocol, he reviewed the C-13 NMR data that told him there were three equivalent carbons in the structure.

That's not a typical ethyl pattern, so that's going to rule that [previous structure] out. Well, I still have a methyl group that is next to a CH₂. That's gonna give, but I've got 2 of those though. Because of the, yeah, the couplet is splitting. So rather than not they are attached directly, they could be CH₃CH₂CCH₂CH₃. (S7-V1, T2)



S7 recognized that the ethyl group was not isolated by itself since the peak at 1.8δ was a multiplet. He recognized there must be at least one other proton next to the methylene carbon to cause the multiplet. His next revision was to draw a methine group dividing the symmetrical ethyls. He attached an amine functional group to the methine, since he had earlier postulated, based on odd numbered mass spectrum, that the unknown contained an amine functional group. However, he then proceeded to eliminate this as a possibility.

Okay, yeah. Um, nitrogen, that's not a match. 1, 2, gets you three carbons [counting equivalent carbons in previous drawing]. That does not get you 15 protons. 10, 13 is here. 2 short. Well, it could be this here then.



CH₃CH₂CH₂, nitrogen, dipropyl amine. That gives me 3 carbons. That gives me 3,5,7,14 and 1 [counting number of protons]. I've got a triplet, 2 triplets, nah, a triplet worth 6. I've got a triplet down field worth 4 and I've got this multiplet here at 1.5 which is a doublet of triplets, and then I've got this nitrogen. So this looks like propyl amine. Some mass add uppers 6, [x12=] 72 and 14 and 15, that's 101. Propyl amine. (S7-V1, T2)

$$\begin{array}{r} 72 \\ 14 \\ \hline 15 \\ 101 \end{array}$$

In his final model revision, he rechecked the proton NMR to make sure that the splitting pattern and integration were appropriate for his structure. He checked the integration, coupling, and chemical shift, absorption peak by absorption peak, to verify a one-to-one correspondence with the dipropyl amine structure.

Infrared Spectroscopy

When used as an evaluative tool, the infrared spectrum was used primarily to confirm the presence or absence of functional groups proposed in the solution. On P5, S3 had proposed decanol; but after using the "revert to Subgoal A" strategy, he concluded that the formula was C₁₀H₂₀O, which contained one degree of unsaturation. He then proceeded to re-inspect the infrared spectrum.

The infrared spectrum confirms it's an alcohol and also confirms that there is no double bond in there. And so, so that means it must be some sort of cyclic alcohol. (S3-V1, T1)

The use of Rappoport (1984) and a derivative allowed the subject to determine that the structure was menthol. In this example, the infrared was scanned for common absorptions. Alcohols produce a broad band in the 3200-3500 cm⁻¹ wave number range,

whereas a C=C non-aromatic double bond typically absorbs in the 1640-1667 cm^{-1} range. For S3, the infrared spectrum of menthol in Figure 18 clearly confirmed the presence of the alcohol functional group and the absence of the C=C functional group.

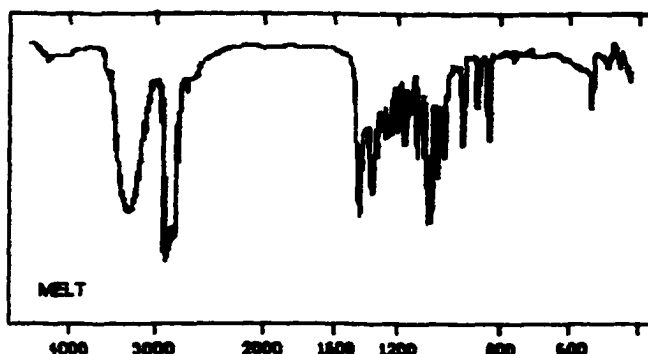


Figure 18. P5, Menthol Infrared Spectrum.

Unlike the previous example, not all scans of the infrared spectrum were used to confirm obvious functional groups. On P7, S3 had correctly identified the compound as 2-methyl-3-butyn-2-ol. He used the infrared to check the reasonableness of the tertiary alcohol he had proposed.

Here's the OH; and it looks a tertiary alcohol, cause there's the C-O at 1150 or so. This looks like the C-H off of the terminal alkyne, and that looks like a carbon-carbon stretch and it seems like I remember using IR tutor that there is a big peak way out here, like that for a terminal alkyne, but I may be wrong. (S3-V1, T2)

Declarative knowledge of the various types of absorptions in tertiary alcohols and terminal alkynes is much more subtle than that of primary absorptions in alcohols or carbonyl groups, for example. The C-O stretch absorption in tertiary alcohols is in the 1124-1205 cm^{-1} range, and the C-H bending absorption is a broad band in the 610-700 cm^{-1} range for a terminal alkyne (Silverstein & Webster, 1998). This knowledge

allowed the subject to verify in his mind that his proposed structure was indeed accurate. Figure 19 shows the infrared spectrum of P7, along with highlights of the absorptions described by S3.

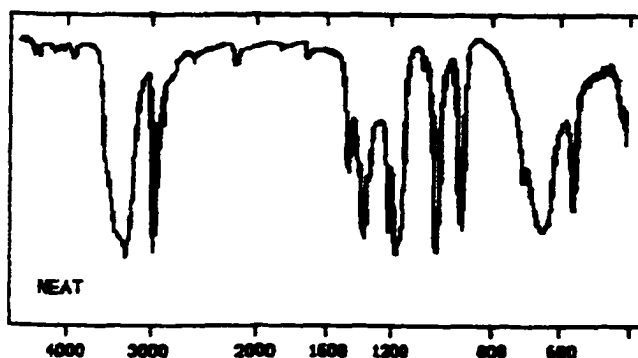


Figure 19. P7, 2-Methyl-3-Butyn-2-ol Infrared Spectrum.

Classification Tests

Classification Tests were used primarily to confirm the presence of functional groups in a proposed model. On occasion, a classification test provided a finer development of the functional group as primary, secondary, or tertiary. After S1 had correctly solved P7, he rechecked the chromic acid test data he had taken earlier.

Well, it looks like that's it. I'm just thinking, thinking through my data. This would give a slow chromic acid, a slow positive chromic acid. Very slow. Tertiary alcohols are very reluctant to oxidize. In fact, they, uh, you typically call them negative. (S1-V4, T8)

The chromic acid test can be used to distinguish tertiary from primary and secondary alcohols. The latter alcohols produce a green color in a few seconds, whereas the tertiary alcohol does not react readily (Shriner, et al, 1998). S1 was using the chromic acid data to provide this confirmation of his structure.

Physical Properties and Percent Composition

The percent composition and melting and boiling point temperatures were used as evaluative checks, as might be expected since the percent composition was used when the subjects determined the percent composition of their proposed formula and compared that with the percent carbon and hydrogen given in the problem. Sometimes this was part of the "revert to Subgoal A" strategy, but usually it was part of the "check Subgoal A" strategy as discussed earlier in this paper.

The melting or boiling point temperature, when used as a check were compared to literature values (Rappoport, 1984) for agreement. S1 had determined P3 to be a methoxybenzaldehyde, but he was not certain whether the ring structure substitution was an ortho-, meta-, or para- arrangement because of abnormalities in the proton NMR.

Well, I think, I think we've nailed it down, Keith, as a disubstituted aromatic aldehyde with a methoxy group somewhere on the ring. Um, at this point I would go to the literature and look up the melting or boiling points of those two compounds. (S1-V1, T2)

S1 proceeded to look up the boiling point temperatures of all three possible structures. The boiling point temperature given in the IOC[®] was 240-246 °C. This limited his possibilities to the ortho- (bp 243-246) or para- (bp 248) structures (Rappoport, 1984). The para-methoxybenzaldehyde was too close to the given boiling point temperature for the subject to eliminate. Consequently, he formed a derivative in an attempt to provide the final confirmatory evidence needed to distinguish between the compounds and solve the problem.

Derivatives

Derivatives were used primarily to provide final confirmatory evidence of a solution. In the preceding section, S1 formed a 2,4-DNP derivative to distinguish be-

tween the ortho- and para- structures on P3, methoxybenzaldehyde. However, each of the derivatives had similar melting point temperatures. Furthermore, Rappoport (1984) described the derivatives as having a red color.

I don't have definitive data here to distinguish between the two [ortho] and the four [para]. What I need to do is make a derivative, get a melting point of the derivative... There we are. 2,4- DNP. All right crystalline derivative is formed. Orange. Solid melting point is 249 to 253. [Reading IOC] And now let me go back to the, all right, there is the two methoxy. . . , I said that was a possibility. The 2,4 DNP is 253.5. [Reading Rappoport] Okay...Now let me try the 4, is page 149 was it? 4-methoxybenzaldehyde. [Laughter] 2,4-DNP is 253-254. Ah, but it's red. And what page was that on? 153. Huh, red. Well we still haven't nailed it down. The, your computer program tells me the 2,4-DNP is orange and both of these are reported as red, so you got a subjective difference there how people are reading colors. Also, the melting [point] is not as definitive as you would like. This is 253.5 compared with, whoa, 253-254. That's just to close to call. (S1-V1, T2)

While S1 took the derivative to distinguish between the possibilities, the results were inconclusive since both choices the ortho- and para- derivatives melted in the same range as the unknown. He finally took a C-13 NMR spectrum and eliminated the para- structure since there were eight peaks in the spectrum. Symmetry in the para-compound would have produced a fewer number of peaks in the C-13 NMR. In this particular example, the formation of the derivative did not supply enough evidence for the subject to declare the problem solved. However, in most cases the formation of the derivative was a straightforward means of confirmation.

On P5, S3 had speculated that the compound was menthol. The boiling point of menthol in the IOC[®] software was 209-211 °C, while Rappoport (1984) reported the boiling point as 216 °C. S3 then chose to form the 3,5-dinitrobenzoate derivative, which provided immediate confirmation in his mind.

Okay, 3,5-dinitrobenzoate. He melts at 155, 153 to 155. [From IOC®]
And so let's see for menthol. [Looking in Rappoport (1984)] Oh, that's
right on. Okay, so I'm ready to say this guy is menthol. (S3-V1, T1)

Derivatives were taken as part of the evaluative process in 27 percent of the problems. Only S(2, 7, 8) failed to take derivatives. As discussed earlier, the two industrial chemists did not possess declarative knowledge about most of the wet chemistry techniques and consequently did not make the formation of derivatives a part of their evaluative problem-solving process. S8 was the one academic who chose to utilize spectroscopic techniques only. With the removal of these three subjects, the remaining chemists used derivatives as part of their evaluative process on 44 % of the problems. This percent does not include the times in which derivatives were used to search for an answer, rather just when they were used to confirm an answer.

Summary

From the data presented in this section, it is reasonable to conclude that there is a positive correlation between success rate at problem-solving and the average number of evaluative experimental searches taken by subjects. The more successful problem-solvers in this study were more likely to perform new experiments or re-check old experiments to make sure that the proposed model conformed to the experimental evidence. The effective subjects in this study generally performed evaluative experimental space searches which spanned all types of experiments in the database. Derivatives were utilized only by the subjects in academia, most likely as a product of what they teach their students. The subjects in industry did not make use of most of the wet chemistry tests and never took a derivative. Their training had been with the contemporary spectrometric techniques only, and they did not possess the declarative knowledge to make effective use of these wet chemistry techniques.

A Model of Expert Problem-Solving in Qualitative Organic Analysis

In the research proposal, this researcher presented a model of problem-solving that was based upon a rational analysis of the domain of qualitative organic analysis. Because this project was the first research of this type in the domain, the analysis was based upon procedural outlines presented in books (Shriner et al., 1998; Feinstein, 1995) on problem-solving in the domain. Some degree of personal problem-solving experience must also have entered this model development. After the subjects in this study completed their participation and a general parsing of the verbal protocols began, it became clear that the hypothesized models did not adequately explain how experts solve these types of problems. Part of the difficulty was that the rational analysis model was very goal-oriented. Even though it was acknowledged that the subjects would move back and forth between subgoals, the model itself was highly specialized according to these subgoals, as if the subjects would systematically work their way through each subgoal. While evidence can be given, based on the protocols, that subjects did indeed engage in particular components of each subgoal, they by no means worked their way through these subgoals in the way originally projected. Part of the reason for this is that a particular chemical or spectrometric test could provide data pertinent to more than one subgoal. For example, inspection of the C-13 NMR can provide information about each of the hypothesized subgoals. Inspecting the C-13 NMR can reveal the number of carbon atoms, which information can be useful in determining the molecular formula and therefore can make this procedure part of Subgoal A. The chemical shift in the C-13 NMR can identify aromaticity and heteroatom functional groups — part of Subgoal B. Finally, it can provide evidence of symmetry and structural proximity of carbon atoms to functional groups, meeting part of Subgoal C. Upon viewing data such as these, experts were likely to infer more than one piece of information, about more than one subgoal, in a brief period of time. Their exploration of the experimental space provided

multiple pieces of information from multiple subgoals and multiple parts of these subgoals. For example, S7 on P3 took a mass spectrum to look for the molecular ion peak and the base peak, then took a C-13 NMR. Below is his protocol on the initial inspection of the C-13 spectrum.

There are lots of carbons in this one. One, two, three, four, five, six, seven, eight non-equivalent carbons. Looks like one is possibly non-substituted at 126.9 ppm. Um, possibly aromatic due to the peaks in the 120-140 [ppm] range. There does not appear to be alkyl atoms based on the fact there are no resonances between 0 and 40 [ppm], or non saturated carbons with hydrogen. Possibly one carbon oxygen bond, or carbon nitrogen at 50-ish. [Pause] 52.4 [ppm]. There is a resonance at 189 [ppm]. Possibly a carbonyl associated with an ester or an aldehyde. The possibility of an ester can be accounted for by the peak at 52.4 and the peak at 189. Although methyl ester, I'm not sure if it could be a methyl ester or not. Okay, so initial information from the C-13, we'll look at the proton spectrum now. (S7-V1, T1)

non-equivalent 8

non-substituted 126.9 ppm

possibly 120-140 ppm

no -CH

C-O or C-N 52.4 ppm

C=O 189

C13

From this inspection of the C-13 spectrum of ortho-methoxybenzaldehyde, S7 gathered information pertaining to each of the three subgoals. The number of non-equivalent carbons can be used to determine the molecular formula (Subgoal A). The chemical shifts indicating aromaticity, a carbonyl, a carbon-oxygen bond, and a lack of alkyl fragments upfield are all part of Subgoal B, determining the functional group fragments in the compound. Finally, the subject was using the chemical shift to infer how the

pieces might be put together when he postulated a methyl ester as a possible arrangement of these fragments (Subgoal C). S7 was indeed working toward the final achievement of the subgoals, but he was not working the problem through the subgoals as presented in the rational analysis. This example is just one of many that could have been given using various instruments and tests. This example, however, illustrates the justification for a major revision of the way the subgoals were presented in the research proposal. The subgoals themselves needed to be compacted, since they illustrated most of the possible outcomes from a data source within a particular Subgoal. This expansiveness was not necessary to capture the nature of expertise in qualitative organic analysis problem solving. The expansive, hypothesized Subgoals in the proposal contributed to the descriptive complexity of the overall model, but not to the productivity or explanatory power of the overall model. Consequently, revisions to the model were necessary, which included an expansion of the overall model, and a compacting of each of the Subgoals found in the proposal.

Revised Qualitative Organic Analysis Problem-Solving Model

The problem-solving process of the subjects in this study was an interaction of searching the experimental space with molecular model building. This search of two spaces: a model space and an experimental space, as discussed in Chapter II of this dissertation—provides a framework for analysis (Hafner & Stewart, 1995). In this research the subjects utilized their own theoretical mental models about the operation of equipment and the significance of peaks in a spectrum or color changes in a chemical reaction as a source of information about the structural models of the unknown organic chemicals they were testing. This model-building process was the result of information inferred through a search of a group of experiments. The three subgoals, defined in

Chapter II, constitute differing aspects of this model-building process. While these subjects may not have worked linearly through each subgoal, the completion of Subgoals B and C were the end result of their experimental operations.

Figure 20 is the finalized model of expert problem-solving derived from this research. It demonstrates how the subjects' interaction with the experimental space and the model space allowed them to solve qualitative organic analysis problems effectively. In this overall model, subjects initially performed experiments that they were comfortable interpreting. The selected experimental procedures, depending on the subject, could emphasize information from any of the three Subgoals. However, the subjects tended to glean a variety of information from the experimental results. Subjects could either use subsequent experiments to confirm the results of the experiment via some other experimental technique, or they could continue to explore various aspects of the Subgoal model space.

While Subgoal A was not utilized as an initial component in the majority of the problems, it was a significant enough part of the problem-solving process for inclusion in the final model. It should be noted that not all of the subjects worked toward the completion of Subgoal A. It is not a necessary component of the model since subjects were able to solve the problem without having to engage Subgoal A in their problem-solving process. Only S1 and S6 regularly made Subgoal A part of their initial strategy. Other subjects, S (2, 3, 4, 5, and 8), did revert to Subgoal A when needed. The determination of the empirical or molecular formulas was utilized as an initial strategy in 24 percent of the problems and as a revert-to-strategy heuristic in 16 percent of the problems when subjects found difficulty in solving the problem. Finally, the percent composition was used as a check of a solution in 15 percent of the problems. Since Subgoal A was utilized in some fashion in 55 percent of the problems, it was still included as part of the finalized model.

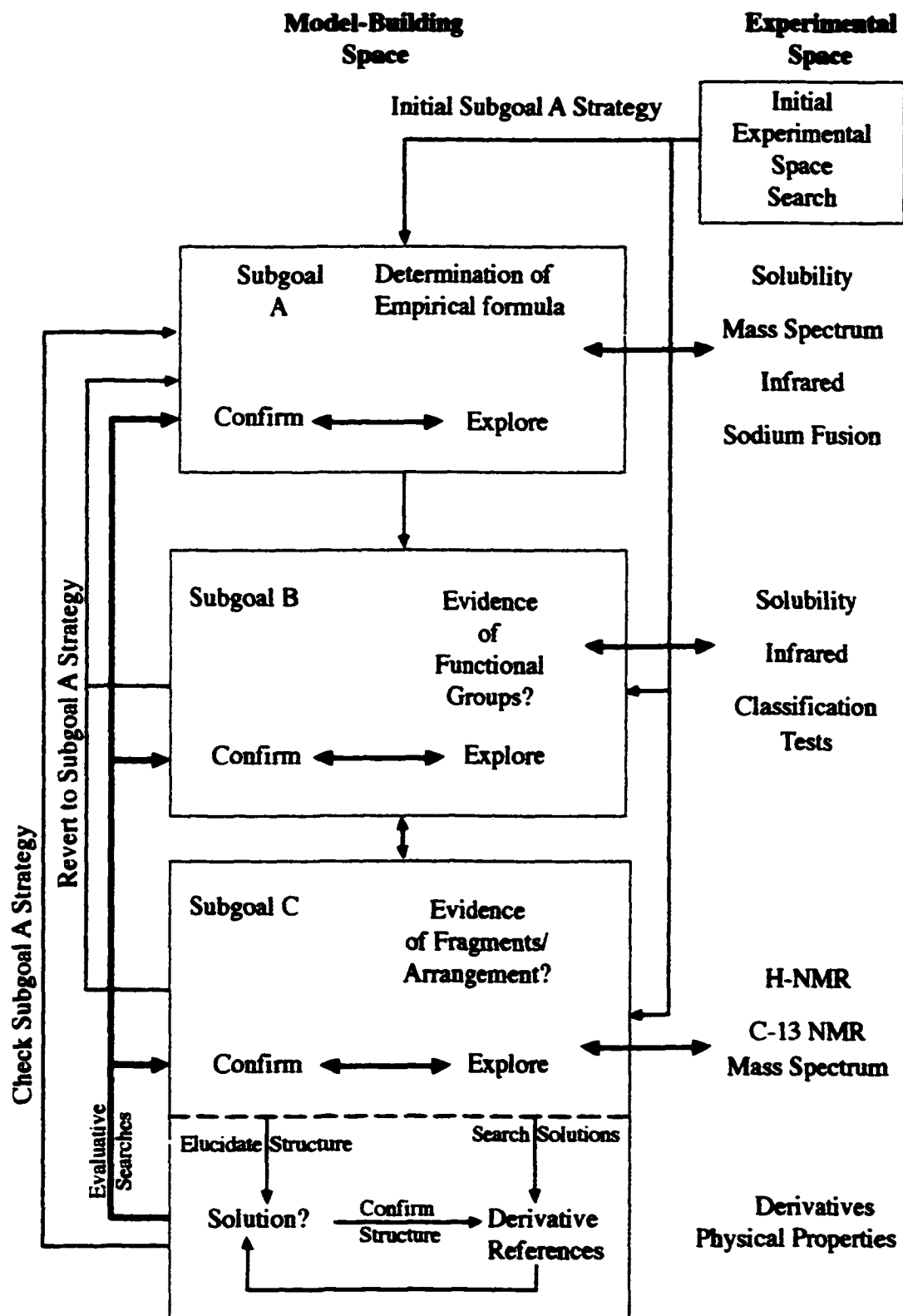


Figure 20. Model of Expert Problem-Solving in Qualitative Organic Analysis.

Initial Experimental Space Search

While S1 and S6 worked toward the completion of Subgoal A, the other subjects most often initially worked toward the development of the molecular model as it pertains to Subgoals B and C rather than attempting to achieve an empirical formula first. While they did gather evidence within Subgoals B and C, it does not appear that the initial exploration of these two Subgoals was entirely goal-driven. The initial exploration of these Subgoals was crouched in a strategy of searching the experimental space of the instrument or chemical tests that the subject felt most comfortable utilizing. Table 14 shows that subjects, on a relatively consistent basis, made similar initial and secondary experimental space moves on these problems. While these initial experimental space moves were fairly consistent within a subject, different subjects utilized different combinations of experiments. These experimental space searches were based, in part, upon the subjects' self-perceived expertise in interpreting the data which could be gleaned from the experiment. A number of examples can be given. S2 stated on P7, "As always, my standard operating procedure is to look at the NMR first." (S2-V2, T3) He made similar comments on P8 and P9. S4 on P4 performed solubility tests as her initial experimental move "just because I like solubility." (S4-V1, T1) When S5 was solving P3, he performed a solubility test, then stated, "I'll just skip to the IR again. It's so useful." (S5-V1, T1) While starting P10, S6 said,

I usually jump to IR first. Gross structural information, and sometimes it's more helpful than NMR in terms of just telling me if I've got a carbonyl, or if I've got an OH, or that kind of thing. That's why that's a common first jump I make. (S6-V2, T2)

Finally, S8 stated during the start of P5, "I really believe in emphasizing spectroscopy and everything that's involved in it." (S8-V1, T1) While verbal protocol evidence is relatively scarce, when combined with the regularity of their initial experimen-

tal moves, it nevertheless seems reasonable to conclude that the initial moves of these subjects was guided by their confidence in interpreting a particular piece of experimental data.

Table 14 shows, in the numerator, the number of times a particular experiment was the initial choice of each experimenter. The Table also shows, in the denominator, the number of times a particular experiment was the second experimental space search for each subject.

Table 14
Initial and Secondary Experimental Moves Conducted by the Subjects
(Number of Times used as 1st / 2nd experimental search.)

	Sol	Fusion	IR	NMR	C-13	Class.	MS	Der.
S1	3 / 6	6 / 2	0 / 1	0 / 1			2 / 1	
S2				11 / 0	0 / 5	0 / 1	0 / 5	
S3	7 / 3	4 / 2	0 / 6					
S4	9 / 0		2 / 9	0 / 2				
S5	11 / 0		0 / 9			0 / 2		
S6	1 / 0	2 / 3	6 / 4	0 / 2		2 / 1	0 / 1	
S7				0 / 1	0 / 10		11 / 0	
S8			11 / 0	0 / 11				
Totals	31 / 9	12 / 7	19 / 29	11 / 17	0 / 15	2 / 4	13 / 7	

This data shows that S (2, 5, 7, 8) never deviated from the same initial experimental move. They always explored the experimental space exactly the same way on each problem. While most of the other subjects tended to utilize the same initial experimental strategy, there were some occurrences which deviated from the pattern. For ex-

ample, S3 used the solubility test, followed by the infrared spectrum on P (1, 3, 4, 5, 6). On P6, 4-chloro-3-nitrobenzoic acid, he had some difficulty solving the problem until he identified (late in the problem-solving process) that nitrogen was present in the compound. Consequently, he altered his problem-solving strategy slightly after this, including a sodium fusion test as his initial move on four of the five remaining problems. He did this to prevent the same situation from recurring. On P7, right after performing solubility tests, he stated, "I'm going to start getting smarter. We're going to do the sodium fusion test." (S3-V1, T2) On P8 he viewed the percent composition and concluded, "12.11 percent something else that I'm going to assume it's oxygen. Ah, shouldn't assume that, should I? Don't make any assumptions. Sodium fusion test." (S3-V1, T2) Clearly, S3 did not want to overlook another heteroatom as he had done in P6. It should be noted that on three of the four problems in which he started with sodium fusion tests, he then went to the solubility tests as his secondary move, similar to his utilizing solubility as the initial experimental move on the first five problems.

Other deviations that occurred in the initial experimental move strategy were case-specific. Something in the physical properties may have evoked a different move on occasion. After viewing the physical properties of cinnamaldehyde and finding that it decomposed at 248 °C on P8, S4 commented immediately,

Okay [laughter]. I have an idea on this one already, just from practical experience. Benzaldehyde does that, or something similar. Aldehydes tend to do that. Let's look at the IR. (S4-V1, T2)

Normally, S4 performed solubility tests as her initial experimental space search, but on this problem she chose to deviate from this pattern because she felt she recognized one of the physical properties. She used the infrared spectrum to confirm the presence of the aldehyde functional group in the compound, instead of trying to infer general functionalities from the solubility data as was her custom on most problems.

Only S1 and S6 used a variety of initial experimental moves. S6 seemed to lack a cohesive initial strategy and utilized four different initial experiments—more than any other subject. On the very first problem S6 calculated an empirical formula and then conducted two different classification tests: 2,4 - DNP and Chromic Acid.

Uh, since it has oxygen in it, the first thing I do is a 2,4 - DNP. No precipitate occurs from that, so I know it's not an aldehyde or a ketone. So then, chromic acid test is the next thing I like to look at. We got a blue-green color, so since it's not a carbonyl compound, I know it's an alcohol. That would have also been obvious from my IR spectrum, which would have gotten me there quicker. (S6-V1, T1)

It appears that S6 was uncertain about how she wanted to approach the problems until after she had started this particular problem. As stated earlier, S6 seemed to be in a hurry at the beginning of the problem-solving session and did not solve any of the first five problems correctly. Like S3, S6 also had difficulty with P6, the nitro- functional group compound. Consequently, on P8, she stated, "Having learned my lesson, I'm going to go to a sodium fusion test." (S6-V1, T2) Aside from deviations like these examples, S6 utilized the infrared spectrum as the initial move on six of the eleven problems.

S1 also used a variety of initial experimental moves, but he favored the sodium fusion test on six of the eleven problems. On P3 he did take a mass spectrum after assuming oxygen in the compound, calculating the empirical formula of C_4H_4O from the percent composition, and determining the degrees of unsaturation. This empirical formula, while possible as a molecular formula, would not be a common formula and therefore gave the subject reason to check the mass spectrum as his initial experimental move. After being prodded to tell what he was thinking, he stated,

I was just thinking that's a little odd and I was going back in my head to see if I've done everything correctly. C_4H_4O with three sites of

unsaturation bothers me a little bit. I think I want to go straight to the mass spectrum and get a molecular weight and see if I'm thinking along the right lines. That's the next thing I'm going to do. Also, this simple molecular formula, in my mind, is not agreeing with the very high boiling point [240 - 246 °C]. And so I'm thinking that my actual molecular formula may be some multiple of this. (S1-V1, T1)

After producing the mass spectrum, he concluded that the molar mass of the compound was 136, exactly twice that of the empirical formula he had calculated.

68 is one-half of 136. So that tells me that was a good move. The molecular formula is $C_8H_8O_2$, and that is more consistent with a boiling point of 240 to 246 degrees. (S1-V1, T1)

On P11 and P12, S1 deviated from the norm of performing a fusion test to do a solubility test because the physical property data reported the compounds as yellow and brown in color, respectively. In both cases, he checked the solubility tests to determine if the amine functional group was present in the compounds. On P11 he stated, "Being a yellow liquid, it could very well be an amine, so, experiments, check solubility tests." (S1-V5, T10) Likewise at the start of P12 he said,

I have a brown liquid, which tells me that it once again may be an amine.... We'll get solubility data and possibly a mass spectrum and find out if nitrogen is present. (S1-V5, T10)

When taken as a whole, each subject had his or her own preferential opening experimental space search. When a subject deviated from this personal pattern of operation, it was typically due to data that was present in the physical properties or because of complications which had arisen on earlier problems. These typical initial experimental space searches were due, in part, to the experimenter's perceived comfort in exploring the data produced by the particular experiment. Table 15 summarizes the initial experimental space search of choice for each subject.

Table 15

Summary of Subjects' Initial Experimental Space Searches		
Subject	Initial experimental space Search	Number of Times
S1	Sodium Fusion	6
S2	Proton NMR	11
S3	Solubility	7
S4	Solubility	9
S5	Solubility	11
S6	Infrared	6
S7	Mass Spectrum	11
S8	Infrared	11

It should be noted that S (2, 7, 8) never made an initial or second experimental space search using wet chemistry techniques. This reinforces other data given previously that the two industrial chemists did not possess much declarative knowledge about the wet chemistry experiments and therefore did not include them in their strategic planning. Only later in the problem-solving process, when the data from the spectroscopic techniques were insufficient for them to solve a particular problem, did they ever utilize the wet chemistry tests. In the case of S8, this appeared to be by choice rather than a lack of declarative knowledge. He seemed determined to use the spectroscopic technology only. At one point he on P5 he said, "I strictly emphasize this [qualitative analysis] from a spectral standpoint. I don't have students do this in a qual scheme [wet chemistry] anymore." (S8-V1, T2) From this quote it can be reasonably concluded that at one point in time he did have the students in his classes perform a series of wet chemistry tests in a scheme similar to that found in Shriner, et al. (1998), but opted to alter his pedagogy to have the students use only spectroscopy. Consequently, the wet chemistry declarative knowledge may have been present but was unused by S8.

The initial experimental space search totals from Table 14 indicate that solubility tests and the infrared spectra were the most commonly used tests at the beginning of the problem-solving process. This is in keeping with the achievement of Subgoal B, the determination of functional groups in the compounds. The solubility tests in these experiments are primarily used to determine the functional groups in an organic compound (Shriner, et al., 1998). Likewise, according to Shriner, et al. (1998), "infrared analysis of organic compounds is nearly synonymous with functional group determination." (p. 126) While the initial experimental search was based upon subject preference pertaining to the interpretation of data, this was for the most part contained in the Subgoal B model-building process. The academic chemists, in particular, worked toward the determination of the functional groups primarily with a combination of solubility tests and infrared spectral data.

Secondary Experimental Space Search

After subjects performed an initial experimental space search, the next search was guided by the information they found or failed to find in the initial search. If the initial search provided evidence of a functional group, S (1, 2, 3, 4, 5, 6) tended to seek confirmatory evidence of the functional group in the next experiment. If the initial experiment was inconclusive or provided little useful information, they would conduct another exploratory search of the experimental space. Table 16 provides data pertaining to the number of times the second experimental space search appeared to be confirmatory or exploratory in nature, based upon evidence from the protocol statements.

Table 16
Strategic Use of Secondary Experimental Space Search

	Confirmatory	Exploratory	Both	Ambiguous
S1	5	5	1	-
S2	4	2	-	5
S3	7	4	-	-
S4	7	2	1	1
S5	3	4	4	-
S6	5	4	-	2
S7	-	11	-	-
S8	-	8	3	-

Regarding S (1, 2, 3, 4, 5, 6), the number of times they performed a confirmatory experimental space search versus an exploratory experimental space search is somewhat equally divided. However, among these subjects the second search was exclusively confirmatory in nature 47% of the problems and exploratory in 32% of the problems. The criteria for the nature of this search was the model-building information gleaned from the initial experimental space search. On P1, S3 performed solubility tests as his initial experiment.

I'm going to do solubility tests. Soluble in water. Insoluble in these guys [5% hydrochloric acid, 5% sodium bicarbonate, 5% sodium hydroxide]. Soluble [in concentrated sulfuric acid]. Okay. So I'm going to guess that it is probably some sort of neutral aldehyde, ketone, alcohol and I'm going to try an infrared [to determine] which of those it is. [He takes Infrared Spectrum.] And it's an alcohol. And there's the OH [peak] and here's the CO [peak], and that CO looks to be at about 975 cm^{-1} . (S3-V1, T1)

By virtue of the unknown's solubility in water and not in any of the 5 percent solutions, S3 hypothesized three possible functional groups in the compound. On the basis of this information, he explicitly stated that he was searching the infrared spectrum to confirm one of these functional groups as the one present in the unknown. The characteristic peaks in the infrared spectrum of his confirmatory experimental space search allowed him to decide that the functional group was an alcohol.

Even when subjects believed they knew the specific functional group from their initial experiment, they often still sought confirmation in the second experiment. On P4, S3 started, once again, with solubility tests. He followed this with an infrared spectrum.

I'm going to do solubility test again. Um, soluble in hot water. Soluble in sodium bicarb. Soluble in sodium hydroxide. So it looks like a carboxylic acid. Oh, let's see. We'll do an infrared spectrum again. [He performs infrared spectrum]. And there is the broad OH [peak] and the carbonyl [peak] for a carboxylic acid. Looks pretty good. (S3-V1, T1)

S3 undoubtedly had confidence that the unknown was most likely a carboxylic acid from the solubility tests, although phenols with electron-drawing constituents on the aromatic ring can also fit this solubility profile. Nevertheless, he chose to confirm his hypothesis by viewing the infrared spectrum.

When the initial experiment provided little information pertaining to Subgoal B, the subjects continued to explore the experimental space. S (1, 2, 3, 4, 5, 6) did this frequently, as Table 16 indicates. For example, S3 on P8 calculated an empirical formula at the beginning, but chose as his first experimental move a fusion test, to rule out the possibility of heteroatoms. The test showed that no heteroatoms were present, so he initiated an exploration of the experimental space for functional groups.

Sodium fusion test. No observable change. No observable change. No observable change. Okay that's good. So the rest of it's oxygen..... C_9H_8O . Sounds like a phenol alcohol of some sort. Let's do an infrared spectrum. Oh, cool. It's not an alcohol. Looks like its got a carbonyl....750

[cm^{-1}], looks like a monosubstituted benzene ring. (S3-V1, T2)

His hypothesis of a phenol was based upon the calculated empirical formula rather than experimental results from the fusion tests. Consequently, he initiated a search of the infrared spectrum in an attempt to fulfill Subgoal B.

The numbers in columns one and two of Table 16 account for those occasions in which it was possible to infer clearly the goal of the second experimental search. Not all of the protocols gave such a clear indication of the subject's intent. Sometimes it was unclear whether the intention was confirmation or exploration, since elements of both were present. This is represented in the column labeled "Both" in Table 16. For example, on P12, S5 conducted a solubility test, apparently concluding that the compound was an amine. Rather than just confirming this in the infrared, he performed a Hinsberg classification test that would both confirm the amine functional group and explore whether the amine was primary, secondary, or tertiary. He stated after looking at the solubility results, "And brown and basic, and that looks like [an amine]. Hinsberg test. It looks like a tertiary amine." It is entirely likely that these subjects gathered information that was both confirmatory and exploratory on more occasions than these listed in Table 16. However, the search was only classified as "Both" if the verbal evidence was not clearly indicative of a search for confirmation and exploration.

The inclusion of a search in the final column from Table 16, labeled "ambiguous," was only necessary when the subject made little or no verbalizations about the experimental move. S2, the subject who needed frequent prodding to speak, most frequently gave no indication of the rationale for his searches in the protocols.

S7 and S8 approached the problems differently than the other subjects in that they nearly always conducted a second experimental search for the purpose of further exploration. Rather than using an approach that would cause them immediately to confirm model components hypothesized from their test results, they chose to explore the

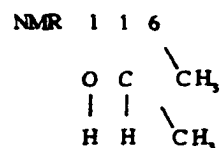
experimental space multiple times, gathering a larger amount of data before attempting to synthesize or confirm results. Their approach was different because they did not appear to be concerned if the conclusions they drew had multiple data substantiation at the early stages of the problem-solving process. They seemed to want to gather as much information as possible from their initial and secondary tests without a need for confirmation at this point. This is supported by the Table 14 data, which shows that their initial and secondary moves were almost always the same two moves. They, too, would ultimately seek to make sure that the data were in agreement. The difference is in the timing of confirmation of the data. For example, S8 always started with an infrared and proton NMR as his opening experimental moves. While these tests can provide corroborating evidence, that did not seem to be his objective. The infrared spectrum was primarily a search of Subgoal B, and the NMR was a search of Subgoal C. P7 provides an example of this strategy.

Spectrum looks like alcohol at 3500 [cm⁻¹]. Absorptions are alkyl, could be sp² CH's. That's what it says over here. Doesn't seem to be anything to draw from. CO bond maybe.... What I'm checking for is double bonds. I've seen double bonds that weak before. [Selects NMR] Okay. 1,1,6 [integration], okay. Well, the easiest way to get that [pattern] is, two methyls, and two other groups of something, and you should have an OH somewhere, but I don't know where. (S8-V2, T2)

alc ~ 3500

alkyl C_{sp}-H

C-O?



S8 went from analysis of alcohol and double bond functional groups in the infrared to proton integration of alkyl fragments in the NMR spectrum. He did not appear

to be seeking corroboration of the infrared data, even though he acknowledged that an OH peak should be somewhere. Rather, S8 worked directly for Subgoal B with the infrared and Subgoal C with the proton NMR. Not until later in the problem-solving process did he attempt to verify conclusions made at this point in his experimental searches.

S7, likewise, searched the experimental space initially without seeking confirmation. His searches were different than S8's. Nevertheless, they were nearly as consistent. He would search the mass spectrum to get a molar mass and any other details he could infer from the spectrum. His next search was consistently the C-13 NMR, with which he searched for the number of non-equivalent carbon atoms. The protocols from P4 provide an example of this.

Mass spec gives an idea of what weight range we are looking at. Mass peak shows up at even 100. 101 fragment. There is a little bit at 133, 134. Don't know if it is noise or not. I'm going to label it as noise right now and say there is a 133 and a 134 [noise] and stick with the 100 and the base peak is 55. So far, percent carbon and hydrogen are right. That is 56%; that means that we would get 34% [mathematical error] is heteroatom of some sort.

And the carbon spectrum, looking for nonequivalent carbons. Oh, we've got three nonequivalent carbons. Let's see, there are so few, I will go ahead and itemize. One carbon at 22 ppms, and one at 31 [ppm] and one way down yonder at 172.4 ppms. (S7-V1, T1)

S7 went on to speculate about symmetry in regard to the low molar mass and the few number of carbons in the spectrum. However, this was typical of his approach of conducting extensive exploration of the experimental space. He always gathered a significant body of evidence before extensively attempting to make sure the data agreed.

Continued Experimental Searches

It becomes difficult to quantify the nature of subsequent searches after the first two experimental searches. Too many variables are dependent upon the results of previous searches to develop a table with numerical values of the nature of these searches. However, a basic problem-solving model can be inferred. Subsequent experimental searches involve the subjects' exploring various aspects of the experimental space, inferring information pertaining to the subgoals, and then either seeking confirmation of information or new exploration to gain new model-building insights.

The model for expertise in qualitative analysis is largely a simple case of exploration and confirmation of data obtained from the experiments. These data are used to obtain various model-building information, until the structure of the compound is satisfactorily solved by the subject. These experts relied on their declarative knowledge pertaining to the various spectrophotometric and wet chemistry tests to solve the problems. (See p. 74-121.) They strategically sought out information, and then confirmation, pertaining to the subgoals of the model. When the subjects were satisfied about various components of the structural model, they would explore new aspects of the experimental space, attempting to expand their understanding of the structure. This recursive process would ultimately allow them either to elucidate the structure of the compound or, if the data would not allow for a final resolution, to identify the compound by derivative formation. Even when they did elucidate the structure, they would often seek confirmation by derivative formation.

Even though these subjects relied heavily on declarative chemical knowledge, they did not scrutinize all of the tests to the same depth of exploration. They tended to utilize the infrared, C-13 NMR, and the mass spectrum to gather basic information that was easy to obtain about each compound's molecular structure (p. 93-112). In using these instruments, they looked for the easy-to-observe, indisputable components of the

spectra to identify basic functional groups and coarse structural components of the compound. The subjects then analyzed the proton NMR for the more detailed aspects of each structure. It was in regard to the proton NMR that these subjects exhibited the most declarative knowledge. This experimental tool provided the greatest amount of detailed information, allowing the subjects to solve problems correctly. The academic chemists also relied heavily on wet chemistry data to initiate and supplement their understanding of the functional groups in the compounds. The industrial chemists, however, did not utilize in a productive way declarative knowledge about the wet chemistry tests available to them.

Problem Solution in Subgoal C

The combinations of C-13 NMR and Proton-NMR can be used to elucidate a structure once the functional groups have been determined from Subgoal B. As a subject would piece together fragments based upon chemical shift, coupling and integration from the proton-NMR, the possibility existed for him or her to elucidate the structure and solve the problem correctly. As discussed in regards to evaluative experimental space searches (p.132-147), the subjects in this study often performed or checked the experimental space to make certain the proposed solution was correct. In 84 percent of the problems, "evaluate solution" searches were performed to make certain the solution was in agreement with a preponderance of the data. Furthermore, the use of evaluative searches was an important component of success. The least effective problem-solvers (S6 and S7) were the least likely to evaluate their solutions. Consequently, they often did not detect errors in their solutions which they probably would have found if they had consistently made evaluative experimental space searches.

Subjects S1 and S8 made evaluative searches on most of the problems (See Table 13, p. 133). When they did not evaluate their solutions, it was because the solu-

tions were so clear in their thinking that they did not need to search the experimental space any longer. Each of these subjects had only one problem in which he did not evaluate his first solution with further experimental study. The remaining subjects S(2-5) made evaluative space searches on every problem.

The academic subjects in this study made derivatives a significant part of the experimental space search. On 27 percent of the problems these subjects, as a whole, used derivatives to "confirm a solution" they had proposed based upon the spectral data. Besides searching the derivative experimental space data to check an elucidated structure, these subjects also searched the experimental space of derivatives at times to find a reasonable solution when the NMR data did not allow for a complete structure elucidation. This "search solutions" derivative experimental space search was performed on 28 percent of the problems. Derivatives were taken on over half of the problems, either to confirm a solution or to search for a solution. Considering that S(2, 7, 8) never performed a derivative, the percentage of problems in which derivatives was used for either of these purposes rises to 73 percent for the remaining subjects from academia. For these subjects, derivatives were used as an integral part of the problem-solving process.

Protocol Example of the Model

In the following section, an entire protocol example is provided to illustrate the application of the model. The protocol is divided into three columns. The first column contains the verbal protocol of the subject divided into frames. The experimental space searches will divide the protocol into the frames and will be inserted into this column in italics. The time that the experiment was first initiated by the subject is included to provide a time reference in the problem-solving process. However, IOC[®] did not have the capability of tracking the time when the subject reexamined a spectrum or wet chem-

istry experimental result. Therefore, only the time of first initiation is included. So that the reader may see what the subject saw, the data provided by the IOC[®] for the subject will be included in the text, with the exception of the spectra. The spectra will be provided in Appendix C. These spectra will be taken from the IOC[®] program. For comparison with comments made in the verbal protocol, specific absorption peaks mentioned by the subject in the protocol will be highlighted in the spectra by this researcher.

The second column consists of the writings the subject made and will be aligned to the time that the verbalizations were made. The third column is this researcher's analysis of the protocol, with application to the model of expert problem-solving and the declarative and strategic knowledge evoked by the subject pertaining to the experimental space search. The model components are italicized in this column to distinguish them from the specific forms of declarative knowledge utilized by the subject.

Since S3 was the most successful problem-solver in this study, evidence from his protocol will be provided. S3 was so successful at problem-solving, that he often solved the problems with a relatively small amount of think-aloud protocols. However, P5 provided a challenge to the subject. P5 was menthol, an alcohol with a non-aromatic ring structure and a significant number of aliphatic chains branching off of the ring in the form of a methyl group and an isopropyl group. Menthol has a complex proton NMR, which makes it difficult to elucidate completely the structure from the NMR. The proton NMR in the IOC[®] was poorly resolved, and the subjects were allowed to view a paper copy of the spectrum from Aldrich[®]. However, this paper copy spectrum was nearly as difficult to fully interpret the finer detail as the IOC[®] NMR spectrum.

Subject 3, Problem 5

R: Yeah, you were going so fast I forgot to turn on the tape recorder.

S3: Oh, I'm sorry, I'll slow down. I actually I'm doing this like I'm running a race, like I've, I've won a prize if I get through first. All right here we go. Uh... new assigned...

R: Save it. Save laboratory.

S3: Save laboratory notebook.

R: All right, new assigned...

S3: New assigned unknown. Okay and we're going to go to five.

R: Unknown five.

Physical Properties (10:04)

Low Melting Solid

bp 209-211 °C

%C=76.86; %H=12.90

S3: Okay, so this again, here's a guy, he's sort of a semisolid, melting point and he's still got oxygen in him, 13, not much oxygen. Looks like maybe just 1 oxygen. If I were doing this with my students I'd probably actually calculate the percent oxygen and try to calculate an empirical formula.

Solubility Tests (10:05)

In water ... slightly soluble

In 5% hydrochloric acid...insoluble

In 5% sodium bicarbonate...insoluble

In 5% sodium hydroxide...insoluble

In conc. sulfuric acid... soluble

Uh... and if it gets to be a difficult prob-

Use of %composition for General Inference

Suggestion of Revert to Strategy for % composition

Initial Experimental Space Search (Subgoal B)

lem I'll probably do that too. This guy's water-soluble. This is misleading when it says its not soluble in 5 percent hydrochloric acid or any of these other guys. Because, in fact, if he's slightly soluble in water, he's going to be slightly soluble in those guys too, um... but any rate, I shouldn't criticize the computer program.

Infrared Spectrum (10:05)
See Appendix C

An infrared spectrum, I'm guessing this guys an alcohol and he is.

And uh... I can't pick out the CO, looks like he might be right there, in which case this guy would be a primary alcohol of some kind.

Physical Properties
Low Melting Solid
bp 209-211 °C
%C=76.86; %H=12.90

Boiling point 209, I'll write that down. Boiling point 209 to 211. I can go look him up in the table but I get more information from the NMR, ooh, normally.

Proton NMR
See Appendix C

This is the proton NMR. Hmm, this guys an aliphatic alcohol, ugly NMR spectrum. No peaks out here past 4 or 5 so he's some sort of saturated alcohol let me go back and look at the alcohol.

Infrared Spectrum

There's the... there's the OH, there's nothing to indicate it's unsaturated. So

Interpretation of solubility rules. No specific functional group stands out.

Explore Subgoal B

Alcohol OH stretch at 3300 cm^{-1}

C-O stretch at 1028 cm^{-1} indicates primary alcohol

BP - 209-211

Writes down boiling point temperature for possible references to literature value

aliphatic alcohol

Explore Subgoal C

Confirm Alcohol from Subgoal B
Chemical shift <5 non-aromatic/saturated

Reinspect to confirm alcohol, confirm no unsaturated peaks in IR

I've got an aliphatic alcohol of some... boils there. So let's, let's go back to the tried and true methods. Look up the boiling point in the table.

Silverstein, et al. (1991)

Alcohol that boils at around 210, and it's a liquid. All right, (pause) well this proton NMR, on this kind of sort of a semisolid, there are not any melting point in this one. See if there are melting points in the other one.

Rappoport, (1984)

Alcohol's boiling point, 210. Melting point... hmm... huh... there's no question it's an aliphatic alcohol, um... NMR spectrum is really funky. It appears to be that there is no, nothing out around 4 so actually it looks like it's a tertiary alcohol. Although I would have thought something else based on the infrared spectrum.
Let's do a C-13 NMR...

C-13 NMR (10:09)

See Appendix C

well, that looks cool. That not exactly what I expected. Uh, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 carbons. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 carbons, now that's something, that's something that I don't know if my students do, they would, they would count those and they and they would assume they got it right the first time.

Proton NMR

Ten carbon atoms and there is what the proton NMR looks like.

Explore Subgoal C

-Reduce problem space by searching references for aliphatic alcohols with boiling points near 210

3

Tertiary alcohols are farther upfield than 1° or 2° alcohols

Conflict of initial interpretation of data regarding type of alcohol

Explore Subgoal C

Searching Number of Nonequivalent carbons
Confirms count

C10

Oh... the 10 carbons are all different. This has got to be something like... looks like 2-decanol, actually is the only one here in the table.

But that doesn't look like the proton NMR. (Mumbling)

Well, there's a cute one. 5 methyl, 2, 1 methyl ethyl, that's uh.... I don't think it could be that. Uh... okay, so let's do a derivative. Uh... oh, I'll go back and do that! Um... let's do a derivative first. Uh... let's see what do I have here?

*alpha-Naphthylurethane Derivative
(10:11)*

No solid derivative was recovered

I have alpha-naphthyl urethane but it doesn't look like its going to be very helpful. No solid derivative was recovered. Uh... well, now I'm puzzled.

Infrared Spectrum

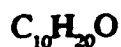
This may not be an alcohol, its gotta be an alcohol. (Humming) okay... go back and do it the way I would teach my students to do it, add those percentages, 76.86 plus 12.9, 89. So that's 11, excuse me, 10.24% oxygen. 76.86% carbon, 12.9% hydrogen. Convert those to moles. 10.24 divided by 16, 0.64 moles. 76.86 divided by 12, 6.4 moles. 12.9 divided by 1, that's something my students would do, 12.9. Divide those, 1, 10, 20... huh. Okay, so this guy has got a ring. 10 carbons, 20 hydrogen's, its got 1 degree

2-decanol

10.24%O → .64 mol 1

76.86%C → 6.4 mol 10

12.9%H → 12.9 20



Exploratory
Proposal of a
Structure

Evaluate structure
with proton NMR
peaks

Finds menthol in
reference. Initially
disregards possibil-
ity

Explore Subgoal C

Since NMR did not
allow for structure
elucidation S3
searches the de-
rivative experimen-
tal space for
compound match.

Lack of a deriva-
tive for an alcohol
creates a conflict in
data.

*Revert to Subgoal
A strategy*

Empirical Formula
algorithm

Degree of unsat-
uration algorithm
(Since no double or

of unsaturation but it's not a double bond, its gotta be a ring. So looking for something like a cyclo-alcohol that boils at 20, around 210. (Humming) well there's menthol. It doesn't look like menthol. Uh, okay... (Humming) What other information I have available? Sodium fusion, classification tests, I don't think derivatives are going to help me cause I don't think he's in either one of those books. Infrared spectrum, so NMR spectrum, I've already got. C13 I've already got. I don't think this is going to help, but lets look at a mass spectrum.

Mass Spectrum (10:15)

74, is the parent, is the base peak. And that sounds like a ring as well. Looks like the molecular ion is... 138, C10 H20 O. 16, 120 plus 20 plus 16, 8 is 158... so that's not the molecular ion. Solids low melting solids... yeah this is when you really start to learn something right? This shouldn't be slightly soluble in water. Who am I to argue?

R: Can you talk while you're looking through?

S3: You want to talk while I'm looking at this, I can do that. Uh... uh, usually I get more information from a proton NMR than anything else and that's probably because I've spent more time doing these guys. At this point in time I've convinced myself that it's an alcohol that has a formula of C10 H20 O. And oh... and, I actually calculated the molecular weight wrong a while ago, it actually has a molecular weight of 156 which uh, which is consistent with, and that's what I'm

74

120

20

16

158

120

20

16

158 156

triple bonds present he proposes a ring structure.)

Inventories possible tests to decide best options

Confirm Subgoal A

Subject error: 74 is not characteristic of a ring structure. (Silverstein & Webster, 1998)

Checking for molecular ion peak to confirm molecular formula

Corrects algorithmic error on Molar mass

looking for now, are things that where one thing agrees with another. Uh... C₁₀H₂₀O would have a molecular weight of 156. And the mass spectrum has uh, uh a molecular ion at 138. And, and there's a little bitty peak out here that could be, looks like, it could be 156, yeah it is 156. Molecular ions for alcohol's are notoriously small, so this guys, at this point in time, I'm looking for things that I know are absolutely true that I, that there's no question about. And one of the things that I think that there is no question about is that it has to be a compound of C₁₀H₂₀O. And that's consistent with the, the elemental analysis and it's also consistent with the mass spectrum. So I'm going to basically hang my hat on that and I don't see anything in the mass spectrum that gives me any further information. One of the things that puzzles me about the, the mass spectrum is that there is a pattern here that actually looks like, looks like a straight chain compound. Its uh, its uh, there are peaks every, roughly every 14 or so carbons and that's not what I guess I would have thought a ring compound would look like but I'm satisfied it's a ring. All right, so that's cool.

Infrared Spectrum

The infrared spectrum uh, confirms its an alcohol and also confirms that there is no double bond in there. And so, so that means that its gotta be some sort of cyclic alcohol, and what really,

C-13 NMR

and the carbon 13 NMR tells me that it is a cyclic alcohol in which every one of

Exploration/
Confirmation
strategy described
by S3

Checks Molecular
ion peak.
Notes characteris-
tic small M⁺ peak
for alcohols.

Check for consis-
tency of data

Reconfirmation of Subgoal B

- Alcohol peak
- saturated ali-
phatic

Reconfirmation of
of carbon atoms -
lack of symmetry

the carbon atoms, the ten carbon atoms are unique and different. Every one gives a different peak.

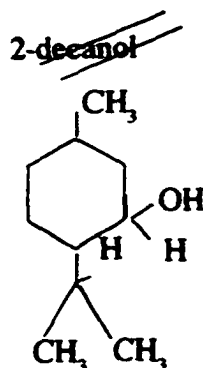
Proton NMR

And uh, and then, if I look at the proton NMR, I get this really, this mess over here that looks like it should be a lot of methyl groups cause they're all right in, and this is what is puzzling me I guess is that there are a lot of methyl groups here um... I guess at this point in time, I uh, it can't be 2-decanol uh...I got uh, two possibilities at this point and neither one of them I'm very comfortable with. I could say its menthol, or I could guess menthol. But if its menthol, it should be a secondary alcohol and there ought to be a peak out here around 4 delta for that hydrogen that on the... Oh wait a minute. All right, oh, wait a minute. Wait a minute, Wait a minute, Wait a minute, Wait a minute, Wait a minute, Wait a minute, Wait a minute, Wait a minute, Wait a minute, what's lenolual. Nope, that not it lenolual is not a ring compound. 216, solubility test. Thank you sir. Yes, so I'm looking, if its menthol then I, then that would account for this,

these things that look like methyl groups out here.

And that would probably account for this mess in here.

And that signal there's a little round thing there somewhere around 3 and a half and I guess I might be able to call uh might be able to call that OH.



S3 eliminates inconsistent proposed structure

Explores Subgoal C
S3 Proposes alternative structure

2° alcohols usually beyond 4

Confirms reasonable match of peaks in H-NMR

methyl peaks <1

Ring CH₂'s ~ 2

alcohol -OH ~3.5

So, so let's, let's see, let's proceed on the, the assumption that it's menthol.

Rappoport (1984)

All right, so it would have a boiling point of 216 it's actually too high, menthol's not a solid, is it? Well, I can't find uh,? Alcohol's, liquids 210, menthol's... I don't find menthol in this book. Wait it's in that book. Okay, let's go back and see if we can find a derivative this guy makes. Experiments, derivatives, all right, we've tried that alpha-naphthyl urethane, benzamide, picrate, 3,5-dinitrobenzoate.

3,5-Dinitrobenzoate (10.25)

A crystalline derivative is formed. Recrystallization yielded a white solid, mp 153-155 °C

Okay ..3,5-dinitrobenzoate he melts at 155... 153 to 155. And so let's see for menthol. Oh, oh that's right on. Okay, so I'm, I'm ready to say this guy is menthol.

R: Okay.

S3: Which is... five methyl, two, one methyl ethyl cyclohexanol.

R: Okay.

S3: All right. I'm ready.

R: That one at least took you, you had to write a few things. So I get a little data from that one. I'm not sure I got much on those first problems.

S3: Well, the deal with that one was that the proton NMR, you want to talk about it?

DNB - 153-155

Confirm Subgoal C

Compare boiling point of menthol

Confirm Solution with derivatives

Problem Solved Correctly

R: Sure.

S3: Yeah, the proton NMR uh, isn't really very definitive and particularly with an alcohol, what I generally do is I look in this region out around 4 for the proton that is attached to carbon that has the OH and it will to generally provide you with a lot of information. And in this case, uh... in this case it's not there. Its not there, here, or here, its not very well defined signals in here from, any where from 1 out to about 4 which I guess is, I should have thought the ring compound on the basis of that cause it does often (mumbling). Uh, the kicker really was really all these peaks here around 1; they're methyl groups. I'm thinking its cyclodeconal or something but it can't be that because those guys are all methyls. Okay are you ready to do another one? Okay, all right. (S3, V1, T1)

Chemical Shift due to alcohol functional group

Chemical Shift of methyl alkyl groups

While S3 was able to solve most of the problems in this study with relative ease, the data for menthol caused him to perform more extensive testing. IOC[®] always gives the basic physical properties of the compound with melting or boiling point temperatures as well as the percent carbon and hydrogen in the compound. It does not provide the identity of specific heteroatoms in the compound. When S3 saw that the percent composition provided was less than 100 percent, he inferred that a small amount of oxygen was present in the compound. This is not necessarily the case, but he operated with this assumption when he performed his initial experimental space search. S3 typically searched solubility tests for evidence of functional groups, Subgoal B, and this experiment was no exception. Solubility in only the concentrated sulfuric acid did not pinpoint any particular functional group since this solubility pattern is characteristic of

several types of neutral functional groups. Consequently, he continued to explore Subgoal B by taking an infrared spectrum. S3 did state that he was “guessing this guy’s an alcohol” before viewing the infrared spectrum, but that is likely due to the common occurrence of alcohols. The slight solubility in water may also have caused him to hypothesize an alcohol. The OH alcohol peak in the infrared spectrum distinctly absorbs as a broad peak at 3300 cm^{-1} . After identifying the compound as an alcohol, S3 made a further search of the spectrum, looking for the C-O stretch that would indicate whether the compound was a primary, secondary, or tertiary alcohol. Based upon the absorption at 1028 cm^{-1} , his initial conclusion was that the compound was a primary alcohol. In reality, menthol is a secondary alcohol; but the wavenumber of absorption is variable and can overlap in the same wavenumber region for primary and secondary alcohols due to coupling with adjacent C-C stretches (Silverstein & Webster, 1998). While his preliminary conclusion was inaccurate, he did not lock his thinking into this conclusion. Rather, he viewed this conclusion as a working hypothesis to be confirmed or denied by future experimental space searches.

After viewing the infrared for the first time, S3 reexamined the physical properties to obtain the boiling point temperature. The only rationale provided for this move was that he could “look him up in a table.”

S3’s next experimental search was the proton NMR. This move allowed for an exploration of Subgoal C, the search for fragments and their arrangements. The NMR spectrum for menthol is not well defined and does not provide a clear indication of coupling or integration. Consequently, he made a cursory scan of the chemical shift at near 4 delta as evidence to confirm that the compound was indeed an alcohol. The lack of peaks beyond this point indicated that the compound was nonaromatic and saturated. In keeping with the pattern of exploration and confirmation, he reexamined the infrared spectrum to search for confirmation that the compound lacked double and triple bond-

ing. The lack of characteristic peaks confirmed in his mind that the compound was indeed an aliphatic saturated alcohol.

While S3 normally would attempt to elucidate the structure of the compound from the NMR data, that did not appear to be possible in this problem. The lack of clarity in the proton NMR forced him to search for aliphatic alcohols in references (Silverstein, et al., 1991; Rappoport, 1984). This was an attempt to limit the problem space by providing a short list of possible solid aliphatic alcohols with boiling points of the liquid phase around 210 °C. At this point he made no specific verbalizations about the compounds in the reference manuals, but at the conclusion of his search he was prompted to think about the chemical shift in the proton NMR and its bearing on whether the alcohol was primary, secondary, or tertiary. Based upon this inspection, he concluded "...it looks like it's a tertiary alcohol. Although I would have thought something else based upon the infrared spectrum." Earlier, he had stated his hypothesis that the compound was a primary alcohol based upon the infrared interpretation. Neither conclusion was correct at this point, but once again S3 did not seem to lock his thinking into one pattern or the other. Instead, he explored Subgoal C, by performing a C-13 NMR and determining the number of nonequivalent carbons in the compound.

With the knowledge that the compound was a ten carbon aliphatic alcohol, S3 proposed a possible solution to the problem with 2-decanol. He then made an evaluative search of the proton NMR to see if the peaks would be consistent with 2-decanol and concluded, "That doesn't look like the proton NMR".

S3 appeared to look at the Rappoport (1984) reference and found menthol in the literature when he stated, "Well, there's a cute one. 5-methyl- 2-(1-methyl ethyl)." He did not finish the name by saying "cyclohexanol," but there is little doubt he was referring to IUPAC name for menthol. He did not give menthol much consideration at this point but dismissed it saying, "I don't think it could be that." Instead, he further ex-

explored Subgoal C by performing a derivative to search for a solution. He recognized that it would be difficult to elucidate the structure by the NMR, so he attempted to limit the possibilities by performing this search. The attempt to perform an alpha-Naphthylurethane derivative was unsuccessful, and no product was recovered. According to Shriner, et al. (1998, p. 315), it is extremely difficult to obtain a derivative for tertiary alcohols using this procedure. Furthermore, the presence of water can interfere with the formation of a derivative of the primary or secondary alcohols. One of the characteristics of the IOC[®] program is that it provides realistic data, in the sense that sometimes the wet chemistry does not perform perfectly according to perfect textbook specifications. The lack of a derivative “puzzled” S3. He did not seem to think of the possibility of a tertiary alcohol as the reason for a lack of solid derivative at this juncture. Rather, he stated, “This may not be an alcohol. It’s gotta be an alcohol.” Based upon his previous experimental space searches, he was convinced that it was an alcohol. The apparent conflict in the data caused him to revert to the Subgoal A strategy at this point in the problem-solving procedure.

In reverting to Subgoal A, S3 calculated the empirical formula of the compound to be $C_{10}H_{20}O$ by performing the standard gram-to-mole algorithm. Immediately, he also performed in his head the degree of unsaturation algorithm. He did not verbalize about the computation; rather, he just stated that the compound had to be a ring compound. A compound with the formula $C_{10}H_{20}O$ has one degree of unsaturation. By his previous experimental searches, S3 knew that the compound did not possess double or triple bonds. This left only a ring structure to account for the single degree of unsaturation since the compound was an alcohol instead of a compound with a carbonyl functional group. “Okay, so this guy has got a ring. Ten carbons, twenty hydrogens, it’s got one degree of unsaturation, but it’s not a double bond. It’s gotta be a ring. So looking for something like a cyclo-alcohol that boils around 210.” The calculation of the empirical

formula and determination of the degrees of freedom caused the subject to search for compounds that fit that description. He postulated menthol, although he did not believe the data really supported menthol at this point.

S3 then paused to look over the experimental possibilities. For some reason, he did not think this compound would be found in one of the references, so he inventoried the experiments and elected to perform a mass spectrum. S3 noted the parent peak at 74 and then attempted to confirm the empirical formula was the molecular formula by finding the molecular ion peak, which is very small in this spectrum. At first he called the peak at 138 the M^+ peak, but then found the small peak at 156, which confirmed the molecular formula to be $C_{10}H_{20}O$.

In the next section, S3 reexamined the infrared, the C-13 NMR, and the proton NMR to make certain his data were consistent with his conclusions to this point in the problem-solving process. The infrared and the C-13 NMR reaffirmed his conclusions, but the new examination of proton NMR created difficulties and a need to propose a new possible structure. "What is puzzling me, I guess, is that there are a lot of methyl groups here [under 1 delta]. I guess at this point it can't be 2-decanol. I've got two possibilities at this point, and neither one of them I'm very comfortable with. I could say it's menthol." He then listed two problems with menthol as the solution. "If it's menthol, it should be a secondary alcohol and there ought to be a peak around 4 delta for that hydrogen on the [oxygen]." Nevertheless, he continued to study the proton NMR after drawing the structural formula for menthol.

If it's menthol, then I, then that would account for this, these things that look like methyl groups out here [at less than 1 delta]. And that [the ring of CH_2 's] would probably account for this mess in here [around 2 delta]. And that signal, there's a little round thing there somewhere around three and a half [delta] and I guess I might be able to call, uh, might be able to call that OH. So let's proceed on the assumption that it's menthol.

Persuaded that menthol was a reasonable choice based upon the evidence to this point, S3 proceeded to search the experimental space for a derivative that would provide confirmatory evidence of the compound's identity. The corresponding match between the compound's boiling point and the 3,5-dinitrobenzoate derivative was sufficient to convince S3 that he had indeed solved the problem correctly.

The strategy of exploring the experimental space in Subgoal B was S3's normal starting operation in qualitative analysis. While he did not start with Subgoal A, or often attempt this part of the model, he was willing to revert to Subgoal A when needed. The proton NMR was not definitive enough in P5 to allow for the complete structural elucidation of this compound, so S3 also explored the derivative experimental space to search for solutions. Finally, he also used derivatives to verify the correct solution to the problem. As was his custom S3, made a significant number of evaluative experimental searches -in this case five- after his initial hypothesis of 2-decanol. Part of S3's success, beyond his firm grasp of the declarative knowledge about the experiments and the data generated by the experiments, was his flexibility in problem-solving. S3 was not locked into a fixed procedure, nor did he place too much confidence in any one piece of data. He took what the data offered and worked accordingly to solve the problems.

CHAPTER V

DISCUSSION

The manner in which the eight subjects in this project solved qualitative organic analysis problems were diverse in many ways. From the beginning it was clear, to this researcher, that these subjects did not use a trivial or algorithmic approach to solving qualitative analysis problems. In every area of the problem-solving process, it seemed there were at least two subjects who would do something different than the other subjects had done. Furthermore, in solving the various problems different subjects deviated from the "norm." As a consequence, much of the discussion of results in this project focuses on the differences rather than the commonalities that the problem-solvers brought to qualitative organic analysis. This made it difficult to generalize a detailed problem-solving model.

The model of expert problem-solving (Figure 20) generated by this project has built into it alternative starting points and pathways that were utilized by various subjects. Nevertheless, it can be generalized that the subjects in this study approached qualitative analysis problem-solving by seeking to reduce the problem space by identifying functional groups (Subgoal B) and by identifying fragments and their arrangement (Subgoal C), although not necessarily in that order. This model-building was a process of exploration of the experimental space for new information and for confirmation of conclusions drawn from previous experimental moves. The specific tests used for both purposes was variable by subject. These experimental space searches were initially based upon the particular tests that each subject felt the most comfortable interpreting.

Rather than utilizing specific strategies of problem-solving found in qualitative organic analysis textbooks, the subjects in this study relied on their declarative knowl-

edge pertaining to the interpretation of spectral data and in most cases classic wet chemistry. In other words, there was not a uniform series of experimental moves either between subjects or within a subject comparable to those listed in a text (Feinstein, 1995). The individualistic approach to problem-solving exhibited by the subjects in this study is significant. Experts do not appear to solve qualitative analysis problems by a set series of pre-prescribed steps, nor does it appear that one particular series of experimental moves is necessarily better or more efficient than another procedure.

The fact that the majority of the subjects did not work initially toward the solution of Subgoal A, the determination of the empirical and/or molecular formula, was surprising. According to Silverstein and Webster, (1998) "If organic chemists had to choose a single item of information above all others that are usually available from spectra or from chemical manipulations, they would certainly choose the molecular formula. (p. 11)" Two of the subjects, S(1, 6), did indeed make the determination of the molecular formula a priority early in their problem-solving process. However, the data collected from the other subjects in this research S(2, 3, 4, 5, 7, 8) would disagree with the claim of Silverstein and Webster. These six subjects did not seem interested in knowing the molecular formula as a tool to limit the problem space. They did, at times, revert to this strategy; and they did, at times, check their solution against the formula generated by the percent composition. However, these subjects did not operate in such a way that would indicate that the molecular formula was the single most important item in the problem-solving process. Rather, it may be that the subjects preferred not to limit their thinking to a particular formula so that their interpretation of specific experimental data would not be inhibited by a formula.

Industrial vs. Academic Chemists

This research found differences in the declarative knowledge, and henceforth the strategies, brought to the problem-solving process by the industrial chemists and the academic chemists. The industrial chemists, S(2, 7), demonstrated very little knowledge about the traditional wet chemistry techniques used in qualitative analysis. These procedures and the significance of their results, for the most part, were not in the long-term memories of these subjects. They approached the problems using only a spectroscopic approach to the searching of the experimental space. They were ineffective in utilizing the traditional methods when the spectral data failed to produce absolute results. It may not be possible to generalize to the entire population of industrial chemists since this study contained only two of these chemists. However, in both cases, the subjects indicated that the types of problems they were solving were not like the problems they would have to solve in the work place. S7 stated,

You know, I am not sure that if you're asking me what would I do if I were in a lab in this day and age, I am not sure I would do many of these [classification tests]. (S7-V1, T1)

When he did resort to wet chemistry on a difficult problem, he stated, "I guess I was starting to give you things I wouldn't normally do in the lab." (S7-V1,T1)

Furthermore, S2 stated that at work he would not have to solve a qualitative organic analysis problem without the benefit of knowing the reactants. In other words, his qualitative analysis was in the context of organic synthesis.

S2: When I put down my compounds, well in the laboratory, I have a big advantage because I know what I have put into the flask, which is enormously helpful. And I'm trying to figure out what has happened to the reactants. (S2-V2, T3)

One of the research questions of this project related to the issue of whether the traditional approach to qualitative organic analysis is outdated (Zubrick, 1992) or whether

the overall process of qualitative organic analysis is still necessary (Zieger, 1993). This research would suggest that, at least in the case of these two subjects, the traditional problem-solving experiments are outdated. On the other hand, when the spectroscopic data failed to produce a definitive solution, these two subjects had great difficulty in solving the problem correctly, whereas the academic chemists had other techniques they could utilize to solve the problem accurately. It may be that one implication for teaching qualitative analysis is that it should be taught in the context of organic synthesis in order to capture a more realistic sense of how it is practiced in industry. This would provide students the added educational experience of seeing the relationship between synthesis and the determination of the structure of the products and by-products made in the process. It would still provide a working knowledge necessary to elucidate structure, but would help the educational experience to be situated in a more realistic context of work in the industrial setting. However, it should be pointed out that there may still be situations when an organic chemist needs to determine the structure of an unknown compound without the benefit of knowing the reactants. Analysis of the structure of potential medicines found in exotic plants would be one example. Their structures must be elucidated without the benefit of the knowledge of starting materials. If the educational experience is to prepare graduates for any possible problem-solving context, it would be beneficial that some of the problems solved would still be independent of the synthesis process. The use of computer software, such as IOC[®], may be able to provide the additional problem-solving experiences necessary for the students to develop the skills to solve qualitative analysis in any setting.

The final conclusion of the matter based upon this research is that qualitative analysis as is traditionally practiced in the undergraduate setting does not correspond to the way it is practiced in industry, if these two subjects are sufficient to make such a

generalization.

Toward a Model of Desired Performance in Qualitative Organic Analysis

This research project has focused upon the knowledge and strategies utilized by experts in organic chemistry as they solve qualitative organic analysis problems using the basic tools often found in the undergraduate programs of universities. The model of expert problem-solving described in this paper provides understanding about how experts solve qualitative organic analysis problems. If education is to utilize this information, a model of desired performance must be specified, making explicit those strategies that will assist a student in becoming a good problem-solver.

This model will use the Revert to Subgoal A strategy rather than determining the empirical formula initially, as is prescribed in texts (See Appendix E). The experts in this study did not, for the most part, make use of Subgoal A as their initial strategy. Consequently, a model of desired performance will reflect this alternative strategy. Table 17 is a prescribed set of steps which will provide a student an initial model of problem-solving that should allow for increased success. This model should be applicable when used in the laboratory setting or in a computer software simulation.

The use of wet chemistry is allowed in this model, even though the industrial chemists did not use these techniques. The use of derivatives to search for solutions and to confirm a proposed solution has an important role in the problem-solving process. The majority of subjects selectively used wet chemistry to supplement the spectroscopic techniques, allowing them to solve a greater range of problems.

Even though some subjects did not search for functional groups initially, the majority demonstrated by their initial and secondary experimental moves that they desired to fulfill Subgoal B by identifying the functional groups (Table 15) in the compound before moving on to Subgoal C.

Table 17

A Model of Desired Performance for Qualitative Organic Analysis

- 1) **Make generalized inferences about the compound based upon color, state, and melting or boiling point temperature.**
 - 2) **Search for Functional Groups utilizing the experiment you have the greatest competency interpreting.**
 - 3) **Perform another experiment to continue exploration or to confirm the results of the initial experiment.**
 - 4) **Perform additional experiments if in doubt about functional groups.**
 - 5) **Search chemical shift, integration, and coupling in Proton NMR to identify alkyl or aryl fragments and their potential arrangement.**
 - 6) **Draw possible structures based upon data collected.**
 - 7) **Confirm interpretations utilizing C-13 NMR or Mass Spectral data.**
 - 8) **If the data do not conclusively support the structure:**
 - a) **Calculate empirical formula to ensure simple molecular formula is correct.**
 - b) **Perform derivatives for a possible match with the compound's properties.**
 - 9) **Perform new experiments and/or reexamine previous experiments to evaluate structure(s).**
 - 10) **Perform Derivative(s) to confirm solution.**
-

It should be pointed out that utilizing the model of desired performance is no guarantee that the student will be successful. As discussed earlier, much of the success of the experts was based upon their declarative knowledge pertaining to the interpretation of the spectra and wet chemistry provided. In order for a student to be successful, he or she must also possess sufficient declarative knowledge to be able to make correct model-building inferences from the data. Performing an infrared to determine functional groups is an excellent way to initiate the problem-solving process, as many of these experts did. However, the inability to interpret the absorptions correctly will lead to poor problem-solving regardless of the strategies used. Qualitative organic analysis is a domain that relies greatly upon the declarative knowledge of the problem-solver, and no prescribed set of strategic steps can guarantee success unless the declarative knowledge of the subject is sufficient to be successful. Nevertheless, this model of desired performance is a first step toward developing proficiency in a student problem-solver.

Theoretical Significance

Problem-Solving and Expertise

Most research in problem-solving has focused on biology (Collins, 1986; Hafner & Stewart, 1995; Brewer, 1996) and physics (Chi, et al. (1981); Larkin, et al., (1980); Reif & Heller, 1982). This research extends the problem-solving tradition into the domain of chemistry.

Most problem-solving research in chemistry has been with algorithmic problems (Yarroch, 1985; Gabel, et al., 1984). Bowen and Bodner (1991) did study the problem-solving processes used by graduate students during organic synthesis, and

Gonzalez (1998) studied how student conceptions of molecular structure relate to proton NMR interpretations; but little has been done in chemistry to research a complex problem-solving domain such as qualitative organic analysis. This study has theoretical significance because it extends the problem-solving research tradition into the understudied domain of organic chemistry to provide insight into how experts solve problems.

Reif (1983b) and Bourne, et al. (1979) break the problem-solving process into three subproblems. These three subproblems are the initial representation of the problem, the synthesis of the solution to the problem and the evaluation for reasonableness and correctness of the solution. One of the differences in experts and novices is in the initial representation of the problem (Larkin, 1979). Chi, et al. (1981) found that novices sorted physics problems based upon the physical objects in the problem, whereas experts sort the problems on the basis of the underlying physics principles found in the problems. While novices were not the focus of this research, it is anecdotally reasonable to assume that their initial representation of the problem would be to determine the empirical formula to reduce the problem space to a particular formula. It was expected based upon the rationale analysis performed before this research was conducted that the experts would also seek to limit the problem space by calculating an empirical formula (Subgoal A) before beginning extensive searches of the experimental space for model-building information pertaining to Subgoals B and C. However, Subgoal A was not used by six of the eight subjects in this study as an initial representation of the problem. Most of these experts chose not to limit the problem space initially; rather, they chose to search for the functional groups in most cases. By determining the functional groups, the subjects were not only representing the components of the problems, but also starting the synthesis of the solution to the problem. The distinction between the initial

representation and problem-solving synthesis is blurred in the case of these experts.

This research found that experts synthesize a solution to the problem by searching the experimental space for evidence of functional groups and fragments. The proton NMR was the primary instrument used to synthesize these various fragments into a molecular structure. While the emphasis was on using spectra to produce the model-building data, the academics also used traditional wet chemistry when necessary, allowing them to be more effective problem-solvers when it was difficult to elucidate the structure from the spectral data provided. Experts did, at times, revert to determining an empirical formula when a solution was not forthcoming.

The data from this research indicate that the experts made considerable evaluative searches of each proposed structure. The most successful problem-solver made an average of nearly four evaluative searches per problem. Furthermore, there was a direct correlation between the number of evaluative searches made by these experts and their relative success rates. These evaluative searches included rechecking old data to confirm the correlation between the structure and the absorptions, chemical shift, etc. in the spectra, and performing new experiments to confirm the structure with a new source of data. The academic chemists also made use of derivatives to confirm the correctness of the problem solution. Reif (1983b) stressed evaluation as an important component of effective problem-solving. The results of this research provide strong evidence of the importance of making multiple evaluations of a solution from a variety of sources. This has practical significance for the teaching of qualitative organic analysis. Students may have a tendency to piece a structure together based on the experimental data, without checking all components of the solution after reaching a conclusion. Professors can make explicit the value of post-solution evaluative experimental space searches in their instructional practice and model this behavior for their students to move them towards a

greater degree of expertise in qualitative organic analysis.

Another characteristic of expert problem-solvers is the ability to store information in chunks. Simon (1974) originally postulated that a chunk may consist of a word, a phrase, or a concept. Larkin (1979) found that expert physicists stored the underlying physics principles in chunks. Simon and Chase (1973) found that chess experts had chess pieces chunked together on the basis of how those pieces would work together offensively or defensively, for example. Experts in this study also appear to have information stored in chunks which would most closely resemble the chunks which chess masters demonstrated in their short-term memory. This was particularly true when interpreting proton NMR data. When viewing a proton NMR, they understood coupling sufficiently enough to postulate ethyl and propyl structures on the basis of absorption patterns in the spectrum. These patterns were recognized very quickly without the need for extensive searching of the spectrum. The ability to organize this knowledge in chunks greatly facilitated the experts' ability to solve the problems since the synthesis of the solution culminates with piecing molecular fragments together into a molecular structure.

Stewart (1988) argued that there are four important learning outcomes from students solving genetics problems. One of those suggested outcomes is that through problem-solving students will gain a better understanding of generic heuristics which are independent of the discipline. While not all of these heuristics may have application in qualitative organic analysis, a number of them were evident in the experts' problem-solving. These general heuristics and examples from qualitative organic analysis protocols are provided in Table 18.

Table 18

General Heuristics with Examples from Qualitative Organic Analysis

1. Redescribe the problem in the problem statement.	• Infer basic chemical properties from the physical properties.
2. Break the problem into subproblems	• Subgoal A, determine empirical formula. • Subgoal B, determine functional groups. • Subgoal C, determine fragments and their arrangement.
3. Use external memory aids	• Write down molecular inferences. • Refer to absorption charts, derivative tables.
4. Select moves that are the most knowledge-producing.	• Perform the experiment most comfortably interpreted.
5. Assume the most simple case first.	• Assume heteroatoms are oxygen.
6. Consolidate your knowledge.	• Confirm inferences with another test for the same functional group.
7. Check results, hypotheses.	• Re-check data already collected. • Perform additional tests/derivatives.
8. Be systematic.	• Find functional groups, then structure.
9. Think of a related problem.	• Recognize characteristic absorption wavenumbers, etc.
10. Use knowledge to construct hypotheses.	• Draw plausible structures.
11. Work backwards.	• Check data against plausible structures.

Practical Significance

Identification of Organic Compounds Computer Software

This research has practical significance in its ability to contribute to the improvement of Identification of Organic Compounds® and other computer-based simulations of qualitative organic analysis problems. The improvement of software will allow educators to use to a greater extent this simulated problem-solving environment to supplement actual laboratory experiences. Elucidating the structure of a compound is very time consuming. The instrumentation - infrared, proton NMR, C-13 NMR, and mass spectrometer - require sample preparation before using. Fourier transformation technology has greatly decreased the time necessary to perform a spectrum, but most universities would only have one of each of these instruments available for student use. When the potential waiting time to use the instrumentation is coupled with the time required to perform the wet chemistry experiments available, it may take several lab periods to collect the necessary data to solve just one problem. This is insufficient time for a student to develop competence in interpreting any one piece of instrumentation, let alone solving qualitative organic analysis problems in their entirety.

Computer software such as IOC® has the potential to supplement this instruction, leading to greater expertise among students at the undergraduate level rather than waiting until the graduate level.

Before IOC® can realize its full potential as an effective problem-solving simulated environment, several changes must be made to supplement those factors which make IOC® a viable tool. IOC® has numerous positive properties in place already. First, it provides the data in a format that would be representative of the observations made in the laboratory, including false positive results which may typically occur in wet

chemistry experiments. The representation of data requires the student to interpret the meaning of the results as they would have to do in the laboratory.

Second, the large selection of problems available and the instructor's ability to create specific problem sets or allow students to solve random problems for practice provides great flexibility to the instructor. The student can print out all of the data collected with his or her results to turn in to the instructor for a grade if necessary.

Third, the pointer on the spectral data allows the user to pinpoint details, for example, the exact wavenumber of absorption. This can compensate for the fact that the spectra in the IOC[®] is rather small and would be impossible to interpret with certainty without the pointer. It would be best to make the spectra larger in order to provide greater resolution of peaks, but the pointer does help to alleviate this problem.

What changes are needed in the IOC[®] to increase its potential ability to serve as a powerful tool in teaching qualitative organic analysis? First, errors which appear in some spectra need to be fixed. Each spectrum needs to be checked to make sure that the peaks register at the appropriate chemical shift, etc. Errors in integration, as in the proton NMR of cinnamaldehyde, need to be corrected. While the subjects only solved 11 problems in this study, several of these types of errors were discovered. It is reasonable to assume that other similar misprints exist in the problems not utilized for this research. This suggestion would be the top priority, since a problem is difficult to solve if faulty data is being used.

Second, integrations of the proton NMR in the IOC[®] must reflect the integration of an actual spectrum. Proton NMR integrations do not give the actual number of protons for each absorption; rather, they provide relative amounts of protons. For hexanedioic acid, IOC[®] provided the integration of 4, 4 and 2, the actual proton numbers for the symmetrical carbon atoms in the compound. A real NMR scan would have

provided a ratio of 2, 2, to 1 for the integration. While the higher ratio might make problem-solving easier for the novice, it does not provide a realistic representation of the data as it would appear in actual problem-solving. Consequently, this should be changed for hexanedioic acid and any other compounds which might have a similar problem with its integration.

Third, the database of possible answers needs to be enlarged. Currently, users can search the database of possible ketone compounds, for example, and be provided with a limited list of possible compounds and their derivatives. This is similar to the database provided in Rappoport (1984), but much more limited in scope. Consequently, students who are using the program can “guess” the correct solution rather easily, since they know the correct answer is contained in the database and there are few competing alternatives with comparable melting points. If possible, the Rappoport (1984) database should be integrated into the program: this type of enlargement is needed to increase the validity of the problem-solving environment. Currently, students using the program do not have to elucidate much of the structure in order to solve the problems with the database in operation in IOC[®]. That is why the subjects in this study were not allowed to utilize this function in the IOC[®] problem-solving environment. If the expansion of the database is not feasible, it would be better to exclude the current database from the program so that students actually have to elucidate the structure or use the actual Rappoport (1984) reference when performing derivatives.

A fourth negative aspect of the IOC[®] is that it is situated much like a “game” in which the students are charged points for each performed experiment. These points are meant to be a way to evaluate the efficiency of the student’s choice of experiments. If, for example, a student starts by performing an infrared spectrum before performing wet chemistry tests such as solubility, he is penalized with more points than if he takes the

spectrum later in the process. This means of "assessment" is tied to a very traditional protocol for solving qualitative organic analysis problems. Now, a student may choose to ignore these points. However, it is human nature to want to perform to the standards established in the game. Even the experts in this study had difficulty ignoring the points they were assessed in spite of the fact that this researcher told them the points did not matter. Based upon the findings from this research, in a desired approach to problem solving, the student may very well justifiably choose, to perform an infrared spectrum as the first experimental option. Therefore, any part of the program that would inhibit students from modeling the expert approach to problems-solving should be removed or modified. The professor evaluating the data sheet of the student is in a better position to judge the merits of the student's problem-solving processes than the computer. As a result, I would recommend that the points assessment part of the program be removed, since it may alter student performance in an undesirable way.

Even with the difficulties with the IOC[®] described in this paper, in its current state it can still be utilized as a computer based problem-solving environment to supplement instruction. These criticisms are not intended to denigrate the program. Rather, based upon the results of this research, they are intended to provide insight into how the program may be improved as an instructional tool.

Undergraduate Organic Chemistry Instruction

This research has indicated that a computer simulation can provide a viable mode of instruction in the undergraduate organic chemistry program. It cannot, by any means, replace the hands-on experiences needed by students to develop competency in qualitative organic analysis. However, the lab time necessary to develop a desired level of proficiency is unavailable at the undergraduate level. Computer-based problem-solv-

ing can bridge the gap needed. When used in conjunction with real laboratory experience qualitative organic analysis software, such as the IOC[®], can be beneficial.

This research has demonstrated that there are a number of pathways available to students to solve problems. The model of desired performance can provide a strategic guideline which professors may find useful for instruction. The model is not rigid in the instrumentation or wet chemistry utilized by the student, but it does emphasize the importance of finding corroborating data before final judgement is made on inferences. It de-emphasizes the role of the empirical formula as an initial first step in the problem-solving process. Finally, it emphasizes the importance of evaluative experimental searches and re-inspections to make sure that the data support the proposed structure. Each of these aspects of the model has the potential to move a student toward a more expert-like approach to qualitative organic analysis problem-solving. Assuming that instruction provides students with the prerequisite declarative knowledge to interpret data properly, the recommendations made as a result of this research have the potential to improve instruction at the undergraduate level.

Questions for Future Research

As a first attempt to study expertise in qualitative organic analysis, this research has raised questions that would be appropriate avenues of further research. Because of the diversity of the eight experts in this study, it might be appropriate to engage other experts, especially chemists who work outside the academic setting, in problem-solving to see if the industrial chemists in this study are truly representative of nonacademic chemists in general. The model of problem-solving generated by this research is not as refined as it might be due to the diverse experimental space search choices and strategies utilized by these particular subjects. An initial investigative research project like

this, which attempts to open up a new domain to be studied, cannot definitively describe all of the strategies and knowledge utilized by subjects who solve qualitative organic analysis problems. Qualitative organic analysis is too complex for this study to be the final word.

This research only allowed subjects to use instrumentation which would most likely be found in the typical undergraduate organic chemistry program. For example, two dimensional proton NMR was not one of the techniques available to the subjects in this study because it was believed at the outset that this was not indicative of the tools an undergraduate would be able to use. It would be valuable to know how the problem-solving strategies would alter if this type of cutting-edge technology were available to the experts.

The subjects in this project often only inspected spectra for crude observations. For example, most often a subject would search an infrared spectrum for carbonyl absorptions and unsaturated carbon groups. This depth of inference was all that was necessary for them to solve the problems. Consequently, this study may not have probed the depth of declarative knowledge possessed in the long term memory of these subjects. It might be possible to provide a set of spectra to experts and ask them to do multiple categorizations of the spectra to investigate specifically their knowledge of the spectra. This would be similar to the study by Chi et al. (1981), in which they had novices and experts categorize various physics problems. This type of project would reveal to a greater extent specifically what experts find important in a spectrum when not in the context of solving a specific qualitative organic analysis problem.

Since the industrial chemists indicated that they solve problems in the context of organic synthesis, the investigator could generate problems which combine synthesis with analysis of the products. This would significantly change the context of the prob-

lem-solving environment and henceforth could alter the strategies used by the subjects.

The next logical step of this research is to study novice performance at qualitative organic analysis. Reif (1983a) elaborated upon four components that must be developed in order to improve the teaching of science based upon research. This research project provided insight into the second of those components, a model of desired performance. Undergraduates at the end of instruction on qualitative organic analysis could engage in solving the same problems the experts solved in this study. This first component of Reif's proposal, the development of a model of students' performance, would make explicit the differences between how novices approach the problem-solving environment and how experts solve the same problems. Once this was completed, models of learning and teaching could be developed to illustrate specific knowledge structures and strategies which need to be addressed in instruction to facilitate the transformation of novices into more expert-like problem-solvers. Research into student conceptions (diSessa 1982; Driver, et al., 1994; Posner et al., 1982) has indicated that these conceptions, even though not scientifically acceptable, are resistant to change by straightforward instruction. The development of a model of student performance would assist in the implementation of teaching strategies which could help to alter these novice-like conceptions found in the research.

Appendix A
Informed Consent Letter

**Western Michigan University
Department of Science Studies**

Principal Investigator: Robert Hafner

Research Associate: Keith A. Schramm

I have been invited to participate in a research project entitled "An Investigation of Expert Problem-Solving in Qualitative Organic Analysis." I understand that this research is intended to study and account for how experts solve qualitative organic analysis problems using a computer simulation program. I also understand that this project is Keith Schramm's dissertation research project at Western Michigan University.

My consent to participate in this project indicates that I am willing to attend one or more problem-solving sessions which may utilize between four and six hours of my time. I understand this meeting will be a private research session with Keith Schramm on the campus of Western Michigan University or at a site of my choosing. This session will involve learning how to use a modified version of the computer software Identification of Organic Compounds® and then to solve problems using the software. I will be asked to "think aloud" while solving these problems. After each problem the researcher may ask clarifying questions.

I am aware that while I am solving these problems, the researcher will video-record the writings I make and the actions I take in the computer environment. I am aware that my think-aloud protocol will be tape-recorded. I understand that my writings will be collected.

I understand that no risks, hazards, or discomforts are foreseen as a consequence of this study. As in all research there may be unforeseen risks to the participant. If an accidental injury occurs, appropriate emergency measures will be taken; however, no compensation or treatment will be made available to me except as otherwise specified in this consent form.

One way I may benefit from this activity is in having the chance to learn about the Identification of Organic Compounds® computer simulation environment for problem-solving in qualitative organic analysis. I also understand that the knowledge gained from this study may contribute to the improvement of instruction and instructional materials in the domain of qualitative organic analysis.

I understand that although no sensitive information is being recorded, all the data collected from me is confidential. My name will not appear on any tapes or papers in which this data is recorded. Participants will be identified with a coded reference, and a master list that shows corresponding names of subjects will be kept separately from the data. Once the data are collected and analyzed, the master list of names will be destroyed. All other forms, tapes, and data will be retained for three years in a locked file in the principal investigator's office.

I understand that I may refuse to participate or quit at any time during the study without prejudice or penalty. If I have questions or concerns about this study, I may contact either Keith Schramm at 616-387-2739 or Robert Hafner at 616-387-5844. I may also contact the Chair of the Human Subjects Institutional Review Board at 616-387-8293 or the Vice President for Research at 616-387-8298 with any concerns I have. My signature below indicates that I have read this informed consent form, that I understand the purpose and requirements of the study, and that I agree to participate.

Signature

Date

Appendix B
Research Checklist

Research Checklist

Set up computer for operation.

Set up video- and/or tape-recorders.

Read and sign Letter of Informed Consent.

Read directions to the subject:

Thank you for agreeing to participate in my research project. I am going to ask you to solve qualitative organic analysis problems using a modified version of the *Identification of Organic Compound (IOC®)* software program produced by Trinity Software, Inc. In a moment I will show you what type of data is available to you and how you can operate the software. I have chosen to have you utilize a simulation to solve qualitative analysis problems because I know that the time required to actually conduct the analysis using real compounds is prohibitive for my research purposes. In this software you can conduct wet chemistry tests and spectrometric tests in a matter of seconds. The data is presented in a format that would be comparable to the results obtained in the laboratory. The interpretation of the results of these tests is up to you. Even though you can obtain test results instantly, I would like you to operate as you normally would in the lab. That is, conduct those tests that you might normally use when you solve qualitative organic analysis problems.

Besides the computer software, I will make several items available for use. First, you may use pencil and paper if you like. Second, I will make available a calculator. Third, you may utilize two references if you need them. These references are *Handbook of Tables for Organic Compound Identification, 3rd edition* and *Spectrometric Identification of Organic Compounds, 6th edition*. Additionally, the IOC® program has a "help" function which provides information about the various tests found in the program.

Now that you understand the problem-solving environment, let me demonstrate how to access all of the available data found in the IOC® program.

Demonstrate the IOC® program.

As you solve the qualitative organic analysis problems I have posed for you, I am interested in hearing you reflect out loud everything you are thinking as you solve these problems. My goal in this research is to gain insight into your thought processes as you solve these problems. However, I do not want you to explain your reasoning to me. Rather, I want you just to verbalize the thoughts you are thinking. Simply try to

Speak the words that are passing through your mind at the time. Many people mumble to themselves while they are solving problems. If this is the case, then just mumble clearly and loudly enough for the tape recorder to hear you. Do not be concerned about whether your thoughts are correct or even sensible. Just say out loud what you are thinking. I may prod you occasionally to keep talking if you remain silent for very long. If you want to write on the paper as you work, that is fine.

It is okay if you need to take a break from problem-solving. However, I would strongly prefer that the break occur between separate problems rather than in the middle of a problem.

Do you have any questions at this point?

In the main menu of the IOC[®] program are unknowns numbered 1-19. I have selected compounds 1 and 2 as warm-up problems so you can gain familiarity with the IOC[®] program and so you can practice thinking aloud. After you have solved these warm-up problems, I would like for you to solve as many of the remaining seventeen problems as time allows. Again, thank you for your assistance in this project. I know you have agreed to volunteer one of your most precious commodities - time. I truly appreciate your time and efforts.

Provide pencil, paper, calculator, and reference materials.

Start tape recorders.

Start practice problems.

Start research problems.

During Interview:

Answer Questions.

Prod Subject to verbalize, if necessary with comments like:

"Can you tell me what you are thinking?"

"That's very clear."

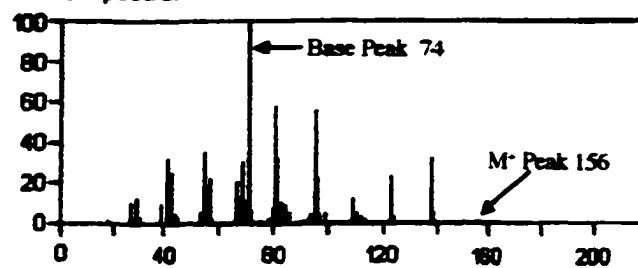
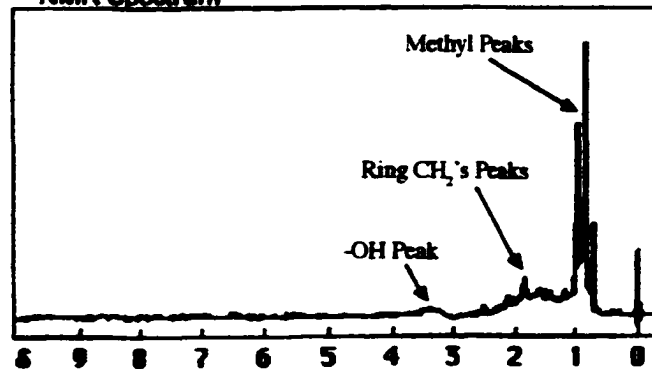
"Please tell me what you are writing."

"Mmm."

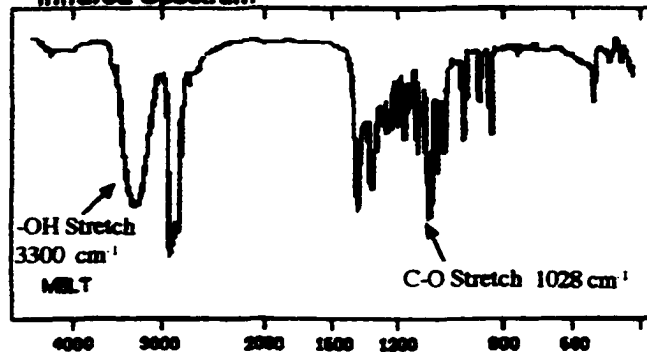
"Okay."

Collect all writings, materials and recording at the end of the session.

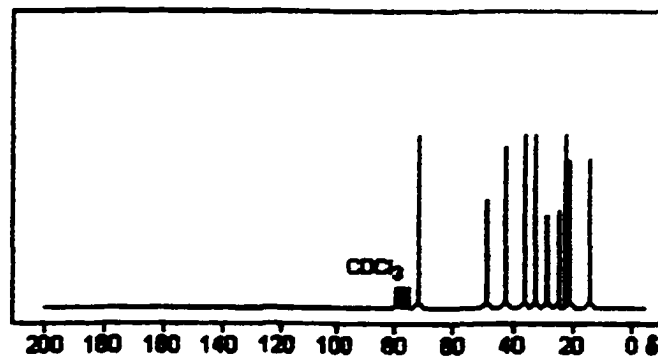
Appendix C
Spectra Used in Problem 5
By Subject 3

Mass Spectrum**• NMR Spectrum**

• Infrared Spectrum



• CMR Spectrum



Appendix D
Protocol Clearance from the Human Subjects
Institutional Review Board

Human Subjects Institutional Review Board

Kalamazoo, Michigan 49006-3899

WESTERN MICHIGAN UNIVERSITY

Date: 26 June 1998**To:** Robert Hafner, Principal Investigator
Keith Schramm, Student Investigator**From:** Richard Wright, Chair *RWright/Haf***Re:** HSIRB Project Number 98-05-04

This letter will serve as confirmation that your research project entitled "The Development of a Model to Account for Expert Problem-solving in Qualitative Organic Analysis" has been **approved** under the **expedited** category of review by the Human Subjects Institutional Review Board. The conditions and duration of this approval are specified in the Policies of Western Michigan University. You may now begin to implement the research as described in the application.

Please note that you may **only** conduct this research exactly in the form it was approved. You must seek specific board approval for any changes in this project. You must also seek reapproval if the project extends beyond the termination date noted below. In addition if there are any unanticipated adverse reactions or unanticipated events associated with the conduct of this research, you should immediately suspend the project and contact the Chair of the HSIRB for consultation.

The Board wishes you success in the pursuit of your research goals.

Approval Termination: 26 June 1999

Appendix E
An Introduction to Qualitative Organic Analysis

Qualitative organic analysis is an extremely important subdivision of organic chemistry. The structure of a compound determines its chemical and physiological properties. Consequently, knowing the structure of a compound is imperative to understanding the properties of the compound. Synthetic organic chemists endeavor to synthesize new compounds in the laboratory, or they attempt to synthesize existing compounds by more efficient pathways. In either case, they must use qualitative analysis techniques to determine and verify the structures of each organic compound they synthesize. Often an organic chemist must determine the composition of an unknown material. This would entail separation and purification of the material if it is a mixture, followed by qualitative analysis of all components in the mixture to determine their individual structures. There are millions of organic compounds in existence, with new compounds synthesized daily. The structures of these compounds can range from very simple to extremely complex. Differences between compounds can be subtle, but important. Qualitative analysis is the only means by which the chemist can analyze and determine the structure of an unknown or new compound. Consequently, its importance in the domain of organic chemistry is highly significant.

Qualitative organic analysis is the process by which a chemist determines the structure of an "unknown" organic compound experimentally. Qualitative analysis can be used to elucidate the structure of novel compounds found in nature or to identify compounds synthesized in the laboratory. Unknown in this context means that the structure and identity of the compound are unknown to the chemist, but may be found in the literature. In the past this process was achieved exclusively by the use of a number of wet chemistry techniques which would allow the properties of the unknown compound to be matched to the properties of compounds previously characterized in tables

(Rappoport, 1984). A compound was classified according to its functional groups based upon data pertaining to the compound's solubility, fusion test results, and classification tests, as well as other physical and chemical properties. Once the functional groups in the compound were determined, the compound was chemically altered into derivatives of the compound, and the melting point temperatures of the purified derivatives were compared to standardized tables (Rappoport, 1984). These tables contain data pertaining to the melting point and boiling point temperatures of derivatives of known compounds. If the derivative of the unknown compound matched the appropriate compound in the table, then the compound was identified, or at least the possibilities were greatly narrowed. This procedure that was used in the past appears algorithmic. Indeed, if the chemical tests are performed in ideal conditions and the derivatives are isolated properly, then the identification of the compound is assured. On the other hand, all of the techniques described here have the potential to yield erroneous results, since the sample purity and reaction conditions are critical for accurate results. Some chemical tests can appear to yield positive or negative results for the presence of a particular functional group due to impurities or a competing reaction which produces a product similar to the expected product. Consequently, these wet chemistry techniques are not as algorithmic as they might appear upon a first inspection. In addition, this process of forming derivatives is only effective if the unknown compound being investigated has previously been classified. Only a small percentage of the compounds in existence are included in tables of derivative melting points.

In recent decades different spectrometric techniques have been used to infer the various functional groups in an unknown compound's structure, as well as its complete molecular structure (Silverstein & Webster, 1998). These spectrometric techniques must be utilized to elucidate the structure of a compound not found in the literature. The use

of spectrometers to assist in the determining of a compound's structure is far from algorithmic. All of these techniques involve bombarding samples of the unknown compound with differing types of energy. The interaction of the compound with the energy produces a spectrum consisting of a characteristic series of signals that can be used to infer different facets of the structure of the compound. Since differences in the spectra produced can often be subtle, proper identification of the compound's complete structure requires a great deal of declarative and strategic knowledge on the part of the chemist. He or she must understand the significance of key signals in each type of spectrum, as well as how each spectrum can be used to "piece" together the structure of the unknown organic compound. The use of these spectrometric techniques allows for the deductive determination of the structures of completely new compounds not found in a table of compound derivatives. As a result, some organic chemists use a combination of the wet chemistry and spectral techniques in most qualitative organic analysis (Shriner, Hermann, Morrill, Curtin, & Fuson, 1998).

Methods of Qualitative Organic Analysis

The methods of qualitative analysis are diverse. Some are rather simple chemical techniques; others require sophisticated and expensive equipment. While the experiments which reveal various characteristics of the structure of a compound are diverse and numerous, most compounds can be determined by a limited number of procedures. One text that defines the experimental space used in most qualitative analysis is *The Systematic Identification of Organic Compounds, 7th edition* by Shriner, Hermann, Morrill, Curtin, and Fuson (1998). This text describes a general procedure that is systematic in its approach and helps to define and limit the types of experiments which are typically used in qualitative analysis. This text provides the guidelines which were used

to select the simulated experimental tools used in this research project. The techniques described by Shriner, et al. (1998) in the following sections are a collection of chemical and spectrometric tests which can be used in various combinations and orders to determine a compound's structure or identity. The outline of this procedure involves limiting the problem space by purification of the sample, determination of functional groups, determination of molecular formula, and finally, determination of atomic arrangement in the compound. Not all of these tests may be used in all cases, nor will the tests necessarily be used in the order presented here. However, the methods described in the following sections are representative of the most common experimental tools used to solve problems within the domain as described by Shriner, et al. (1998) and Silverstein and Webster (1998).

Purification of the Sample

In order for the chemist to analyze the structure of an organic compound, the sample should be pure. If the sample is not a "pure" compound, it must be purified by various procedures such as distillation, fractional crystallization, or chromatographic techniques before a systematic analysis can begin. For the purpose of this research, all samples were considered pure. While a chemist may have to purify an unknown substance, these procedures are not part of the determination of the compound's structure. Rather, purification is preparation of the sample and does not determine the way in which the chemist conducts the qualitative analysis of the purified substance.

Physical properties

Inspection of the compound for odor and color can be helpful. Color and odor can indicate the presence or absence of certain types of functional groups in the com-

pound. While these observations are not definitive, they can help to guide preliminary search of the experimental space. Color was given on each problem for the subjects in this research, but odor was not given. Compounds such as menthol and cinnamaldehyde would be easy to solve if odor observations were presented to the subjects.

Melting point and/or boiling point temperatures can provide confirmatory evidence of the compound, but they also give an indication of the types of functional groups in the compound. A high melting or boiling point temperature can indicate large molar mass or highly polar functional groups, suggesting strong intermolecular forces in the compound. Likewise, a liquid compound with a relatively low boiling point temperature can indicate a compound of small molar mass or slight polarity in its structure.

Solubility Tests

The solubility of a compound is determined largely by the functional groups present in the compound. This procedure utilizes differences in Bronsted acid/base activity so that compounds can be classified according to functional group by the use of a mental flow chart and the compound's solubility in water, 5% sodium hydroxide, 5% sodium bicarbonate, 5% hydrochloric acid, and concentrated sulfuric acid. The solubility of a sample may be difficult to determine since the observations are qualitative in nature and since the chemist often has a limited sample of unknown.

Sodium Fusion

The sodium fusion test allows for the determination of the presence of the heteroatoms: nitrogen, sulfur, and the halogens. Elemental sodium is reacted with a sample of the compound. The sodium destroys the sample and produces aqueous sodium cyanide if nitrogen is present, sodium sulfide if sulfur is present, and a sodium halide salt if

a halogen is present. The reacted sodium sample can be divided into three samples, and each sample can be run through a series of wet chemistry tests which will indicate which, if any, of these heteroatoms are present. This is accomplished if there are characteristic changes to the samples color.

Molecular Weight Determination and Elemental Analysis

Combustion analysis can indicate the percent of carbon and hydrogen present in a compound. Fusion tests can then be used to determine the presence of nitrogen, halogens, or sulfur. From this data, the empirical formula can be calculated. If the molecular mass of the compound is known from mass spectrometry, then the simple molecular formula may be inferred. This significantly limits the problem space, since there is a vastly smaller subset of compounds for a specific molecular formula. However, the molecular ion peak is not present in every mass spectrum. This has the potential to mislead a subject who may infer a significant peak as the molecular ion peak. If the subject concludes that the molecular ion peak is not present in the spectrum, he or she can only qualitatively reason about the molecular mass and molecular formula of the compound.

Classification Tests

Classification tests are a large set of chemical reactions which are specific to particular functional groups and react in a reproducible manner. When a functional group is suspected to be present in the unknown, the chemist can perform the appropriate reaction for confirmation of the presence of that functional group. While classification tests can give erroneous results due to impurities or experimental error, they can be very useful in the confirmation or denial of functional groups in the compound as indicated

by other data sources such as solubility or infrared spectroscopy. Furthermore, certain classification tests can be used to determine if a functional groups, such as alcohols and amines are primary, secondary, or tertiary in structure.

Preparation of Derivatives

A derivative is a compound which has been synthesized from the original sample. Based upon the indication of functional groups, the chemist can synthesize and purify the derivative and compare the properties of the derivative, including melting point and boiling point temperatures, with a standardized set of values of derivatives (Rappoport, 1984). For this to be effective, the parent compound (the unknown) and its derivatives must be included in the tables. The use of derivatives can be a very powerful technique, especially for compounds that are hard to elucidate by spectroscopic means. In a compound like 4-chloro-3-nitro-benzoic acid, the subject may have the basic functional groups of the compound determined, but may not be able to distinguish the exact position of the functional groups on the benzene ring. The use of derivatives has the potential to provide conclusive evidence of the compound, especially if more than one derivative can be formed and the compound is found in the tables (Rappoport, 1984).

Spectroscopic Techniques

The pure wet chemistry techniques described above can only identify established compounds since those procedures attempt to match in a perfect one-to-one correspondence with the properties of a compound found in the literature (Rappoport, 1984). The spectrometric techniques described below allow for the elucidation of compounds that are not found in the literature since the spectra produced provide clues about the actual molecular arrangement. This makes them more powerful since these techniques

can elucidate the molecular structure of a completely original compound.

Mass Spectrometry

In a typical Electron Ionization (EI) mass spectrometer, the unknown sample is bombarded with a high energy beam of electrons which ionizes the compound. The compound is, essentially, blown apart into fragments. Many of these fragments are positive ions which can be accelerated by a magnetic field. These ions are separated based upon their mass-to-charge ratio. A detector senses the arrival of the particles, and a spectrum of relative intensity can be plotted versus the mass-to-charge ratio. Most particles have a charge of positive one, so the spectrum essentially shows the mass of the positive ions created. Often present is the molecular ion peak which gives information as to the molecular mass. Furthermore, peaks heavier than the molecular mass peak are due to the presence of isotopes in the sample. These peaks can indicate the presence of nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens in the compound. Finally, the spectrum can give an indication of the structure of the compound since aromatic rings, aliphatic chains and other functional groups tend to break apart in a general characteristic manner from compound to compound. Mass spectrometry is most valuable in providing information about the molecular mass, although the spectrum can provide direction in the research or confirmatory evidence of a proposed structure.

Infrared Spectrometry

When a compound is irradiated with infrared radiation of the proper energy, chemical bonds within the molecule absorb the energy, causing the atoms to vibrate about the chemical bonds. The frequency of the energy absorbed depends upon the mass of atoms, the strength of the chemical bonds (force constant), and the spatial rela-

tionship of the atoms to each other. If a change in dipole occurs within the chemical bond an absorption occurs and a spectrum is produced. The spectrum can give indication of the types of functional groups present in the compounds, since these absorb energy at nearly the same frequency from compound to compound. Infrared spectra are complicated by the presence or absence of a number of absorptions that can occur for various reasons. For example, some absorption bands are too weak to observe, some absorption bands are too close in frequency to distinguish, and some bands are formed by overtone absorptions. Nevertheless, infrared spectroscopy is a powerful tool to determine the presence of functional groups in the compound.

Proton Nuclear Magnetic Resonance (NMR) Spectrometry

Some nuclei absorb radio frequency energy in the presence of a magnetic field. The nucleus of ^1H is one such nucleus. This nucleus is of particular importance since every organic compound contains a ^1H nucleus, which is the primary isotope of hydrogen. The spectrum that is produced can suggest several characteristics of a compound's structure. First, the chemical shift can indicate the chemical environment of the proton. That is, it can suggest the type of functional group on the adjacent carbon atom. Second, the area of the absorption peak is proportional to the number of equivalent hydrogen atoms producing the peak. Hence, it can indicate the number of hydrogen atoms per peak and the chemical environment within the molecule. Third, protons on a carbon atom are coupled to protons on adjacent carbon atoms. This coupling produces a splitting pattern in the spectrum. Associating these peaks allows the chemist to infer relative positions of the protons, and the carbon atoms to which they are bonded, within the structure of the molecule. Proton NMR is an especially effective tool, since it not only provides some evidence of the presence of functional groups, but also is used to infer

the arrangement of atoms within the compound. This allows the chemist to put the pieces of the molecular puzzle together.

Carbon-13 Nuclear Magnetic Resonance (NMR) Spectrometry

The ^{13}C nucleus can also absorb radio frequency radiation in the presence of a magnetic field. The ^{13}C nucleus is an isotope of carbon which is present in small quantities. However, even a small sample of an organic compound will contain enough ^{13}C nuclei to produce an absorption spectrum with modern instruments and fast computers. The primary information that can be gained from ^{13}C or carbon-13 NMR spectrometry is the indication of the number of chemically nonequivalent carbon atoms in the compound. Compounds with symmetry produce fewer peaks in the carbon-13 NMR spectrum than are actually present in the compound. To the trained subject, a small number of peaks indicates this symmetry and often makes the problem easier to solve. Finally, chemical shift can provide information about functional groups present in the compound and their structural proximity to particular carbon atoms.

Ultraviolet Spectrometry

Some molecules can absorb ultraviolet (UV) radiation. This absorption is primarily limited to molecules with conjugated π electron bonding systems. Consequently, UV spectra can be useful in distinguishing between similar compounds which have different conjugated systems. However, since this same information can be inferred from NMR spectrometry, the usefulness of UV spectrometry has diminished. The most recent edition of *Spectrometric Identification of Organic Compounds* (Silverstein & Webster, 1998) deleted UV spectrometry for this very reason. Consequently, ultraviolet spectra were not utilized in this research as a tool to be used by the subjects.

Summary of Qualitative Organic Analysis Methods

The procedures that the organic chemist can use to elucidate the structure of an organic compound are numerous. The specific and exhaustive characterization for any compound consists of the determination of its molecular formula, functional groups, and arrangement of its atoms within the compound. Using various combinations of the instruments and tests described previously definitely has the potential to identify and characterize all of these components of a compound. However, most of these tests are not absolutely definitive in isolation and usually require verification from other tests the chemist may elect to use. Consequently, the experimental space of qualitative organic chemistry is extensive, with many possible pathways available to the chemist. While texts have been written about the content knowledge and strategies of qualitative analysis, no research has been conducted to provide an indication of the declarative and strategic knowledge actually used by organic chemists as they solve problems within the domain. It was hoped that this research would provide insight into the knowledge structures and strategies used by organic chemists within the important domain of qualitative organic analysis.

Qualitative Organic Analysis in the Curriculum

Qualitative organic analysis is a highly specialized content area within the domain of organic chemistry. In the United States, an in-depth study of organic chemistry is generally not attempted until the second year of a student's undergraduate collegiate career, after the student has successfully completed a year-long general inorganic chemistry course. Although some high school students have received training in qualitative analysis as part of a third-year high school chemistry course (Liebermann, 1985), it is in undergraduate college organic chemistry textbooks (Streitwieser, Heathcock, & Kosower,

1992; Morrison & Boyd, 1992; Loudon, 1995; Solomons, 1996) and lab manuals (Campbell & Ali, 1994; Landgrebe, 1993) such as the ones cited here that students are introduced to the knowledge and strategies used in qualitative organic analysis. Additionally, graduate programs in chemistry offer courses devoted entirely to the domain of qualitative organic analysis (Western Michigan University Graduate College, 1996).

Appendix F
An Introduction to Identification of Organic Compounds®

IOC[®] (Clough & Pavia, 1998) stands for Identification of Organic Compounds. Trinity software has developed several software packages for qualitative organic analysis. Both the IOC[®] program for PCs and the MacSQUALOR[®] (Pavia, 1991) program written for Macintosh[®] computers were developed by Trinity Software for the purpose of giving students an opportunity to solve a greater number of problems than is afforded from actual laboratory experiences. As stated in the MacSQUALOR[®] Instructor's Manual (Pavia, 1991), the software provides students "with an opportunity to think more broadly about the problem and concentrate on the logic and implications of the tests". The manual claims that after working with this program, "students will spend their time in the wet laboratory more productively" (p.1).

Originally, the MacSQUALOR[®] program was going to be the software used in this research. Permission was obtained by Trinity Software to use the MacSQUALOR[®] software; however, the president of Trinity Software was in the process of developing a new program for PCs and substituted the IOC[®] program in place of the MacSQUALOR[®]. The substitution was made because this researcher had asked for modifications to the program and Trinity decided that those modifications better fit into the development of the new program than the modification of MacSQUALOR[®]. Consequently, Trinity decided that from their perspective it would be better for the IOC[®] to be used for this research. While there are minor differences in the format of the IOC[®] and the MacSQUALOR[®], the experimental data contained in the programs is the same and did not adversely affect this research.

The IOC[®] program is formatted so that the student decides what tests to run and determines the order of operation. Results of tests are always given as observations, and the student is left to determine the significance of the test results. When using the program, the student starts in the IOC[®] main menu, which allows the student to select an

unknown first. Once the unknown is selected, the student is presented with physical properties (physical state, color, as well as melting or boiling point temperatures) and elemental analysis for the percent carbon and hydrogen only. The layout of the computer screen is that of a laboratory notebook. When a student chooses wet chemistry tests, the observations are written in the notebook. Data are given in the form which would be received in the laboratory. That is, only the observations of test results are given. The significance and meaning of the tests are not given to the student. If the student chooses to perform one of spectroscopic techniques, the spectrum is displayed in the upper right hand side of the lab notebook. The displayed spectrum is rather small, but the mouse can be used to point at specific peaks in the spectrum and the computer shows the precise wavenumber or delta shift of the peak in question. Only one spectrum can be viewed at a time unless the spectrum is physically printed from the computer. The student may choose fusion test results, solubility test results, classification test results, infrared, proton NMR, C-13 NMR, and mass spectral data, and derivative formation results in any order he or she chooses.

Figure 21 is an example of the results of the physical properties, solubility tests, fusion tests, a classification test, and a derivative in the lab notebook as a subject would see it on the computer screen. The data for these tests is presented as descriptive of the observations rather than the significance of the observations. The subject must interpret the significance of each result in his or her molecular model refinement.

Figure 22 shows an infrared, proton NMR, carbon-13 NMR, and mass spectra as printed from the IOC[®] lab notebook.

Identification of Organic Compounds — Laboratory Report

• Physical Properties

Jan. 14 (10:05 a.m.)

Yellow Liquid

bp 200-209°C

%C = 77.87; %H = 11.76

• Solubility Tests

Jan. 14 (10:07 a.m.)

In water . . . insoluble

In 5% hydrochloric acid . . . insoluble

In 5% sodium hydroxide . . . insoluble

In conc. sulfuric acid . . . soluble

• Fusion Tests

Jan 14 (10:08 a.m.)

A part of the fusion mixture was treated with ferrous ammonium sulfate and KF. It was heated and acidified with sulfuric acid. There was no observable change.

Another portion was acidified and treated with lead acetate. There was no observable change.

Another portion was acidified and boiled. Silver nitrate was added. There was no observable change.

The fusion mixture was acidified with sulfuric acid, boiled chlorine water was added and the mixture was extracted with methylene chloride. The organic layer was clear.

Classification Tests

• Tollen's Test

Jan. 14 (10: 15 a.m.)

Fresh reagent is prepared by adding 1 drop of NaOH to a silver nitrate solution. Then enough ammonia is added to dissolve the precipitate. When the unknown is added, a bright, silvery mirror forms on the inside of the test tube.

• Derivatives

• 2, 4-DNP Derivative

Jan. 14 (10.23 a.m.)

A crystalline derivative is formed. Re-crystallization yielded a Yellow Solid, mp 75-78°C.

Figure 21. An IOC[®] Notebook Entry with Physical Properties, Solubility, Fusion Tests, Classification Test, and Derivative Lab Test Results.

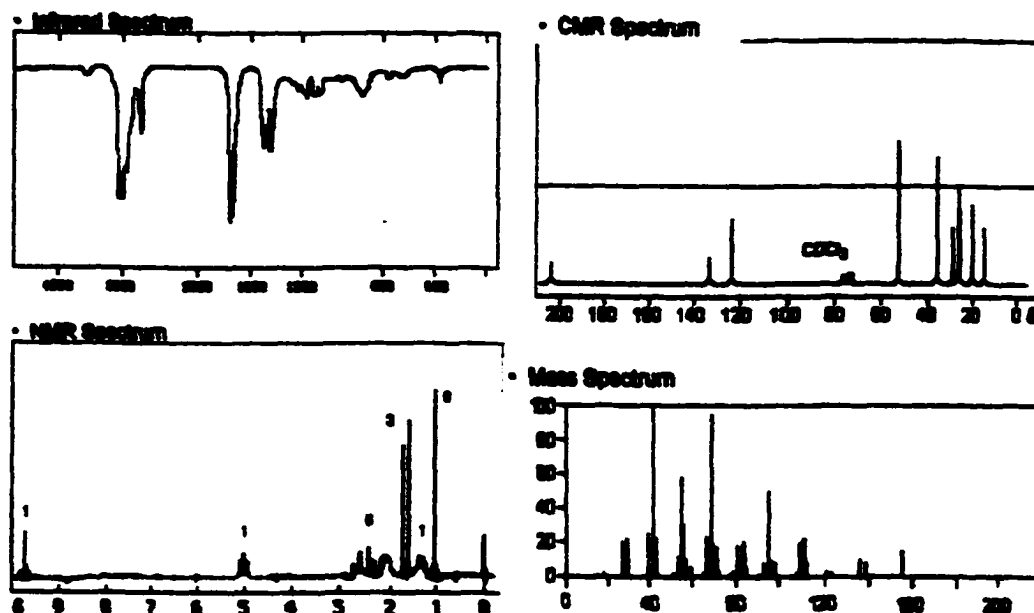


Figure 22. An IOC[®] Infrared, Proton NMR, Carbon-13 NMR, and Mass Spectra.

IOC[®] does have a “Help” function that will explain the chemistry of a particular test if needed. An additional function in IOC[®] is a table of derivatives listed according to functional groups. In using this feature, the student may compare his or her derivative melting point temperatures with those in the table. This table is similar to the reference book by Rappoport (1984), but much smaller in scope. Finally, there is an “Answer Trial” function that allows the student to type in the name of the unknown from a list of possible compounds divided by functional groups. The program then responds as to the correctness of the solution. The Answer Trial database in the program is limited. Both of these features, the derivative table and answer trial, would have greatly limited the richness of problem space, therefore, the subjects participating in this study were not allowed to use them. The subjects could utilize the Rappoport (1984) reference, but they were required to announce the identity or structure of the compound without the use of the database of possible compounds found in the program.

In terms of the number and variety of compounds in the IOC[®] program, 93

unknowns are available, with 21 classification tests and 15 derivative-forming reactions for several different functional groups (IOC[®] Instructor's Manual, 1998). Infrared and proton NMR spectra were included for most, but not all, of the unknowns.

The primary data that was missing from MacSQUALOR[®], and also from the IOC[®], were ultraviolet spectra, mass spectra, and carbon-13 NMR spectra. Several reasons may be given for this: (1) Most likely, the instruments are inaccessible to most undergraduate students, and (2) as stated previously, the importance of UV spectrometry has diminished in qualitative analysis problem-solving (Silverstein & Webster, 1998). Additionally, (3) mass spectrometry and ¹³C NMR spectrometry are excluded in some undergraduate lab manuals (Campbell & Ali, 1994) and receive a sparse treatment in undergraduate textbooks (Morrison & Boyd, 1992; Loudon, 1995; Solomons, 1996; and Streitwieser, Heathcock, & Kosower, 1992) when compared to infrared and proton NMR spectroscopy, possibly for the same reasons. This did cause a problem when the IOC[®] was to be used as a problem-based research simulation. On the one hand, experts in the domain may very well use ¹³C NMR, mass spectra, and UV spectra when solving problems. On the other hand, in the educational system for undergraduates, this type of data is either only briefly introduced or entirely neglected. In the future, however, it is likely that undergraduates will be exposed to more and more interpretation of mass spectral and ¹³C NMR spectral data in qualitative organic analysis; therefore, the researcher requested that Trinity[®] Software add this data to the software package. Trinity[®] agreed to the request and added this spectral data to the problems in the IOC[®] program that were chosen for this research.

One additional feature of the IOC[®] program that makes it useful for educational purposes is that the professor has the option of allowing students to solve random problems found in the program on their own for practice or can assign specific problems to be solved as part of an assignment. When utilizing the program in this manner, the

professor selects a group of problems and assigns them to a file. Each student logging on to the program must enter an assigned password specific to that individual. Each student can then turn in a computer-generated notebook which keeps a record of the experiments conducted and the answers entered into the Answer Trial function. The printout can be graded on the correctness of the solutions as well as the appropriateness of the experimental space search as perceived by the instructor. When used in either manner, this program would allow undergraduate students more opportunities to utilize their declarative knowledge and refine their problem-solving strategies than can be afforded in the laboratory class.

In summary, permission was obtained from Trinity[®] Software to use the IOC[®] program. Trinity[®] agreed to make the modifications to the program (adding ¹³C and mass spectral data) for the purpose of this research. The president of the company placed the following restrictions: Trinity[®] wanted to receive proper credit in the dissertation, and the company wishes to receive a copy of the finished work.

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