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**Improved Response to Hazardous Spills:
Conceptual Design of the Teleoperated Hazmat Laboratory**

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ABSTRACT

Spills of hazardous materials expose emergency response personnel and the public to the risk of explosion, fire, and contamination. This report investigates the use of automation and remote control to reduce response time and improve safety in the identification phase of highway spill response. Currently available technologies for identification are reviewed. A survey of Caltrans Hazardous Materials Specialists was undertaken to assess the usefulness of improved identification technology; results indicate that automated or remotely controlled systems with a cost of \$5000 to \$10,000 would be attractive to Caltrans districts. A variety of conceptual approaches to improved identification technology are presented. Three of these (two versions of a remotely controlled laboratory and a prepackaged set of test cells) warrant further investigation by Caltrans. Two other approaches (a fully automated laboratory and test strips capable of detecting commonly spilled materials) are promising, but require substantial research and development investment.

EXECUTIVE SUMMARY

To effectively manage a hazardous spill, identification, containment, and cleanup must be carried out with minimum human exposure and property damage. Reducing the time required for these activities is critical, particularly for highway spills, when the cost to society due to highway closures can be significant.

This project investigates the automation of the identification process. Based on a review of available laboratory and field technology, discussions with Caltrans personnel and other experts, and a survey of Caltrans Hazmat Specialists, several alternatives to current practice were proposed. Of these, two versions of a remotely controlled laboratory (Subset 1 THL and Subset 2 THL), and a self-contained test-cell system (Testblock-ID) warrant further investigation by Caltrans. Two other approaches, test strips to identify frequently spilly materials and a fully automated laboratory, are promising ideas, but require too great an R&D investment to be carried out by Caltrans. Instead, Caltrans should pursue low cost means of motivating others to work on these approaches. It is recommended that Caltrans

- Meet with developers of field chemistry systems (HazCat and HeinzCat) to determine the usefulness of subsets of the systems in assessing hazard class and identify modifications in the test procedures that would facilitate automation. In particular, tests proposed for the Subsets 1 and 2 THL and tests feasible within the Testblock-ID approach should be reviewed.
- Pursue low cost means of promoting the development of the test strip and AHL approaches. This includes the submission of articles and queries describing technology needs to relevant trade magazines, and perhaps organizing a workshop to bring together the developers of field chemistry systems, analytical laboratory equipment, and others involved in identifying unknown spills (local health agencies, fire departments, contractors, in-house industry response teams).
- Review the frequency and impact of unknown spills to determine the cost in terms of (1) risk to health and safety of responders, (2) direct costs of identification efforts, (3) cost to society of road closures.

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DISCLOSURE SECTION

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The contents of this report reflect the views of the author, who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the STATE OF CALIFORNIA or the FEDERAL HIGHWAY ADMINISTRATION and the UNIVERSITY OF CALIFORNIA. This report does not constitute a standard, specification, or regulation.

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CHAPTER ONE

INTRODUCTION

1.1 Highway Spills

The call comes in from a passing motorist: "There is yellowish white powder in the right lane of northbound I-5 north of Redding." Ten minutes after the call is received, a Caltrans maintenance worker is the first to arrive at the scene. No one is in the area. There is no indication of what the material is or where it came from. The spill is relatively small and is at the right side of the right lane. It is a calm day in a rural area and this stretch of the road is straight and not obstructed by trees; it is not likely that anyone will wander on to the road. The maintenance worker closes the lane to traffic in the affected area, and radios in to the district office and the highway patrol. The district office has already dispatched a spill response team. Forty minutes later, the response team arrives at the site. A Caltrans HazMat Specialist suits up in level A protective clothing and a respirator, and obtains a sample of the powder. The Hazmat Specialist then conducts a series of tests on the sample to determine the hazard level and the appropriate procedure for containment and clean up. The identification process takes about 45 minutes. The spilled material does not appear to be in any of the hazard categories, and does contain flour (it is later identified as a baking mix). It is quickly swept up, and the lane is reopened two hours after the initial call was received.

In the "cake mix" scenario above, the unknown substance turned out not to be harmful to response personnel or the public. Only one lane of Interstate 5 had to be closed, and in an area not usually congested. Response, identification, and cleanup took place rapidly and safely. Even in this case, though, a significant component of response time was due to the need for a HazMat Specialist to suit up, retrieve a sample, and run a series of tests to identify the unknown material.

In many instances, the situation is more complicated and more costly. Had the substance in the "cake mix" scenario been hazardous, there would have been a risk to the health and safety of the public, the Caltrans employee first on the scene, and even to personnel wearing protective gear. In 1988, there were over 6000 hazardous materials transportation incidents in the U.S., resulting in 15 deaths, over 150 injuries, and damages exceeding \$20 million. All of the fatalities and over 85% of the damages resulted from hazardous materials spilled on highways [DOT 1988]. For 1991, the number of highway hazardous materials incidents is estimated to be over 7500 [NCHRP 1994]. In California alone there were over 300 incidents during 1988, resulting in close to \$2 million in damages [DOT 1988]).

1.2 Current Spill Response Practice

Current spill response practice involves several organizations. Typically, either Caltrans personnel or the California Highway Patrol (CHP) are the first responsible parties to arrive at the scene of a spill. Often, the particular Caltrans or CHP employee involved does not have significant training in the handling of hazardous materials. In this case, the employee functions at the First Responder Awareness Level, authorized only to secure and

control access to the spill site and to begin the emergency response procedure by contacting the appropriate authorities.

Upon receiving word of a spill, Caltrans will send out a spill response team that includes personnel with more hazmat training and authority. At a minimum, this includes a First Responder Operations Level, who will attempt to contain the spill from a safe distance, keep it from spreading, and prevent the public or other workers from exposure to the spilled substance. The First Responder Operations Level will attempt to identify the substance through labels, placards, manifests, or other information at the scene. If the material can be identified, information sources such as CHEMTREC (the Chemical Transportation Emergency Center) will be used to carry out a hazard assessment.

If the material cannot be readily identified, additional expertise must be obtained. Within Caltrans, identification of an unknown substance can be carried out by a Hazardous Materials Technician or by a Hazardous Materials Specialist. Depending on the nature and location of the spill and the qualifications of available personnel, identification may be carried out by other organizations including cleanup contractors and local fire departments. Identification is carried out only to the degree necessary to complete a hazard assessment. In some cases, additional post-cleanup identification must be carried out prior to disposal.

Once the spilled substance has been identified, the hazard assessment completed, and the spill contained, cleanup begins. Depending again on the nature and location of the spill and the qualifications of available personnel, cleanup may be carried out Caltrans, by cleanup contractors, or by the spiller of the substance (if known).

1.3 Improving Spill Response through Automation

Even with state-of-the-art equipment, current practice puts response personnel at risk. Protective clothing may not be adequate; clothing may protect against one chemical, yet be readily penetrated by another. In addition to the human risk, the dollar cost of current practice is significant. Roads remain closed until a contractor arrives at the site, identifies the spilled substance, and cleans up the spill. Supporting equipment and protective gear are costly, and equipment and gear which cannot be decontaminated must be thrown out and replaced.

Problems of human exposure make a remotely controlled system a logical approach. Remotely controlled vehicles have been developed for use in the cleanup of nuclear and other hazardous waste sites. However, these systems are for the most part too large and too expensive to be used on highway spills. To minimize response time, a system for highway use should be small enough to be stored in a variety of Caltrans vehicles. It should be easily operated by employees whose primary function is not hazardous spill response. In addition, it should be easy to decontaminate, and inexpensive enough to be placed in districts throughout the state and to be discarded when decontamination is not possible. Finally, the system must be intrinsically safe, since many highway spills involve flammable and/or explosive materials.

Identifying an unknown substance can be thought of as a two step process: obtain a sample of the unknown and then identify the unknown substance. These steps require very different capabilities. The former is primarily physical; whatever is obtaining the sample must get first to the site and then to the exact location of the spill, and must pick up a sample of the spilled substance. Although some initial testing (e.g. for explosivity) may be carried out while obtaining the sample, safety and weight considerations dictate that the

bulk of the identification process be carried out at a location slightly removed from the actual spill. The process of identifying the unknown is largely observational. Using existing field chemistry procedures, small amounts of the unknown substance and various reagents are combined in a series of test tubes, and the resulting reactions are observed.

Because the requirements for sampling and for identification are so different, it makes sense to consider the development of separate devices for these tasks. Caltrans has sponsored a pair of projects that demonstrate this approach. A prototype Teleoperated Hazmat Vehicle (THV) capable of obtaining liquid and solid samples has been developed at California State University, Chico [Hoff 1992, Internet 1995a]. This report addresses the analysis identification phase of highway spill response, and describes possible configurations for a portable Teleoperated Hazmat Laboratory (THL). Figure 1 shows how these devices would be used together. Upon arriving at the scene of a spill, Caltrans personnel would deploy the THV. Using a video camera mounted on the THL, response personnel would inspect the site, looking for labels or placards, without the need to suit up in protective gear. If no identifying information is found, the THV would obtain a sample of the spilled substance. At the same time, response personnel would deploy the THL in a location slightly removed from the spill, but also removed from people at the site. The THV would deposit the sample in the THL. Testing in the THL would be controlled and monitored remotely. Response personnel would not come into contact with the unknown until an appropriate containment and clean up procedure is identified.

1.4 Contents of this Report

Chapter 2 of this report discusses unknown spills and the means available for their identification. In Chapter 3, the tradeoff between cost and capability is investigated through a survey of Caltrans response personnel. Conceptual designs of the THL are presented in Chapter 4. Conclusions and recommendations are included in Chapter 5. A questionnaire used to gather information from Caltrans districts is provided as Appendix A. Responses to the questionnaire are shown in Appendix B.

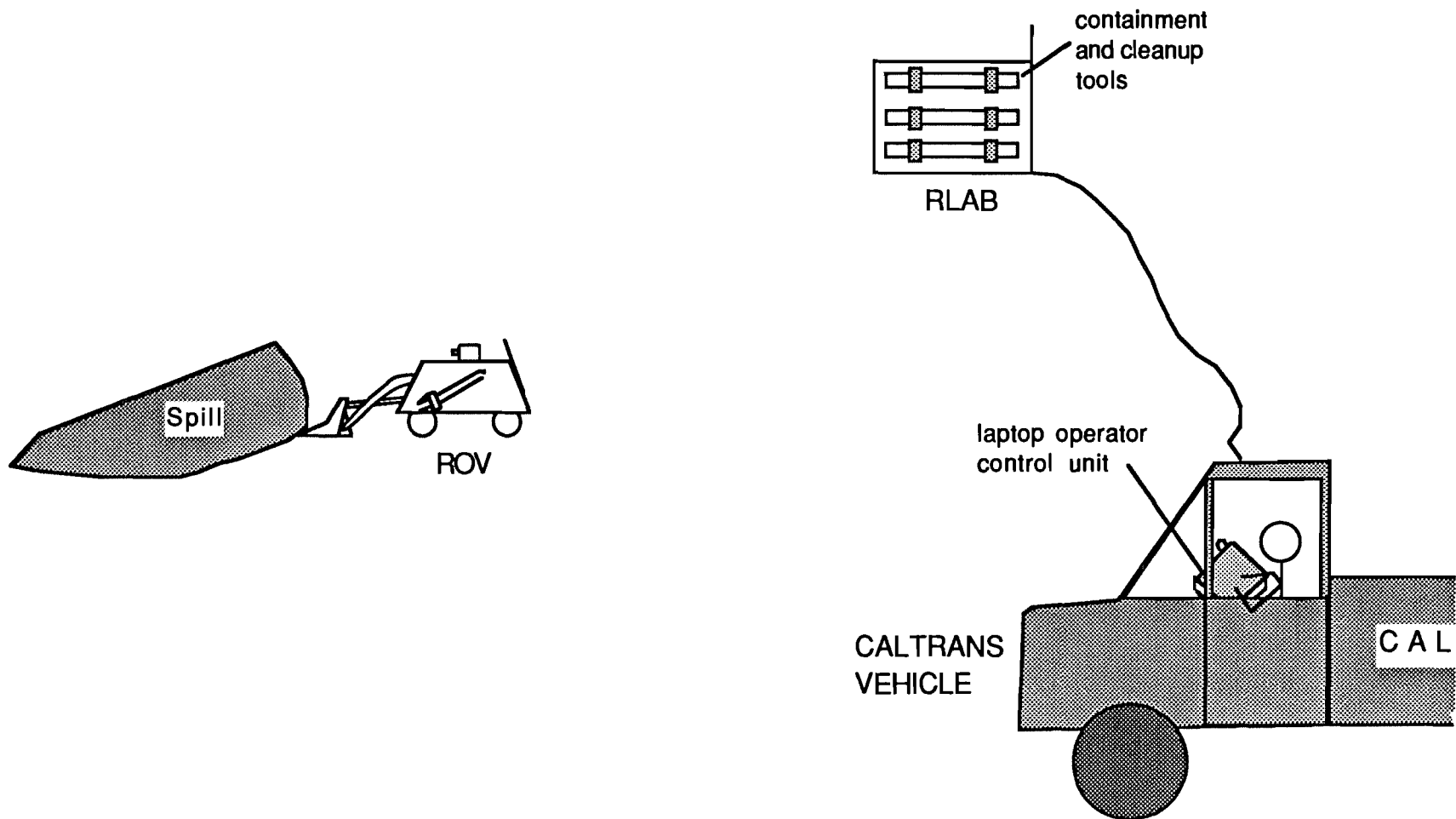


Figure 1. THV/THL Coordinated Operation

CHAPTER TWO

UNKNOWN SPILLS

When the composition of a spilled material is not readily evident from labels, placards, or shipping manifests, it must be determined by the spill response team. A precise determination of the chemical content of the unknown is not required. Rather, it is necessary to proceed through the analysis only until an appropriate containment and clean up strategy is indicated. In most cases, a more detailed quantitative analysis will be needed prior to disposing of the material. However, this detailed analysis can be carried out in a controlled laboratory environment without the time pressure caused by roadway closure.

Three broad categories of equipment and methods may be used in identifying unknowns: field meters, field chemistry systems, and analytical laboratory equipment. Before discussing these systems, it is useful to review the types of substances considered to be hazardous and what is known about previous unknown spills.

2.1 Hazardous Materials

Definitions of the term hazardous vary widely, but are typically based on the concept of risk to human health and the environment. The EPA defines a hazardous substance, with respect to hazardous wastes, as

"anything which, because of its quantity, concentration, or physical, chemical, or infectious characteristics may cause, or significantly contribute to, an increase in mortality; or cause an increase in serious irreversible, or incapacitating reversible, illness; or pose a substantial present or potential hazard to human health and the environment when improperly treated, stored transported, to disposed of, or otherwise managed" [Masters 1991]

The definitions of hazardous substances for the EPA are found under the Resource Conservation and Recovery Act (RCRA). A substance is hazardous if it is a listed waste or if it possesses any of four attributes (based on Wentz 1989 and Masters 1991):

Ignitability Ignitable substances are easily ignited and burn vigorously and persistently. Examples include volatile liquids, such as solvents, whose vapors ignite at relatively low temperatures (60° C or less).

Corrosivity Corrosive substances have a pH of less than 2 or greater than 12, and can react dangerously with other wastes or cause toxic contaminants to migrate from certain wastes. This category also includes substances that are capable of corroding metal containers.

Reactivity Reactive substances are unstable under normal conditions. They can cause explosions and/or liberate toxic fumes, gases, and vapors when mixed with water.

Toxicity Toxic substances are harmful or fatal when ingested or absorbed. Toxicity is determined by using a standardized laboratory test called the toxicity characteristic leaching procedure. A toxic substance is capable of killing, injuring, or otherwise impairing organisms which it contacts. The risk depends upon the pathway and amount of exposure.

The Hazardous Material Transportation Act (HMTA) authorizes the Department of Transportation (DOT) to regulate the movement of substances within the United States which pose a threat to health, safety, property, or the environment when transported by air, highway, rail, or water. Sixteen thousand substances are regulated under the HMTA. The HMTA describes several groups of hazardous substances, including explosives, flammables, oxidizing materials, organic peroxides, corrosives, gases, irritants, poisons, etiologic agents, radioactive materials, and other regulated matter (ORM). A summary of the DOT Hazard Classes is supplied in Table 1.

The Registry of Toxic Effects of Chemical Substances (RTECS) is a list of toxic substances designated by the National Institute of Occupational Health (NIOSH), and is used jointly by OSHA and the EPA. The list currently includes over 100,000 entries based on the risk of adverse effects to human health. Substances are divided into carcinogenic and non-carcinogenic categories. Carcinogenic substances are assumed to be hazardous at any exposure level. Non-carcinogenic substances are typically tested to determine Time Weighted Averages for Threshold Limit Values and Permissible Exposure Limits for each chemical. These values represent exposure limits beyond which a designated percent of individuals in a general population would be adversely affected. Toxicological studies are performed to determine acceptable levels of exposure. A common acceptable exposure risk would be one adverse effect in an at risk population of one million; for some substances, this would result from a chemical concentration in the parts per million or parts per billion range.

2.2 Hazard Assessment for Containment and Cleanup

For hazardous spills that occur on the highway, clean-up and containment can be carried out more efficiently if identification is thought of as a two part process: initial identification on site to allow hazard assessment and to guide containment and cleanup, and comprehensive identification prior to disposal. The Department of Transportation Emergency Response Guidebook provides recommendations for actions to be taken at the site, in the form of a series of guides keyed to specific substances or characteristics [DOT 1990].

For initial identification, it is necessary to determine the type of hazard the unknown presents, so that appropriate containment and cleanup measures can be taken. Because a conservative, but practical, approach must be followed in the absence of information, more detailed knowledge of the spilled substance will allow safer, faster, and less expensive containment and cleanup. For example, if no information is available, the first responder is instructed in DOT 1990 to follow Guide 11, which contains only general emergency response actions, and notes that self-contained breathing apparatus and structural firefighter's protective clothing will provide limited protection. Small fires are recommended to be handled with dry chemical, CO₂, water spray or regular foam. Small spills are to be taken up with sand or other noncombustible absorbent material and placed in containers for later disposal.

Hazard Class	Definition	Examples
Flammable liquid	Any liquid having a flash point below 100° F.	Ethyl alcohol, gasoline, acetone, benzene, dimethyl sulfide
Combustible liquid	Any liquid having a flash point at or above 100° F and below 200 ° F.	Ink, fuel oil
Flammable solid	Any solid material, other than an explosive, liable to cause fires through friction or retained heat from manufacturing or processing or which can be ignited readily, creating a serious transportation hazard because it burns vigorously and persistently.	Nitrocellulose, phosphorous, charcoal
Oxidizer	A substance, such as chlorate, permanganate, inorganic peroxide, or a nitrate, that yields oxygen readily to stimulate the combustion of organic matter.	Potassium bromate, hydrogen peroxide solution, chromic acid
Organic peroxide	An organic compound containing the bivalent -O-O- structure and which may be considered a derivative of hydrogen peroxide where one or more of the hydrogen atoms have been replaced by organic radicals.	Urea peroxide, benzoyl peroxide
Corrosive	Liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact, including liquids that severely corrode steel.	Bromine, soda lime, hydrochloric acid, sodium hydroxide solution
Flammable gas	A compressed gas that meets certain flammability requirements.	Butadiene, engine starting fluid, hydrogen, liquified petroleum gas
Nonflammable gas	A compressed gas other than a flammable gas.	Chlorine, xenon, neon, anhydrous ammonia
Irritating material	A liquid or solid substance which on contact with fire or when exposed to air gives off dangerous or intensely irritating fumes.	Tear gas, monochloroacetone

Table 1. Department of Transportation Hazard Classes

Hazard Class	Definition	Examples
Poison A	Extremely dangerous poison gases or liquids belong to this class. Very small amounts of these gases or vapors of these liquids, mixed with air, are dangerous to life	Hydrocyanic acid, bromoacetone, nitric oxide phosgene
Poison B	Substances, liquids or solids (including pastes and semisolids), other than poison A or irritating materials, that are known to be toxic to humans. In the absence of adequate data on human toxicity materials are presumed to be toxic to humans if they are toxic to laboratory animals.	Phenol, nitroaniline, parathion, cyanide, mercury-based pesticides, disinfectants
Etiologic agents	A viable microorganism, or its toxin, which causes or may cause human disease. These materials are limited to agents listed by the Department of Health and Human Services.	Vibrio cholerae, clostridium botulinum, polio virus, salmonella, all serotypes
Radioactive material	A material that spontaneously emits ionizing radiation having a specific activity greater than 0.002 microcuries per gram (mCi/g).	Thorium nitrate, uranium hexafluoride
Explosive	Any chemical compound, mixture, or device, the primary or common purpose of which is to function by explosion, unless such compound, mixture, or device is otherwise classified.	
Class A	Detonating explosives.	Just trust unit, explosive booster
Class B	Explosives that generally function by rapid combustion rather than detonation.	Torpedo, propellant explosive
Class C	Manufactured articles, such as small arms ammunition, that contain restricted quantities of class A and/or class B explosives, and certain types of fireworks.	Toy caps, trick matches, signal flare, fireworks
Blasting agent	A material designed for blasting, but so insensitive that there is very little probability of ignition during transport.	Blasting cap

Table 1. Department of Transportation Hazard Classes (continued)

Hazard Class	Definition	Examples
ORM (other regulated materials)	Any material that does not meet the definition of the other hazard classes ORMs are divided into five substances:	
ORM-A	A material which has an anesthetic, irritating, noxious, toxic, or other similar property and can cause extreme annoyance or discomfort to passengers and crew in the event of leakage during transportation.	Trichloroethylene, carbon tetrachloride, ethylene dibromide, chloroform
ORM-B fluoride	A material capable of causing significant damage to a transport vehicle or vessel if leaked. This class includes materials that may be corrosive to aluminum.	Calcium oxide, ferric chloride, potassium
ORM-C	A material which has other inherent characteristics not described as an ORM-A or ORM-B, but which make it unsuitable for shipment unless properly identified and prepared for transportation.	Castor beans, cotton, inflatable life rafts
ORM-D	A material such as a consumer commodity which, although otherwise subject to regulation, presents a limited hazard during transportation due to its form, quantity, and packaging. ammunition	Consumer commodity not otherwise specified, such as nail polish, small arms
ORM-E	A material that is not included in any other hazard class but is subject to the requirements of this subchapter. Materials in this class include hazardous wastes and hazardous substances.	Kepone, lead iodide, heptachlor, polychlorinated biphenyls

Table 1. Department of Transportation Hazard Classes (continued)

If it can be determined that the material is, for example, an oxidizer, Guide 47 is used. In this case small fires are to be handled using water only, with no use of dry chemical, CO₂, or Halon. Small spills are to be handled by flushing the area with flooding amounts of water. If the material can further be identified as a hydrogen peroxide solution of 20% to 52% peroxide, Guide 45 is used, and there is an added caution not to get water inside a container holding the material. If the hydrogen peroxide solution has 8% to 20% peroxide, however, Guide 60 is used. Although it is noted that the material may react violently with water, the lower peroxide content permits small fires to be handled by dry chemical, CO₂, regular foam, or water spray. Small spills are to be taken up with sand or other noncombustible absorbent material.

If it can be determined that the material is corrosive, Guide 59 is used. In this case, it is noted that structural firefighter's protective clothing is not effective, and that fully-encapsulating, vapor-protective clothing should be worn for spills and leaks with no fire. Small fires and small spills are handled as in Guide 11. If it can be determined that the corrosive material is a sodium hydroxide solution, however, firefighter's protective clothing will provide limited protection.

2.3 Unknown Spill Incidents

In many spill incidents, the substance is readily identifiable by a combination of labels or placards visible at the site, shipping papers, and information provided by the driver of the vehicle. However, there are several circumstances under which the identity of a spilled material may be unknown. A vehicle may be badly damaged and the driver unable to provide information. The material may have been spilled without the driver's knowledge, and neither vehicle nor driver remain on the scene. The material may have been illegally dumped on the roadway. Caltrans personnel report that the dumping of supplies used to process illegal drugs is an increasing problem.

There are no readily available nationwide statistics on the frequency of unknown spills. In California, releases of hazardous substances are tracked by the Office of Emergency Services through the California Hazardous Material Incident Reporting System (CHMIRS). Section J on the CHMIRS response form deals with hazmat identification sources. Respondents are requested to "check the best descriptor/s" of identification source from the following list: on-site fire services, off-site fire services, on-site non-fire services, off-site non-fire services, chemist, tox center, dot manual, msds, placards/signs, shipping papers, contract info sources, computer software, other. Multiple identification sources may be indicated for each incident. For 1988, on-site services (fire and non-fire) were the source of hazmat identification in 62% of roadway spills (derived from information in [OES 1989]). However, this indicates only that personnel on site made the identification; identification through visual inspection of a label is not differentiated from identification by a series of chemical tests carried out on-site.

Caltrans also tracks hazardous material incidents, though this information is not published regularly. Records of hazardous spills from 1986 through 1992 were obtained from Caltrans. Table 2 shows the percentage of incidents for each year in which an unknown substance was involved. Note that while the average over all records was 8.7%, the percentage of unknown spills decreased over the six year period. From 1988 to 1992, the number of unknown spills decreased as well. This could be due to a variety of factors, including better documentation of cargo or better labeling of containers. Because the

development of a field ready version of either the THL or the AHL will require a significant investment, it will important to evaluate the likelihood of a continued reduction in the incidence of unknown spills.

Year	All Spills	Unknown Spills	<u>Unknown All</u>
1986-87	268	38	.142
1987-88	407	53	.113
1988-89	705	59	.084
1989-90	540	51	.094
1990-91	598	38	.064
1991-92	427	22	.052
total, 1986-92	3008	261	.087

source: derived from Caltrans yearly summaries

Table 2. Frequency of Unknown Highway Spills in California

It is of interest to note that, of the great number of hazardous materials transported on the highways nationwide, only 14 substances account for more than 50% of the spill incidents, and 50 substances account for more than 77.5% of the incidents [NCHRP 1994]. If these same statistics held true for unknown spills, a system that could identify the "top 20" spilled materials quickly and safely would be beneficial. Statistical information on the actual identification of spills reported as unknown is not readily available.

2.4 Tools for Identifying Unknowns

When a spill involves an unknown substance, it is necessary to identify at least the hazard class of the material as quickly as possible, and preferably at the spill site. There are three general categories of tools that can be used for identification of unknown spills: field meters, field chemistry systems, and analytical equipment. These are described briefly in the paragraphs that follow, with an emphasis on characteristics relevant to an automated or remotely controlled system for spill response: substances or characteristics detected, ease of use, portability, durability, availability of electronic output, power requirements, and cost.

2.4.1 Field Meters

Portable hand-held field meters are available to measure pH, to monitor radioactivity, and to detect a variety of gases. A summary of commonly available meters is provided below.

2.4.1.1 pH Meters

pH is an indication of acidity or alkalinity. The simplest form of a pH "meter" is the familiar pH paper, whose color changes according to the pH of the solution used to wet it. pH paper is inexpensive (pennies per use), easy to use, portable, durable, and requires no power to actually carry out the measurement (though power may be required to place the solution in contact with the paper). pH paper must be interpreted visually. This could be

done remotely, if a video camera were used to display the wetted paper and a color comparison sheet. It is possible that image processing software could be developed to automatically determine pH from the video image, but this would not be cost effective (compared to other pH measurement technologies) unless the image processing was used for a large portion of the identification process.

pH can also be measured using a variety of handheld battery powered "testers" that provide output in the form of a liquid crystal display (LCD). These have self contained sensing media (as opposed to the detachable electrodes found in more expensive pH meters), and range in price from \$25 to \$200. The LCD output indicates that pH is converted to an electronic signal within the tester; it may be possible to modify these testers so that pH can be electronically transmitted to a remote location, allowing automated sensing.

More sophisticated pH meters typically make use of detachable electrodes and can correct for the temperature effect associated with pH readings. Field models are battery powered. Some models include an RS232 communications port. pH meters range in price from \$100 to over \$1000, depending on accuracy and other features.

For identification at the site of a spill, great accuracy is not required. The most promising options for automated or teleoperated determination of pH in spill response are (1) pH paper or pH testers viewed remotely through a video camera and (2) pH testers modified to allow electronic transmission of the pH reading.

2.4.1.2 Radiation Meters

General purpose radiation meters measure alpha, beta, gamma, and X-ray radiation. The meters are battery powered, with output displayed either through LCD readouts or through an analog scale. Most models contain an additional visual (flashing LED) or audio indicator of radiation level. The meters range in price from approximately \$250 to over \$1200. It may be possible to modify portable meters so that output is provided electronically, allowing automated or teleoperated use. An advantage of this approach is that the existing "factory built" output (visual or audio) could be monitored with a video camera to provide a backup.

2.4.1.3 Gas Detection Meters

Hand-held meters are available to detect a variety of gases and groups of gases. For example, combustibility meters detect the presence of combustible gases or vapors. Toxic gas meters detect the presence of gases such as O₂, CO, H₂S, SO₂, NO_x, and NO₂. In addition, meters exist that can detect a variety of gases, including mercury vapor, freon and other refrigerants, and chlorine and other halogen gases. These meters have either an audio alarm, an analog scale, a digital readout, or some combination. As with other meters, it is likely that these could be modified to provide output electronically. The cost for most of these meters is between \$250 and \$700, although at least one intrinsically safe model which detects any non-flammable gas for which the thermal conductivity is different from ambient air sells for over \$3000.

2.4.2 Field chemistry systems

At present, the identification of unknown roadway spills is most frequently accomplished through the use of field chemistry systems in which small amounts of an

unknown are combined with a series of reagents. Several proprietary systems have been developed to lead response personnel through a sequence of tests. Typically, the tests can be divided into two types: screen tests and definitive tests. Screen tests are carried out to detect properties which indicate that a substance is hazardous. Based on the results of screen tests, a sequence of definitive tests is carried out to identify common materials. In some tests, the direct reaction of an unknown with a reagent is visually observed. In others, the gas given off as the unknown undergoes a reaction is drawn into a prepackaged detector tube containing a reagent. A change of color in the tube indicates the presence or absence of a particular material.

The actions required to carry out the various tests in common field chemistry systems include adding one material to another, shaking a test tube, heating a test tube, tilting a test tube. Nearly all the motions required could be carried out remotely or automatically in a fairly straightforward manner. The exception is the loading/unloading of detector tubes into the pump that is used to draw in a gas sample. For nearly all tests, the result is monitored visually. Monitoring could be carried out remotely via video if a system with high color fidelity was used or if appropriate color coded markers were included in the field of view. Thus, in concept, remotely controlled or automated versions of available field chemistry systems could be developed.

Most of the components of field chemistry systems are relatively inexpensive. The most costly item is typically the set of detector tubes and the pump used with them. Hand powered pumps cost between \$250 and \$400. At least one company makes an electrically powered pump. However, loading the detector tubes into the pump still presents difficulties.

Field chemistry systems have been developed taking into account the safety of the person carrying out the tests. In an automated or remotely controlled system, the distance between the test and the person carrying it out provides a much safer environment. A field chemistry system designed for an automated environment might contain different types of tests, or carry out the tests in different order. For example, instead of first screening for hazards that put the person carrying out the tests at risk, the first tests could be carried out to identify frequently spilled substances. This could reduce the average time required for identification.

2.4.3 Analytical Equipment

In a laboratory environment, the goal of analysis is typically the precise identification of materials, including the detection of very small (parts per million) quantities of a contaminant. Techniques such as chromatography and spectroscopy support this goal. They are designed for situations in which the operator suspects the presence of a particular substance. In each case, the operator compares the observations of the unknown (its signature, in terms of absorption peaks in chromatography, resonance or emission peaks in spectroscopy) with observations of a known substance. Compared to field meters and field chemistry systems, analytical equipment is expensive (starting at around \$5000 and increasing to over \$50,000), needs frequent recalibration, and requires trained operators. Although most analytical equipment is designed for use in a laboratory setting, there now exist portable models of some types of equipment, with on-board computer systems that assist in comparing the signature of the unknown to reference signatures. Several special purpose portable analytical systems are under development, primarily with funding from the U.S. Department of Energy. These vary in size from a "backpack" to a van, with costs estimated to be \$150,000 to \$1,000,000.

It would be possible, though not necessarily straightforward, to develop hardware that would allow the loading of samples into existing equipment. However, the high cost of the equipment, even before modification, may be prohibitive for initial spill response. At least some of the cost associated with analytical equipment is due to features (such as the ability to quantify substances on a parts per million level) that are not important in initial spill response. It is possible that lower cost and perhaps more rugged systems could be developed to meet only the identification requirements of highway spills.

2.4.4 Other Automated Systems

Two other efforts to automate the identification of unknown substances are described here. The first is more directly relevant to the problem of highway spills. To assist their on-site hazardous materials response team, the Jet Propulsion Laboratory has developed HAZBOT III, a remotely controlled emergency response robot. The following description of the HAZBOT III is drawn from several sources [Hazardous 1995, Welch 1994, Internet 1995b]. HAZBOT III has been used in a demonstration to navigate 30-50 meters into a building, unlock and open doors, move in and out of rooms, sense for the presence of combustible gases and level of oxygen, climb over a 10 inch berm to get into a chemical storeroom, and locate and identify a simulated spill. On-board sensors include audio and color video communications, an AIM USA 3300 chemical gas detector, a general combustible gas sensor, and sensors for oxygen and carbon monoxide. The HAZBOT III weighs 600 pounds, measures 28" wide x 42" long x 40" tall when stowed, and can operate safely in a combustible atmosphere.

The HAZBOT III is capable of greater mobility and manipulation that would be required for most highway spills. It carries out analysis of gases only. In the HAZBOT's current configuration, size, price, and the inability to analyze liquids and solids keep it from being a realistic alternative for highway spills. However, future versions of the device may be appropriate for use by Caltrans, at least on an experimental basis.

On a much larger scale, the U.S. Department of Energy is developing an integrated system for contaminant analysis automation (CAA). The goal is to reduce the time and cost of carrying out analysis by automating the process in a facility that can be located at a remediation site. Much of the effort of this project is directed toward the definition of "a standard laboratory automation formalism that addresses sample preparation, analysis, and data interpretation" [Internet 1995c]. The initial application area investigated is the extraction, cleaning, and identification of PCBs in solid samples.

The technology developed and used under the CAA project is much more sophisticated than that required for highway spills. However, it is possible that work done on this project will have spin-offs that would be applicable in the Caltrans environment.

2.4 Evaluation

Based on existing identification technology and other efforts toward automating the identification process, two approaches to the automated identification of unknown highway spills seem worthy of further investigation. In each approach, it is assumed that the THV or other sampling device obtains a sample of the spilled material, and that one or more field meters could be mounted on the THV if necessary.

The first approach is based on existing field chemistry systems. A Teleoperated Hazmat Laboratory (THL) would allow Caltrans personnel to remotely view and control the sequence of tests prescribed by a field chemistry system. One advantage of this approach is that it makes use of identification technology familiar to the Caltrans personnel who would operate the system; little or no new training would be required. A THL could likely be constructed from readily available parts, keeping costs low. The major disadvantage is that the approach represents an attempt to automate a process that has been designed to be carried out by humans, rather than redesigning the identification process for automation. This may lead to higher costs and poorer performance than would otherwise be obtained.

The second approach is based on existing analytical laboratory equipment, and modify these to carry out automatic identification of most substances. The resulting Automated Hazmat Laboratory (AHL) would be a "black box" to the operator, who would need to be trained only in how to set it up on site. The advantages of this approach are that it would be easy to use on site even by personnel who have not received training beyond that of First Responder Operations Level. The system could be designed to provide information beyond just the hazard level, perhaps providing a detailed quantitative analysis of the unknown. The disadvantages of this approach are that the technology required does not now exist on the market, and that even if it did, it would likely be expensive.

The appropriateness of each of these approaches in the Caltrans environment is addressed in the next section.

CHAPTER THREE

COST-CAPABILITY TRADEOFF

The field chemistry systems currently in use for spill response provide an indication of the hazard category of a substance and, in some cases, an indication of the particular substance. In a few instances, the systems do not yield enough information to initiate cleanup, and a sample of the unknown must be sent to a lab for analysis. An automated or remotely controlled approach to spill response could be designed to duplicate the current level of identification (that is, determine hazard class and identify some specific substances), or it could be designed to allow more or less detailed identification.

In general, the more detailed the identification, the more costly the equipment. To assess the tradeoff between cost and capability within Caltrans, a questionnaire regarding current response practice and the desirability of a more automated approach was prepared and sent to each District Office.

3.1 The Caltrans Questionnaire

The questionnaire was designed to gather information about current spill response practice, assess the need within Caltrans for improved technologies for identifying unknowns, and determine the value of such technologies. The first portion of the questionnaire dealt with current response practice: the personnel involved, the time required, and the techniques used. The second portion of the questionnaire solicited feedback on the importance of various screen tests and specific tests in spill response, and on the value of a system that could carry out these tests with exposing the operator to the unknown. The final portion of the questionnaire investigated the value of additional identification information, including the particular chemicals in an unknown and the quantities of these chemical present.

A presentation on this research project was made to Caltrans personnel at the Hazardous Material Coordinators meeting on November 4, 1992. The questionnaire was distributed to each Caltrans district office to the attention of personnel who had attended the Hazardous Materials Coordinators meeting. An initial mailing did not reach most districts, so a copy was faxed to each office. The questionnaire is reproduced in Appendix A.

3.2 Questionnaire Responses

Responses to the faxed questionnaire were received from ten Caltrans districts; Districts 7 and 8 did not respond. The detailed responses are shown in Appendix B. Summaries and implications are discussed in the paragraphs below. The small number of samples, the brief time available to respondents, and the prior conceptions of the respondents with respect to this project all argue against a statistical analysis of the results. Instead, the responses are viewed as giving a sense of the attitudes and experiences of Caltrans HazMat Coordinators with respect to more automated spill response.

3.2.1 Section I - Current Practice

Responses to questions in this section indicated that while Caltrans personnel (most often supervisors/superintendents) and the California Highway Patrol are often first to arrive at the scene of a spill, they seldom carry out the identification of an unknown substance. Instead, roughly one to two hours after the spill is reported, clean up contractors or local health departments arrive and begin to identify the substance. HazCat¹ and HeinzCat² (proprietary field chemistry systems) were the only method of analysis reported, with HazCat reported by more respondents. The identification process typically takes 20 to 30 minutes (and perhaps longer if the time required to don protective gear is included). On-site identification most often results in a determination of the hazard level or hazard class of the substance, though the chemical group is identified in many cases as well. Small cleanups or cleanups of non-hazardous materials may be handled by Caltrans, and typically start within 1-2 hours after the spill is reported. Cleanup of larger and hazardous spills are handled by contractors, and may start within 1-2 hours of the spill or much later (4 - 10 hours). The time required for cleanup varies greatly. Most respondents indicated a cleanup time of at least one hour and up to four hours, but some indicated that cleanup can take days or weeks. In most districts, the role of Caltrans in identification and clean-up of unknown spills is that of coordinator, though in a few districts Caltrans itself will carry out identification and cleanup.

With respect to the material spilled, by far the most frequently spilled materials are fuels and oils. Asked how often these substances were unknown at the time of the spill, respondents provided a wide variety of answers, with several "seldom" responses, several in the 10-15% range, and several at 70% or greater (it is possible that this last group misinterpreted the question).

For the most part, responses to questions in this section supported the information obtained through a review of the literature and through earlier conversations with Caltrans personnel. One of the motivations for a more automated approach to spill identification is speed; the quicker the roadway is reopened, the better. Road closure time could be reduced a bit if identification were carried out more quickly. However, because identification takes only 20-30 minutes under current practice, larger reductions are possible only if identification can be carried out by the first party at the scene (typically Caltrans or CHP) while waiting for cleanup contractors to arrive. Even if only a portion of the unknown spills could be identified by the first on the scene, the benefits might be significant. The most frequently spilled substances are petroleum based fuels and oils. Therefore, equipping Caltrans and CHP personnel with an inexpensive means of identifying fuel and oil might be worthwhile.

3.2.2 Section II - Screen Tests

Questions in this section addressed the relative importance of various meters and screen tests and the price that HazMat specialists would be willing to pay for a system that would enable them to carry out a set of screen tests remotely.

¹ HazCat is a registered trademark of Haztech Systems, Inc., 2218 Old Middlefield Way, Suite J. Mountain View, California, 94043.

² HeinzCat is a system developed by Dieter Heinz, San Luis Obispo, California.

Of the typically available hand-held meters, a combustibility meter was considered very important by all respondents, followed by other gas detection meters and pH meters. Radiation meters were considered less important by roughly half the respondents. Of the field chemistry tests considered for the THL (evaporation, combustibility, oxidizer peroxide, water reaction, pH, char/ignition, iodine crystal, ammonia, cyanide), the combustibility test was felt to be the most important, followed closely by the oxidizer test and the pH test. Somewhat less important were tests for peroxide, water reaction, ammonia, cyanide, and an iodine crystal test that identifies gasoline, oil, and diesel. Of less importance still were the char/ignition test and the evaporation test.

The next question provides an indication of the perceived value of a remotely controlled lab capable of carrying out the following field chemistry tests: evaporation, combustibility, oxidizer peroxide, water reaction, pH, char/ignition, iodine crystal, ammonia, cyanide. Seven of 10 respondents felt that such a device would be very useful to their districts if it were available for between \$500 and \$1000. At a price of \$1000 to \$5000, the response drops off somewhat (from a mean of 2.3/3.0 to a mean of 2.0/3.0). At still higher prices, the device is perceived to much less useful.

The last question in this section investigates the usefulness of tests to identify specific substances. Based on discussion at the 11/4/92 Hazardous Materials Coordination Meeting, it appeared that it would be useful to include tests for cement, fertilizer, lime, arsenic, asbestos, and pesticides. The questionnaire responses verified that HazMat specialists would be interested in being able to identify these substances quickly and easily.

3.2.3 Section III - Automated Testing Technology

The final section of the questionnaire dealt with a hypothetical fully automated identification lab. A series of three questions addressed the value of information beyond that currently provide through field chemistry analysis. Specifically, respondents were asked in turn to indicate the usefulness of (1) an automated system capable of duplicating a HazCat analysis, (2) an automated system capable of carrying out a qualitative analysis that would indicate the chemicals present in an unknown, and (3) an automated system that would carry out a quantitative analysis of the unknown similar to what would be done by a testing lab. The responses are indicative of the need to consider regulatory requirements in the design process. Option (1), which provided results similar to those obtained in current practice, was considered useful at a price of \$5000 to \$10,000 by seven out of 10 respondents; usefulness dropped off rapidly as the price increased. Options (2) and (3) were considered less useful, with one respondent noting that lab certification would still be needed for disposal.

3.3 Evaluation of Questionnaire Responses

The questionnaire responses provide insight into four major questions regarding an automated approach to spill response: Who is the target market? How can spill response time be minimized? What capabilities should a new technology have? At what price would new technology for identification be considered?

3.3.1 Target Market

In most districts, Caltrans does not carry out the identification of spilled substances on a regular basis. Local health agencies and spill clean up contractors do most of the identification work. Under current practice, Caltrans represents only a portion of the target market for THL/AHL; health agencies and contractors would be the primary purchasers of automated devices. Caltrans could, of course, promote the use of a specific device by recommending or requiring that it be used by contractors, or by including in spill response contracts a financial incentive to reopen roadways as quickly as possible. If a technology such as the THL does reduce response time, contractors would then have an incentive to use it.

It is possible that the availability of a faster, safer way of identifying unknowns could change the role that Caltrans plays in spill response. Under one scenario, Caltrans could elect to carry out identification in more districts, training additional personnel in these districts in hazmat response. Spill response would be the highest priority task for these personnel, and they would be dispatched as soon as Caltrans learned of a spill. In some cases, for example, if the spill response unit happened to be housed very close to the location of a spill, this could lead to a significant reduction in the one to two hour time it now takes for contractors or local health authorities to arrive at the spill site. In most cases, however, a CHP officer or Caltrans worker not trained in spill response will happen upon a spill, and call in the spill response unit. Because spill response would be the highest priority of this unit, it might arrive at the spill site faster than a contractor or local health agency. However, it will still take time for the Caltrans unit to travel to the spill site, and the average reduction in road closure time would probably not be large. In another scenario, all Caltrans and CHP personnel on the road would be provided with a simple, easy to use device that would allow identification of at least the most commonly spilled substances by the first party on site. This is discussed in more detail in Section 4.3 below.

A broader target market for the THL/AHL could be considered as well, including those who respond to spills that occur in industrial, commercial, and educational facilities. JPL's HAZBOT III has been developed to address one portion of this market. If the THL/AHL meets the needs of these organizations (contractors, local health agencies, and in-house response teams) as well as the needs of Caltrans, development costs could be spread over a much larger group of purchasers (either initially, through joint sponsorship of development efforts, or ultimately through the cost of the device).

3.3.2 Spill Response Time

The time required to respond to a highway spill is made up of the following components: the time between spill occurrence and spill discovery (T_{OD}), the time between spill discovery and arrival of the first responder (T_{DR}), the time between arrival of the first responder and identification of the substance (T_{RI}), the time between identification of the substance and the start of cleanup (T_{IC}), and the time between the start of cleanup and its finish (T_{CF}). In most spills, the driver is aware of the spill, the vehicle remains on the scene, and the spilled substance is readily identified through placards, labels, manifests, or other information at the scene. In these cases, T_{OD} is close to zero. T_{DR} is the time it takes for Caltrans or the CHP to arrive at the scene, and depends on the location of the spill. Because the spilled substance is readily identified, T_{RI} is close to zero. T_{IC} depends on the location of the spill, on the spilled material, and on who will carry out the cleanup. Based on the questionnaire responses, T_{IC} is typically either 1 -2 hours (substance

routinely handled by Caltrans or contractors, location is not remote, clean up contractors called when spill first reported) or in the 4 - 10 hour range (substance is not handled by Caltrans, location is remote, contractors not readily available). T_{CF} depends on the specifics of the spill.

In the case of an unknown spill (8.6% of spills in recent years, as shown in Table 2), T_{RI} is no longer close to zero. Questionnaire results indicate that it takes 1 - 2 hours for contractors or the local health agency to arrive at the scene and begin the identification process, and another 20-30 minutes to identify at least the hazard posed by the spill. Thus, under current practice, improvements in identification technology would save at most 20-30 minutes. However, if identification could be carried out by the initial Caltrans or CHP officer on the site, much of the 1 - 2 hour travel component of T_{RI} could be eliminated. It is not clear what effect this would have on spill response time. If, in present practice, the clean up crew is different from the identification crew, and is dispatched only after the substance is identified, as much as two hours could be saved by having the initial responder carry out identification. However, if the clean up crew is dispatched to the scene as soon as an incident is reported, it is again the case that only the 20-30 minutes of identification time would be reduced.

The aspects of the cleanup process that have the biggest impact on time, getting the clean up contractor to the site and completing the cleanup, are not likely to be changed much through use of an automated system. If a cleanup contractor could be dispatched at the time the spill is first reported, it seems likely that even an automated system capable of rapidly determining the hazard level of an unknown would reduce response time by only 20-30 minutes plus the time required to don protective clothing. One respondent noted that the societal cost of a one hour closure of Interstate 5 is \$1 million. No attempt was made to verify this cost as a part of this report. However, if it is in the right "ballpark", then reducing response time by even 20 or 30 minutes for several spills each year would be worthwhile. In addition, a THL/AHL approach that minimizes contact with hazardous substances should also yield a safety benefit.

3.3.3 Capabilities

Under current practice, capabilities beyond that of the current field chemistry systems are not viewed as being of value to Caltrans, perhaps because lab certification is still needed prior to disposal. However, if there existed a system that could quickly carry out a quantitative analysis on site, perhaps the certification procedures would be modified so that the users of the system could issue their own certification. This might make an automated device capable of quantitative analysis more valuable to Caltrans than the survey results show.

A system with only limited capabilities might be of value if it were inexpensive enough to be issued to all Caltrans and CHP personnel, so that it allowed identification of some substances to be carried out by the first responder.

3.3.4 Cost

Questionnaire responses indicate that Caltrans HazMat coordinators would be willing to pay as much as \$1000 to \$5000 for a device that allowed a hazard analysis to be carried out automatically or under remote control. At this price, would all first responders

(Caltrans and CHP personnel) be equipped with and trained to use the system? Probably not, given the large number of potential first responders, the relatively small percentage of spills that are unknown, and the relatively small portion of overall spill response time that would be saved.

Is there a low cost alternative that first responders could safely use to speed up the identification process? Diesel, gasoline, and motor oil are by far the most commonly spilled substances [OES 1989, NCHRP 1994]. Based on questionnaire responses, these are also the most commonly unknown spills. A quick, safe, and easy way to identify these materials that could be packaged in a delivery system small enough and inexpensive enough to be routinely carried in all Caltrans and CHP vehicles might be of significant benefit.

3.4 Cost-Capability Summary

Based on questionnaire responses, three strategies for improving the identification phase of spill response warrant investigation: a remotely controlled system capable of duplicating at least portions of current field chemistry systems (THL), a fully automated portable hazardous analysis laboratory (AHL), and an inexpensive means of providing first responders with the ability to identify frequently spilled substances. These strategies are discussed in detail in the next section.

CHAPTER FOUR

CONCEPTUAL DESIGNS

This section presents four candidate approaches to spill identification. Three versions of the THL are described: a full system that would replicate the HazCat identification system currently used by many Caltrans districts, and two systems that would enable selected HazCat tests to be carried out. A mock up of one of these subset systems was constructed and is documented here. Comments from a Caltrans employee at a technology fair where the mock up was displayed led to the development of the second candidate approach: the testblock ID system. The third approach, test strips, evolved from the desire to provide first responders with the ability to quickly identify the most frequently spilled substances. The final approach is the AHL, a self-contained analysis lab..

4.1 Teleoperated Hazmat Laboratory (THL)

In its original concept, the THL is a remotely controlled laboratory that enables the operator to carry out identification using a field chemistry system such as HazCat without actually handling the unknown (and therefore without needing to suit up in protective clothing). The THV would drive up a ramp and deposit a solid or liquid sample into the top of the THL. A major THL design decision is whether the unit must be intrinsically safe (that is, designed so that its operation will not cause an explosion even if vapors from the substance being tested are flammable or combustible). Using only intrinsically safe actuators increases the cost of the THL. In the descriptions that follow, it is assumed that a combustible gas detector would be mounted on the THV, and that components of the THL that are not intrinsically safe (for example, open flame) would not be used in the presence of combustible or flammable gas.

Basing the THL on existing field chemistry techniques has the advantage of building new equipment around a familiar identification method, one that uses readily available supplies and is already used by response personnel. The drawback is that by doing no more than remotely controlling existing practice, the opportunity to take advantage of automation may not be fully realized. The tests currently used in systems like HazCat were designed to be safe and easy for a person to carry out; there may be other types of tests or other orders in which the tests could be carried out that would be more efficient to automate.

The tests in field chemistry systems involve combining small amounts of the unknown with a series of reagents and observing the resulting reaction, including color. In some cases, the unknown is to be added to the reagent; in other cases, the reagent is to be added to the unknown. Some tests involve stirring or shaking. Some require that the vapor given off by a reaction be drawn in to a prepackaged detector tube and observed. There are tests that require the unknown to be heated, and others that require a heated object be placed in the unknown.

A remotely controlled laboratory that could carry out, for example, the tests included in the HazCat system, would at a minimum require the following capabilities: drop unknown into test tube or watch dish, add liquid reagent(s), add solid reagent(s), measure pH of unknown, measure pH of unknown plus reagent, add water, shake, heat gradually

along the length of test tube, touch a lighted match to the substance, ignite the vapor over a sample or a sample/reagent mixture, draw vapor into prepackaged detector tubes. Because the results of most tests are indicated by color changes, the visual feedback provided to the operator (most likely through a video camera) must either be of high color fidelity or must include a color reference chart. The THL must also be small enough, light enough, and rugged enough to be transported easily to the spill site, fast and easy to set up, easy to use, and easy to clean, and capable of being powered by batteries (either vehicle batteries or batteries that travel with the device).

4.1.1 Full system

A conceptual design of a version of the THL that could carry out the full HazCat system is shown in Figure 2. The full system THL is built around three carousels. Carousel #1 contains the test tubes in which reactions will be observed. The unknown material is ejected from the THV collection syringe (or tube, in the case of a solid) into a storage tube. A valve at the base of the tube allows the appropriate amount of unknown to flow into a test tube. Water is dispensed as needed from a second storage tube. Of the test tubes mounted on the carousel, some are preloaded with the reagents required for frequently used HazCat tests. Others are empty; less frequently used reagents can be dispensed from carousel #2 into these tubes as needed. Carousel #3 houses auxiliary devices such as agitators and heaters, shown as compact devices in this conceptual drawing. Some of these devices, such as stirrers and heaters, do indeed exist in compact form. Others, such as a means of heating an object and bringing it into contact with the unknown, would require special design fit into the limited space shown in Figure 2. A video camera with remote focus is mounted so that the operator can observe the reactions that occur as the unknown is added to the test tube. Not included in this conceptual drawing, but necessary if the full HazCat analysis is to be carried out, is an automated pump positioned so that it can draw vapor samples into prepackaged detector tubes. The pumps exist, the means of automatically loading and unloading the specific tubes called for as the analysis progresses does not.

The full system version of the THL as shown in Figure 2 requires at least three rotary motion systems (most likely stepping motors and encoders) and at least four metering valves (two of which must be able to handle either liquids or solids) in addition to the actuators or sensor required by auxiliary equipment. The system would be feasible to construct, perhaps for under \$5000 but more likely for closer to \$10,000. The major drawback to the full system THL is the large number of reagents that must be available if identification process is indeed to be carried out remotely. When a HazCat analysis is carried out manually, only those reagents required for the specific test sequence that is carried out must be opened and available. In the case of the THL, however, any reagent that could be required by any HazCat test must be included on either Carousel #1 or Carousel #2. This means either the THL must be brought to the site preloaded or that reagents must be added prior to identification. In either case, it is likely that the time required for set up and identification would be at least as long as the 20-30 minutes currently required. Thus, the only benefit of this version of the THL is that responders would not come into contact with the unknown substance.

Regardless of the configuration used, any version of the THL capable of carrying out a complete HazCat analysis will suffer that same drawback as the system shown in Figure 2. Some of the clutter in Figure 2 could be eliminated, but there remain unsolved problems: how to load and unload detector tubes, how to incorporate some of the auxiliary devices, particularly those that require an open flame, without significant increases in cost

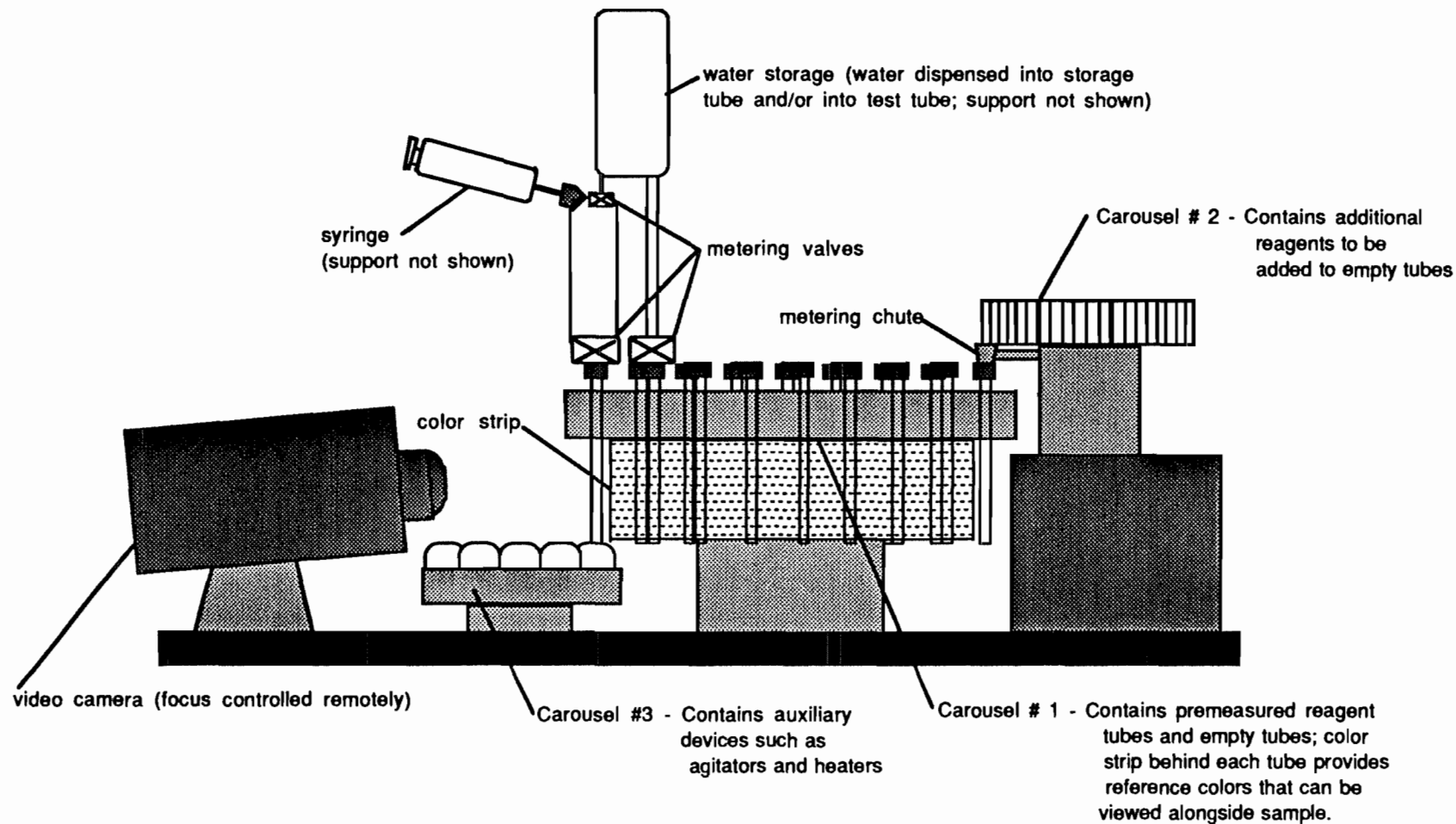


Figure 2. Full System THL Conceptual Design

or in the size of the THL. A full system THL could be designed and constructed. However, it does not appear to represent a significant improvement over current practice (when first responders take necessary precautions).

4.1.2 Subset 1

If only a few preselected HazCat tests were carried out, the resulting THL would be significantly simpler, less expensive, and faster to set up and run. First priority should be to the screen tests used to determine general hazard class; additional specific tests should be added as space permits. Table 3 outlines the tests proposed for inclusion in the Subset 1 version of the THL: screen tests plus the iodine crystal, ammonia, and cyanide tests. The descriptions in Table 3 are based on HazCat and HeinzCat.

Figures 3a and 3b show the conceptual design of a THL that includes Subset 1 tests. In this configuration, the entire THL is roughly the size of an automobile tire. The individual tests are laid out in a circle. It is assumed that a video camera mounted on the THV is available to allow remote viewing of the tests. The THV drives onto a ramp above the THL and unloads the sample into the dispenser. The dispenser rotates about the center of the lab; the operator dictates the order of the tests by controlling the rotation of the dispenser. Fire walls isolate the char and combustibility tests from the remainder of the THL. To avoid splashing, the dispenser tip should be kept close to test tubes and watch dishes. Therefore, the dispenser must be retracted slightly to pass over the fire walls.

The Subset 1 THL is considerably smaller and simpler than the Full System THL. Including all auxiliary devices, the Subset 1 THL requires 5 actuators (dispenser rotation, dispenser tip retraction, char test flame movement, detector tube insertion/ejection, water reaction agitator) and six valves (dispenser, iodine crystal, water reaction, propane supply for each side of char test, propane supply for combustibility test), and two switches (flame source on/off, automatic pump on/off)

The Subset 1 THL as shown in Figure 3 presents several design issues: the retractable dispenser, the flame source from the char and combustibility tests, the detector tube insertion/ejection mechanism, and the modified test tubes for the water reaction and iodine crystal tests. However, none of these (with the possible exception of the detector tube insertion/ejection mechanism) should be too difficult to implement. Control for the Subset 1 THL is straightforward as well. With the visual feedback provided to the operator through the THV video camera, only open loop control is required (the operator closes the loop). The operator's control panel would consist of three variable input mechanisms (i.e. knobs, possibly with start/stop buttons) to allow the operator to control dispenser rotation, char test flame movement, and water reaction agitation, a toggle button to raise and lower the dispenser tip, another toggle switch to insert/eject dispenser tubes, and eight push buttons to control the valves and on/off switches.

The Subset 1 THL could most likely be built for under \$5000 (after the detailed design has been worked out). The limited preloading of chemicals and test papers could be done prior to transportation or at the site. The THL includes tests that were considered very useful or somewhat useful by Caltrans personnel (as expressed in the questionnaire). In cases where the tests contained in the Subset 1 THL are sufficient to determine hazard level and a cleanup procedure, it should provide safety benefits and even save 5 - 10 minutes of identification time (compared to current practice). However, there may be substances for which the 11 tests included in the Subset 1 THL do not provide enough information to determine the hazard level. In this case, a member of the spill response team

Evaporation test

Information gained: screens for inhalation hazard and possible flammability

Method: place a small amount of unknown in dish, see if it evaporates

Possible reactions: quickly evaporates, leaves a residual, does not evaporate

Alternative methods: compare evaporation rate with water, acetone, etc.

Limitations: liquids only

Possible extensions: warm dish for faster results

Space requirements: one or two watch dishes

Combustibility test

Information gained: flammability

Method:

1a place a small amount of sample in dish, bring flame source towards dish

1b heat hairpin, stick into solid

2 put sample on Q-tip, stick into flame.

Possible reactions: material burns rapidly, slowly, or not at all

Alternative methods: don't touch flame to liquid in dish

Limitations: safety

Space requirements: one watch dish, space for flame and source

Char/ignition test

Information gained: screens for organic/inorganic, but can ID some substances

Method: heat unknown gently starting at top of tube and working down to sample; observe reaction, continue to heat until no change; try to ignite vapor

Possible reactions: many

Alternative methods: none

Limitations: safety, combustibility test must be performed first

Space requirements: two test tubes, torch, several flame outlets

Char/ignition test with HCl & cyanide detector tubes

Information gained: cyanide tube screens for urethane plastics in solids, nitriles in liquid; HCl tube screens for PVC plastic in solids, PCBs in oils

Method: pump vapor into tube during char test.

Possible reactions: change in color of tube

Alternative methods: none

Limitations: no information for many unknowns

Possible expansions: additional detector tubes

Space requirements: automatic pump dimensions (100x190x270 mm)

Water reaction test

Information gained: places unknown in one of several major categories

Method: place 1 ml water in angled test tube; add several drops of liquid (or small amounts of solid) unknown, one at a time, to water.; observe behavior

Possible reactions: reacts violently or less so w/water, dissolves, floats, sink

Alternative methods: rotate test tube; drop unknown directly into water

Limitations: specialized test tube required

Space requirements: equivalent of one watch dish

Table 3. Subset 1 Tests

Oxidizer test

Information gained: screens for oxidizers

Method: place KI starch paper with 1-2 drops HCl in watch dish; add unknown

Possible reactions: paper changes color

Alternative methods: put KMnO₄ in test tube with unknown; add water to solid

Limitations: must pre-wet paper or add dispensers

Possible expansions: none

Space requirements: one watch dish

Peroxide test

Information gained: explosive hazard; finds oxidizer missed by KI starch paper

Method: wet peroxide paper with distilled water in watch dish; add unknown

Possible reactions: paper changes color

Alternative methods: none

Limitations: must pre-wet paper or add dispensers

Possible expansions: none

Space requirements: one watch dish

pH test

Information gained: screens for corrosivity, yields pH.

Method: place unknown from water reaction test onto pH paper.

Possible reactions: pH paper changes color

Alternative methods: pH meter; place pH paper in water reaction test tube

Limitations: water reaction test must be done first

Space requirements: one watch dish

Ammonia test

Information gained: screens for ammonia and amines

Method: place unknown on watch dish with Nessler's solution

Possible reactions: color change

Alternative methods: carry out in test tube

Limitations: none

Possible expansions: none

Space requirements: one watch dish or test tube

Cyanide test

Information gained: screens for cyanide radical

Method: place unknown in watch dish with test paper wetted with HCl

Possible reactions: color change

Alternative methods: use cyanide indicator solutions in test tube

Limitations: none

Possible expansions: none

Space requirements: one watch dish or test tube

Iodine crystal test

Information gained: IDs diesel, gasoline, turpentine, kerosene, other hydrocarbons

Method: place organic unknown in test tube with iodine crystals

Possible reactions: color change, no color change

Alternative methods: none

Limitations: must do char test first

Possible expansions: none

Space requirements: one test tube

Table 3. Subset 1 Tests (continued)

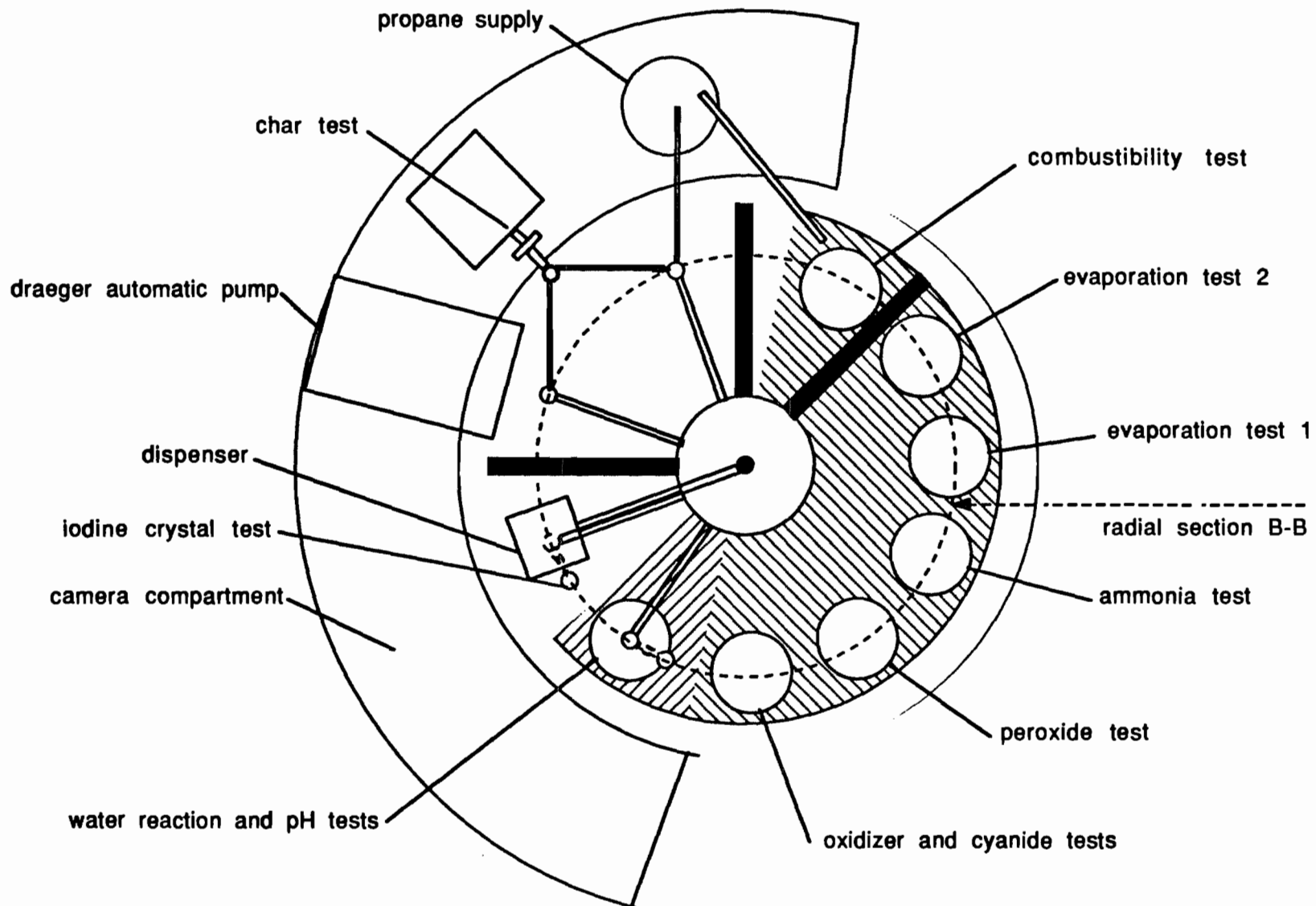


Figure 3a. Subset 1 THL Conceptual Design, Top View

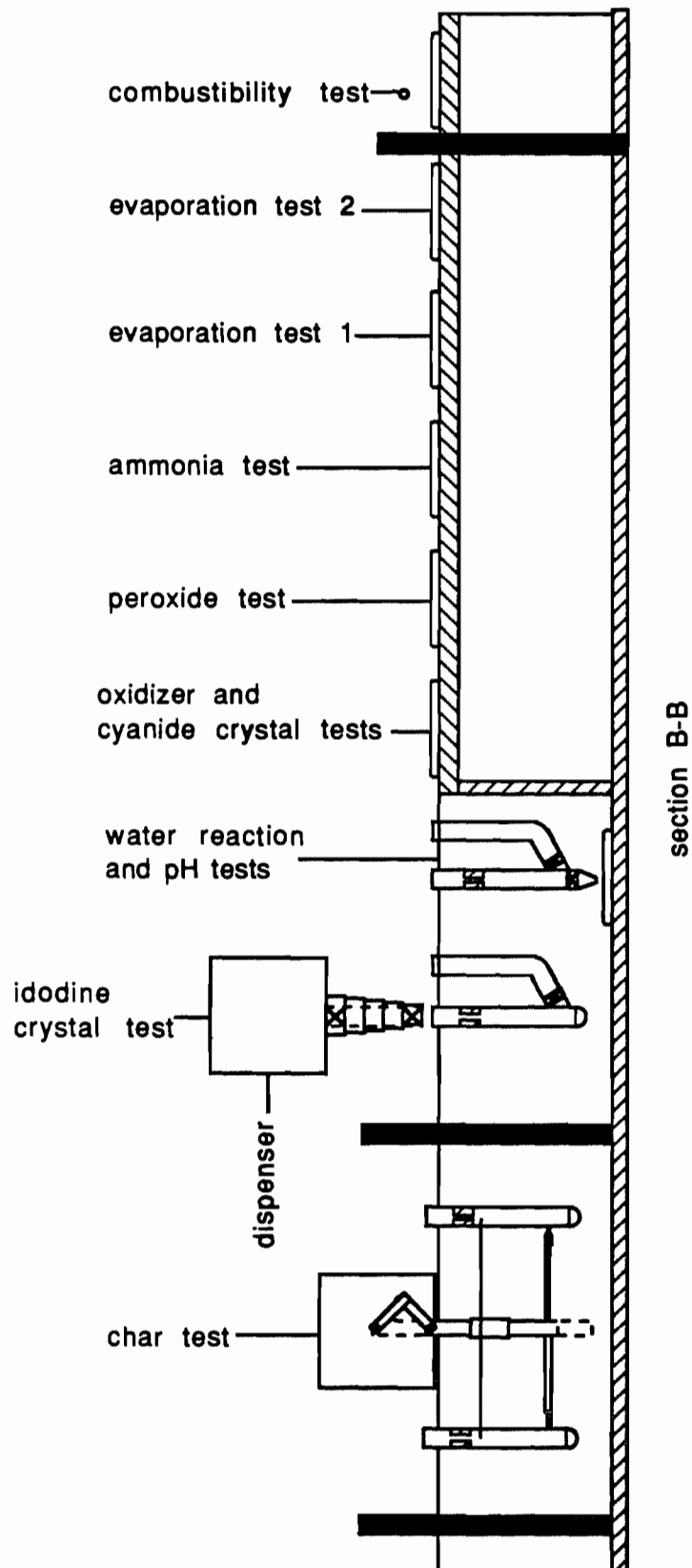


Figure 3b. Subset 1 THL Conceptual Design, Side View

would have to complete the analysis manually (after suiting up in protective gear). In this case, the THL would provide some safety benefits (tests with a high risk of flame or explosion are still carried out remotely), but little or no reduction in identification time. Based on the limited HazCat and HeinzCat knowledge obtained in this research, and on knowledge of spill frequencies, this scenario does not seem very likely. However, it will occur, so response teams using the Subset 1 THL will have to be prepared to carry out manual HazCat analysis as well.

4.1.3 Subset 2

The major components that add cost and complexity to the Subset 1 THL are the heat/flame source required for the char/ignition and combustibility tests and the detector tubes and pump used to supplement the char/ignition tests. Questionnaire responses from Caltrans personnel indicate that the char/ignition test is not considered to be as useful as the other tests included on the Subset 1 THL. The combustibility test is considered to be very important. However, much of the information obtained through this test (that is, the combustible nature of the vapor over an unknown) could safely be obtained through a combustibility meter mounted on the THL.

If the use of a THV-mounted combustibility meter provides sufficient information to forego the THL combustibility test, and if the char/ignition test can be eliminated, the resulting Subset 2 THL would be very inexpensive; less than \$500 if the most straightforward methods for each of the remaining tests were implemented. It would require only two actuators: dispenser rotation and water reaction agitation. A single valve would be required to dispense the unknown. If the Subset 2 THL were viewed as disposable if contaminated, the cost could be reduced even more.

The Subset 2 THL would contain the following tests: evaporation, water reaction, oxidizer, peroxide, pH, ammonia, cyanide, iodine crystal. It would be intended for use only with a combustible gas meter (mounted on the THV). Further work with the developers of field chemistry systems such as HazCat or HeinzCat would be required to (1) determine the feasibility of carrying out a hazard determination without the char/ignition test, and (2) modify the sequence of testing to reflect the absence of the char/ignition test. For example, the current HazCat system identifies gasoline and diesel (fuels) by the following series of tests and results: no or slow evaporation, negative oxidizer test, no rotten egg odor, floats in water solubility test, flammable in combustibility test, purple in iodine crystal test. If the use of a combustibility meter and a toxic gas meter on the THV eliminated the need for the combustibility test and "rotten egg" smell detection, the Subset 2 THL could be used to carry out the remainder of the identification process.

4.1.4 THL Mock-Up

To provide a more tangible sense of the portability of the THL, a mock-up of the configuration for the Subsets 1 and 2 THL was constructed. The mock-up shows the proposed layout for the THL, and includes the actuators and valves required for the Subset 2 configuration. Figure 4a shows the THL mock-up and control panel. Figure 4b shows a top view of the THL mock-up. The mock-up is powered by two 12-volt batteries.

An inexpensive model railway turntable (\$50) is used for dispenser rotation. The turntable is geared so that it pauses at each of 10 positions. This greatly simplifies the position control strategy; the operator holds the turntable forward/reverse switch in the

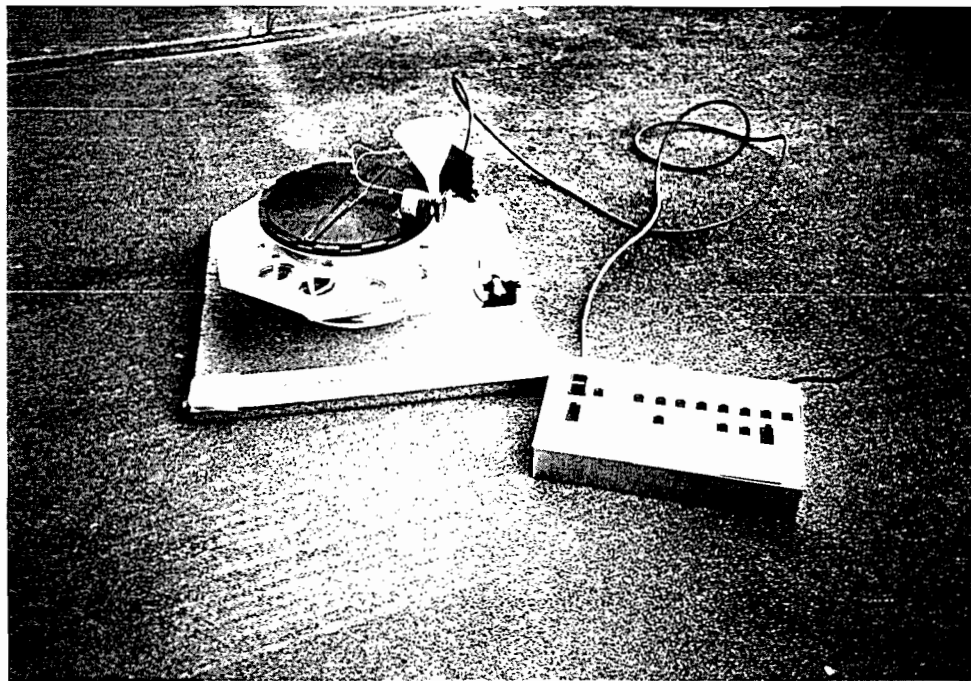


Figure 4a. THL Mock-Up, Lab and Control Panel

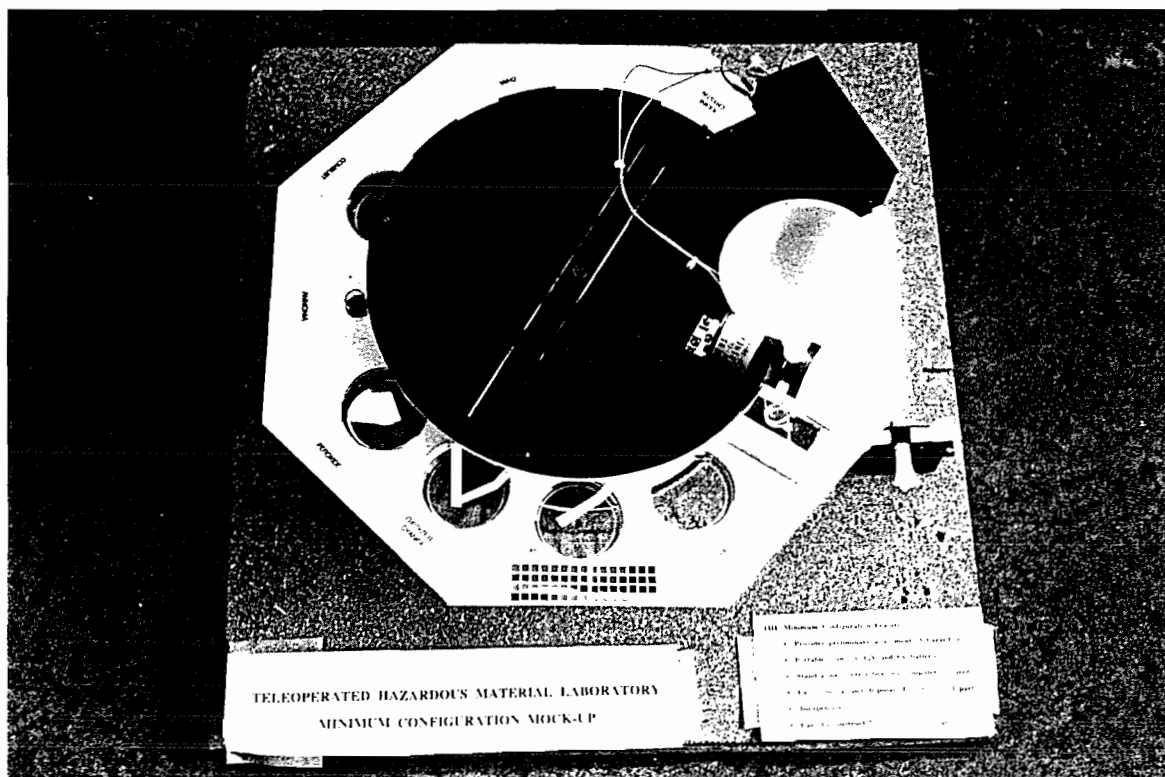


Figure 4b. THL Mock-Up, Top View of Lab



Figure 4c. THL Mock-Up, Dispenser

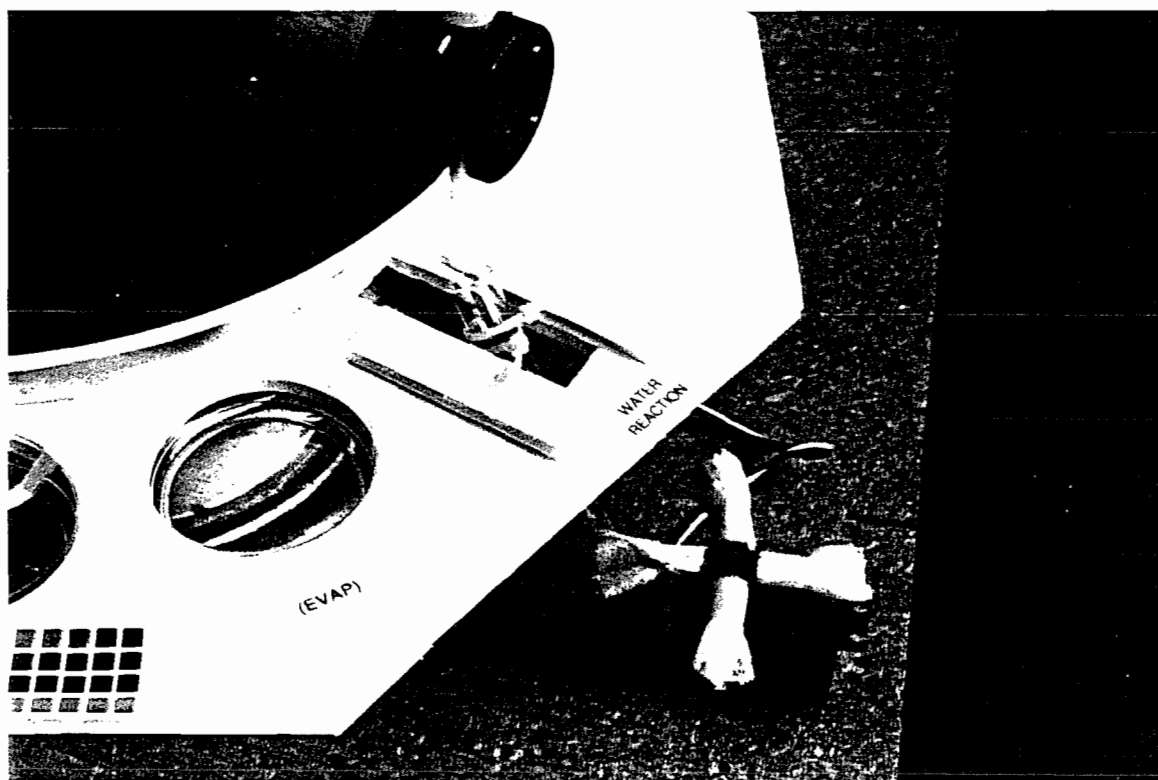


Figure 4d. THL Mock-Up, Agitator

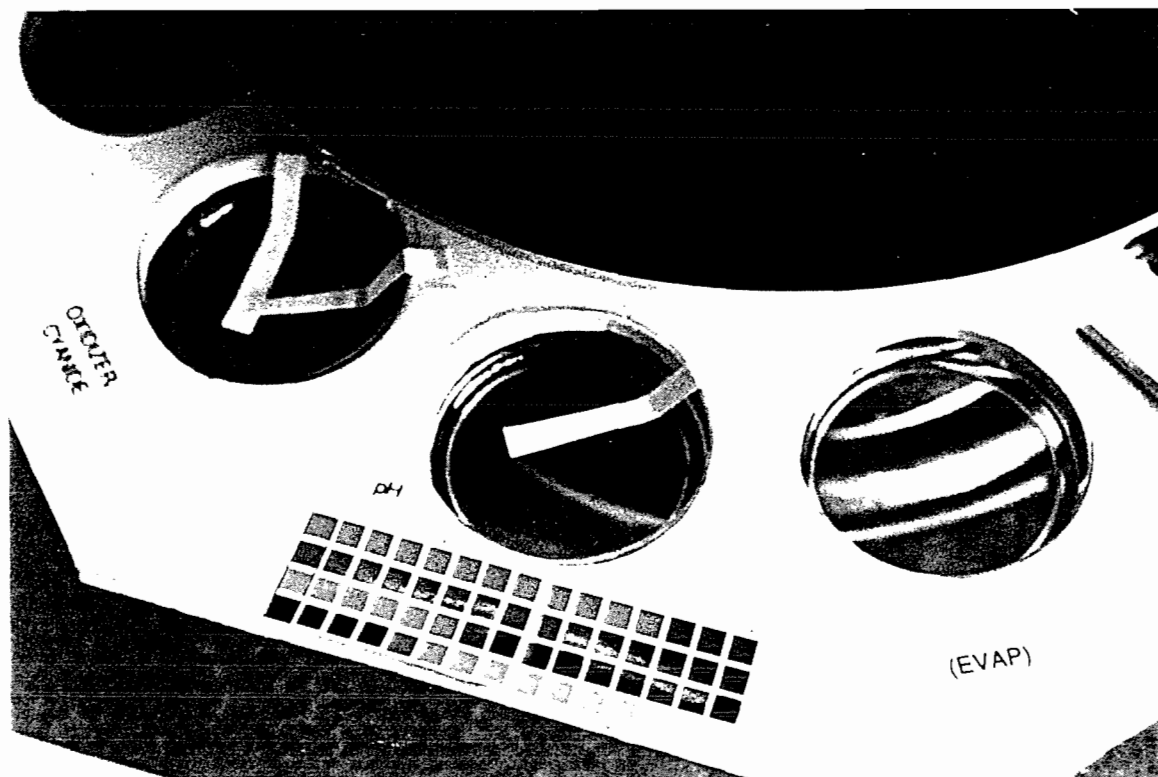


Figure 4e. THL Mock-Up, Platen with Watch Dishes

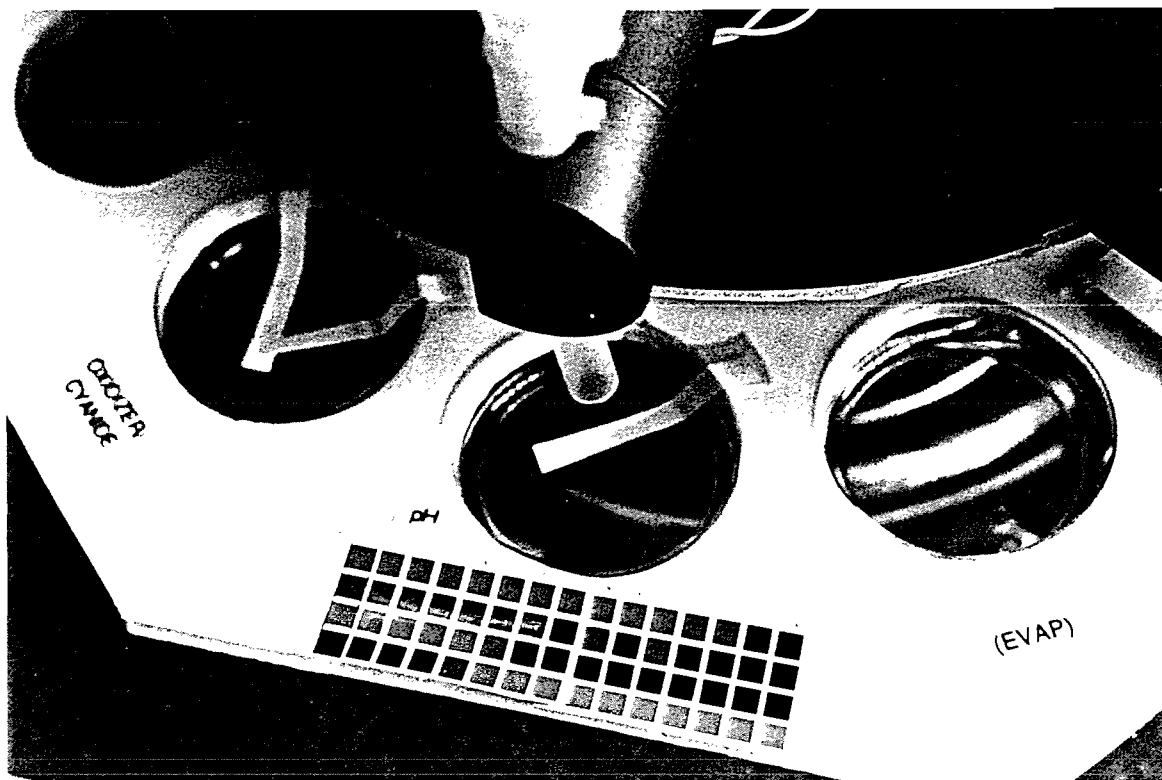


Figure 4f. THL Mock-Up, Dispenser over pH Watch Dish

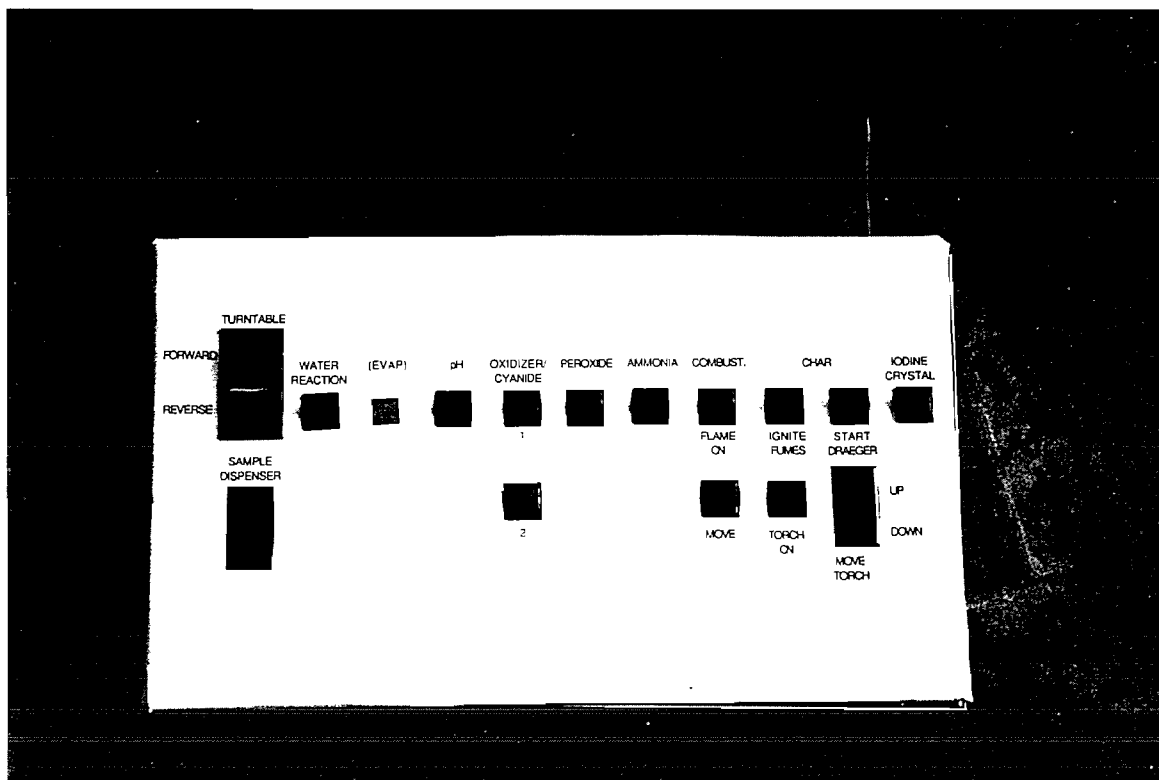


Figure 4g. THL Mock-Up, Control Panel

appropriate position until the desired test station (usually the next station) is reached, then releases the switch during the built-in pause. The dispenser consists of a funnel mounted above a pinch valve, which allows liquids, powders, and small diameter solids to be dispensed. Only the funnel and replaceable tube come into contact with the unknown. The dispenser is shown in Figure 4c. Figure 4d shows the agitator for the water reaction test, a modified steering actuator from a model race car (approximately \$30). Its "blades" are padded and positioned so that it gently bumps the test tube containing water and the unknown.

In the mock-up, the test platen is constructed of foam core board. This allows watch dishes and test tubes to be "press fit" into holes, with no other attachment required. For a disposable model of the THL, this approach would be sufficient. Even in a "field hardened" version, a disposal foam-core test platen is a worthy idea. Only the platen, with its watch glasses and test tube, and the dispenser tube and funnel would need to be replaced to clean the THL. The more costly actuators never come into contact with the unknown.

Watch dishes for the evaporation, pH, and oxidizer/cyanide tests are shown in Figure 4e. Test papers are preloaded into the watch dishes (and secured to the test platten). Where appropriate, color keys are mounted near the watch dish. Figure 4f shows the dispenser in position over the pH test watch dish.

The control panel for the mock-up, Figure 4g contains the controls that would be required for the Subset 1 version of the THL, which includes the char/ignition and combustibility tests. The control panel for the Subset 2 version would be even more compact.

The mock-up shows that it is feasible to construct and operate a portable THL. Little additional effort would be required to implement a field version of the Subset 2 THL. Additional design work would be required for the Subset 1 THL.

4.2 Testblock Identification System (T-ID)

The THL mock-up was displayed at the 1994 AHMCT Technology Fair. A comment and sketch from a Caltrans hazmat specialist (Manuel Miranda) motivated the development of a second conceptual approach, the Testblock Identification System (T-ID). Figure 5 shows a conceptual sketch of the T-ID. The T-ID would carry out only field chemistry tests that required no moving parts. It would consist of a three main components: upper and lower halves of a transparent plastic testblock with an interior test cell for each test, and a control strip. Reagents and/or test papers would be preloaded into the lower half of the test cell. The control strip would be placed over the lower half of cell. The top half of the test cell would be screwed or clamped to the lower half, sandwiching the control strip within the test cell.

The test cell would be placed in an area accessible to the THV, bolted to a reaction frame. The control strip would be extended to the operator in a safe area. The THV would deposit the unknown in a well on the top half of the test strip, and the unknown would flow into the upper half of each of the test cells (solid unknowns would require a more sophisticated delivery system). The operator would pull the test strip (or turn on a motor mounted on the T-ID block that would pull the test strip), allowing the unknown to fall into the bottom left-most test cell. After observing the reaction (remotely, using the THV's video camera), the operator would pull the test strip again (or again turn on the control strip

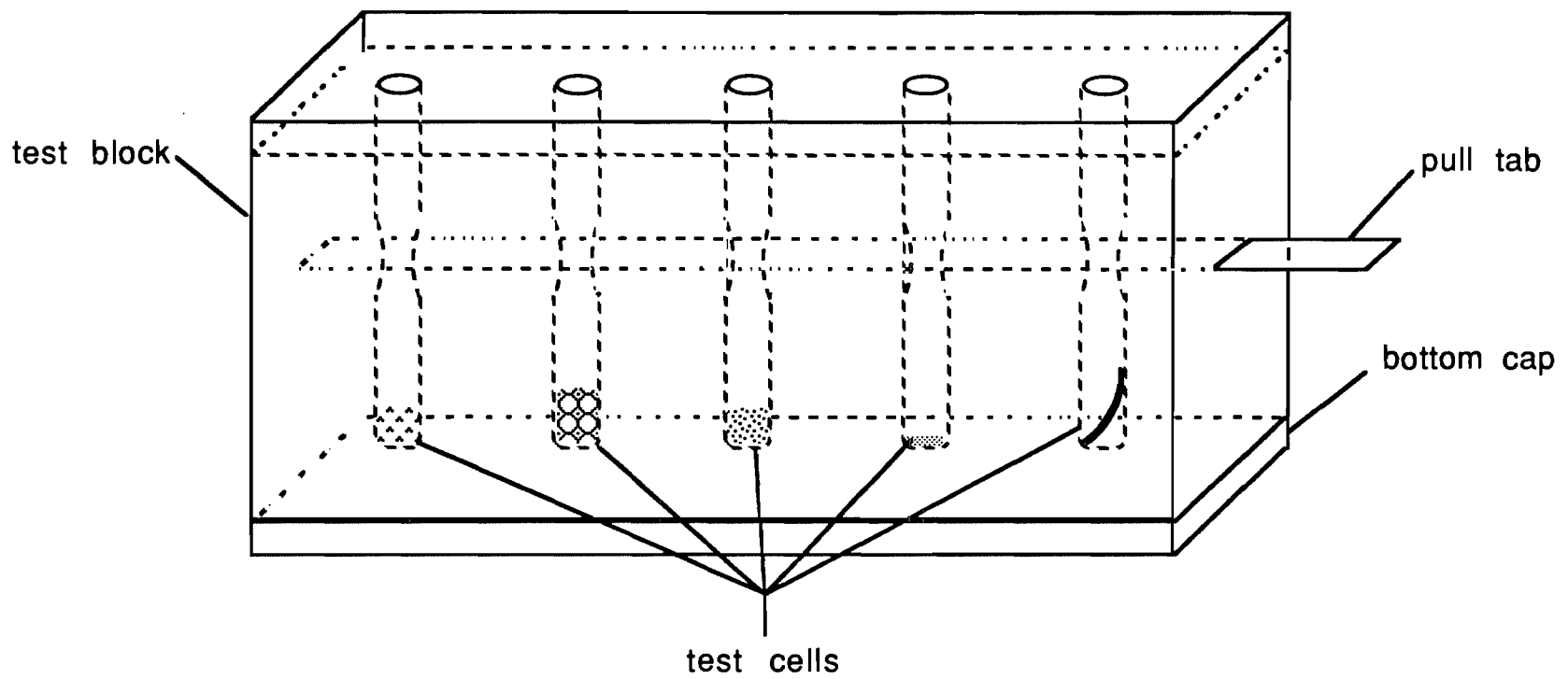


Figure 5. Testblock-ID Conceptual Design

winding motor), and allow the sample to fall into the bottom of the next test cell. The same procedure would be followed to complete all necessary tests.

The T-ID is straightforward to implement, requiring at most one actuator (the control strip winding motor). Once a suitable material for the test block is found, manufacturing costs should be small. The T-ID will be inexpensive enough (certainly under \$100 and probably under \$50) to be disposable. However, the ultimate usefulness of this configuration depends on whether hazard class and clean-up strategy can be determined from tests that require no heat source and no motion (stirring). Further consultation with developers of field chemistry systems will be required before the benefits of the T-ID as an identification tool can be determined.

4.3 Test Strips

The T-ID will be both small enough and inexpensive enough that it could be provided to every first responder (CHP or Caltrans). However, use of the T-ID still requires the availability of the THV or some other means of obtaining a sample and remotely viewing the test cells. But the size and cost of the THV are such that it will be used by Hazmat Specialists in each district, and will not be available to each Caltrans or CHP vehicle.

Improved identification can significantly decrease overall spill response time only if the first responder can carry out identification of at least the most commonly spilled materials. It would be desirable to have a system that would allow first responders to identify at least diesel, gasoline, and motor oil. Such a system would have to be deployable and readable from a distance without risk of ignition or explosion. In the current HazCat system, fuels are identified by a series of tests and results: no or slow evaporation, negative oxidizer test, no rotten egg odor, floats in water solubility test, flammable in combustibility test, purple in iodine crystal test. Determining whether these tests could be combined into a single "test strip" similar to pH paper is beyond the scope of this project. However, if the chemistry for such a test strip could be worked out, there are several promising concepts for delivery: foam that is sprayed from a distance and changes color upon contact with the unknown, bubbles that could be blown onto the spill and change color upon contact with the unknown, long rolls of test paper that are rolled on to the spill and change color upon contact with the unknown, a paper airplane that glides on to the site and changes color upon contact with the unknown, "dandelion" seed delivery systems that float onto the unknown and change color. Further work on these concepts should not be undertaken until the feasibility of a test strip to identify fuels and oils is determined.

4.4 Automated Hazmat Laboratory

The final approach to increased automation in the identification of unknown spills is based not on existing field chemistry systems, but on existing analytical laboratory equipment. This equipment has been developed under goals and constraints that are very different from the spill response scenario: the need to detect very small concentrations of specific substances, the need to determine the precise composition of an unknown, and the availability of space and power in a laboratory environment. It is possible that the underlying technology in existing analytical equipment could be modified to address spill identification needs, and that the resulting equipment would be less costly than currently available laboratory models. The goal would be a portable automated hazmat laboratory (AHL), which would carry out identification on site.

There are two approaches that could be taken to the AHL. The first is to assume that the system will have a highly trained operator. In this case, the operator would understand the identification technologies used by the AHL, and could carry out interpretation of the results. The second approach assumes the operator has received First Responder Operations level training only. In this case, the AHL must function as a "black box"; the THV inserts a sample, the analysis is carried out and interpreted by software resident in the AHL, and the AHL returns the hazard class (and perhaps more detailed information on the composition of the unknown). Based on the limited percent of spills for which Caltrans carried out identification, the latter approach is more appropriate for Caltrans use. However, for local health agencies and clean up contractors, it may be reasonable to assume a trained operator will be available to interpret the results.

Under either approach, the AHL should be portable and self contained. It should weigh no more than 80 pounds, be able to be easily loaded and unloaded from a pickup truck or van, and be powered by a portable battery pack.

Either approach is likely to yield a system that is at least at the top of and probably higher than the \$5000- \$10,000 price range at which questionnaire respondents felt the AHL would be useful under current procedures. It is possible that the AHL would be valuable even at a higher price tag to local health agencies and clean up contractors.

4.5 Conceptual Design Analysis

The four concepts and their variations presented above span a wide range of cost and capability. A summary and evaluation of each approach is provided below, including additional research required, anticipated cost of resulting system, and recommendations for further action.

Full System THL

Description: Remotely controlled implementation of full HazCat system; assumes use of THV to obtain sample of unknown.

Additional chemistry r&d: Review of HazCat system with remotely controlled testing in mind.

Additional equipment r&d: Significant design effort required to modify auxiliary equipment.

Anticipated cost: \$5000-\$10,000 (probably higher end of range)

Comments: Will not reduce response time significantly. Too complex, too costly for the functions it provides.

Recommendation: Do not pursue.

Subset 1 THL

Description: Remotely controlled implementation of selected field chemistry tests (screen tests plus selected definitive tests); assumes use of THV to obtain sample of unknown and provide visual feedback during use.

Additional chemistry r&d: Review of selected tests to determine usefulness in assessing hazard level and modifications that facilitate remote control.

Additional equipment r&d: Several design issues must be resolved, including use of open flame and mechanism for inserting/ejecting detectors tubes out/of pump.

Anticipated cost: \$5000 or less

Comments: May reduce identification time by 5-10 minutes. May not yield sufficient information for some substances, so response team must still be capable of carrying out analysis by hand.

Recommendation: May be worthwhile for the few districts where Caltrans carries out significant identification; discuss further with those districts.

Subset 2 THL

Description: Remotely controlled implementation of selected field chemistry tests; assumes use of THV to obtain sample of unknown and provide visual feedback during use.

Additional chemistry r&d: Review of selected tests to determine usefulness in assessing hazard level and modifications that facilitate remote control.

Additional equipment r&d: Minimal effort required to move from mock-up to field prototype.

Anticipated cost: \$500

Comments: May reduce identification time by 5-10 minutes. May not yield sufficient information for some substances, so response team must still be capable of carrying out analysis by hand.

Recommendation: If tests included allow clean up strategy to be selected for most substances, worthwhile for the few districts where Caltrans carries out significant identification and perhaps for other districts. Review capabilities of selected tests with developers of field chemistry systems.

Testblock-ID

Description: Self-contained block of test cells preloaded with reagents; assumes use of THV to obtain sample of unknown and provide visual feedback during use.

Additional chemistry r&d: Determine subset of tests that can be carried out merely by placing unknown and reagent in same space (no stirring or heating required). Determine usefulness in assessing hazard level.

Additional equipment r&d: Minimal. Must select material that is transparent and resistant to most substances.

Anticipated cost: \$50-\$100

Comments: May reduce identification time by 5-10 minutes. May not yield sufficient information for some substances, so response team must still be capable of carrying out analysis by hand. To provide safety benefits, should be used with THV. However, may also be of use when sample obtained manually.

Recommendation: Work with field chemistry system developers to identify candidate tests and assess usefulness of these tests in determining hazard class and response strategy. If a suitable subset of tests exists, this approach would be useful for all Caltrans districts.

Test strips

Description: Test papers or foam/liquid equivalents that change color when placed in contact with frequently spilled substances (e.g. diesel fuel, gasoline, motor oil), and delivery systems that allow deployment without human exposure to unknown; would be issued to all Caltrans and CHP personnel.

Additional chemistry r&d: Significant research required to develop test strip materials.

Additional equipment r&d: Significant research required to develop delivery systems compatible with test strip materials

Anticipated cost: \$50 or less

Comments: Potential to allow identification of frequently spilled substances by first responder on scene, significantly reducing road closure time. Would be of use to all Caltrans and CHP personnel in the field. Significant uncertainty in feasibility of developing test strip materials.

Recommendation: Pursue low cost means of identifying test strip materials or promoting their development, for example, queries or articles in trade magazines such as Sensors or R&D.

AHL

Description: Fully automated laboratory capable of determining at least hazard class and possibly more detailed information on composition of unknown.

Additional chemistry r&d: Significant research required.

Additional equipment r&d: Significant research required.

Anticipated cost: Over \$10,000

Comments: If such a system existed, it might be useful for the few districts that regularly carry out identification.

Recommendation: Pursue low cost means of identifying relevant research and promoting development of usable hardware, for example, queries or articles in trade magazines such as Sensors or R&D.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

Unknown spills represent a small portion of all highway spills. In recent years, the number of unknown spills has decreased. Even so, safety concerns and the high cost of road closures warrant improvement of the identification phase of spill response.

Although Caltrans or the CHP are typically the first responders to arrive at the scene of a spill, identification is most often carried out by local health agencies or contractors using field chemistry systems. Only a few Caltrans districts carry out identification on a regular basis. If improved identification methods existed, it is possible that some Caltrans districts would do more identification in-house.

Under current practice, Caltrans Hazmat Specialists see remotely controlled or automated approaches to the identification of unknowns as useful to their districts, but only if the cost is relatively low (up to \$5000 for a remotely controlled system, \$5000-\$10,000 for a fully automated system). Systems that would carry out subsets of field chemistry systems were viewed as potentially useful. Systems that go beyond field chemistry systems to provide quantitative analysis were not viewed as useful to Caltrans.

Four approaches to improved identification (and several variations of one approach) were presented in this report. The Subset 1 THL, Subset 2 THL, and Testblock-ID systems warrant further investigation by Caltrans, starting with input from the developers of field chemistry systems. Test strips and the AHL are promising ideas, but require too great an R&D investment to be carried out by Caltrans. Instead, Caltrans should pursue low cost means of motivating others to work on these approaches. The Full System THL would be too costly for the functions provided, and should not be investigated further.

Based on the research described in this report, it is recommended that Caltrans

- Meet with the developers of field chemistry systems (HazCat and HeinzCat) to (1) determine the usefulness of subsets of the systems in assessing hazard class and (2) identify modifications in the test procedures that would facilitate automation. In particular, the tests proposed for the Subsets 1 and 2 THL and the test that would be feasible with the Testblock-ID approach should be reviewed.
- Pursue low cost means of promoting the development of the test strip and AHL approaches. This includes submitting articles and queries on unknown highway spills to relevant trade magazines such as Sensors and R&D Magazine, and perhaps organizing a workshop to bring together the developers of field chemistry systems, analytical laboratory equipment, and others involved in identifying unknown spills (local health agencies, fire departments, contractors, in-house industry response teams).
- Review the frequency and impact of unknown spills to determine the cost in terms of (1) risk to health and safety of responders, (2) direct costs of identification efforts, (3) cost to society of road closures.

REFERENCES

DOT. See United States Department of Transportation.

Hazardous-Materials Robot, 1995. *NASA Tech Briefs*, March, pp 42,44.

Hoff, P. and Critchlow, A., 1992. *Automated Hazardous Spill Pick-Up, Draft Report to Caltrans*, 1992.

Internet 1995a. Internet document http://www-ahmct.engr.ucdavis.edu/ahmct/AHMCT_projects/hvehicle.html, August 16, 1995.

Internet 1995b. Internet document <http://robotics.jpl.nasa.gov/./tasks/hazbot/homepage.html>, August 10, 1995.

Internet 1995c. Internet document http://eclipse.esa.lanl.gov/CAA/tech_briefs.html, August 10, 1995

Masters, G.M., 1991. *Introduction to Environmental Engineering and Science*, Prentice-Hall, Englewood Cliffs, NJ.

National Cooperative Highway Research Program, 1994. *Highway Maintenance Procedures Dealing with Hazardous Materials Incidents*, NCHRP Synthesis 196, Transportation Research Board.

NCHRP. See National Cooperative Highway Research Program.

OES. See Office of Emergency Services.

Office of Emergency Services, 1989. *Hazardous Material Incidents, California, January-December 1988*, Office of Emergency Services, California, December 1989.

United States Department of Transportation, 1988. *Annual Report on Hazardous Materials Transportation, Calendar Year 1988*.

United States Department of Transportation, 1990. *1990 Emergency Response Guidebook*. Research and Special Programs Administration.

Welch, R.V., 1994. A Mobile Robot for Remote Response to Incidents Involving Hazardous Materials, *Proceedings of the ASCE Specialty Conference on Robotics for Challenging Environments*, Feb./March 1994.

Richard V. Welch

Wentz, C.A, 1989. *Hazardous Waste Management*, McGraw Hill, New York.

APPENDIX A
QUESTIONNAIRE

**Identification of Unknown Spills:
Survey of Caltrans' Needs**

This survey is a follow-up to the presentation on the RLAB project by Laura Demsetz at the Hazardous Material Coordinators meeting on November 4. The RLAB project is investigating a range of technologies to aid in the identification of unknown spills. We are currently designing a portable lab that allows screen tests to be controlled remotely. In addition, we are developing a "wish list" of specifications for an automated testing system based technologies currently used in the laboratory. To ensure that the results of this project are of use to Caltrans, we hope you will take a few minutes to complete this survey. Further comments on this project are welcome at any time; contact Laura Demsetz (phone: 510 642-1927; fax: 510 643-5264). The survey is self addressed; after completing it, please fold and staple. Thank you for your time.

Your name (optional): _____

Your position (optional): _____

Your district (optional): _____

Please use the space below for any additional comments you have after completing the survey.

I. CURRENT PRACTICE

Who is typically first to arrive at the scene of a spill?

Who typically carries out the on-site identification of an unknown?

How long after the spill is reported does this person arrive at the scene?

What method is used for on-site identification (e.g. HazCat, HeinzCat, etc.)

How long does the on-site identification take?

What is the end result of the on-site identification (e.g. specific chemical composition, chemical group, class of unknown, hazard level, etc.)

For what percent of unknowns is off-site lab analysis required prior to clean up?

Who carries out clean-up?

How long after the spill is reported does this person arrive at the scene?

How long does the clean-up take?

What is Caltrans' role in identification and clean-up in your district?

What are the most frequently spilled substances in your district? How often are these substances "unknown" at the time of the spill?

What percent of the spills in your district are of a sludge rather than a pure compound?

Additional comments on current practice (good points, bad points, problems):

II. SCREEN TESTS

In our current design, the RLAB does not attempt to carry out a definitive analysis. Rather, it allows a group of screen tests to be carried out remotely. The information from these screen tests should be of use in planning spill response.

Please indicate the importance of each of these tests in determining spill response:

Mounted on next generation ROV:

	not important	0	1	2	3	very important
radiation meter		0	1	2	3	
organic and inorganic gas meters		0	1	2	3	
combustibility meter		0	1	2	3	
pH meter		0	1	2	3	

Included in RLAB:

	not important	0	1	2	3	very important
evaporation test		0	1	2	3	
combustibility test		0	1	2	3	
oxidizer test		0	1	2	3	
peroxide test		0	1	2	3	
water reaction test		0	1	2	3	
pH test		0	1	2	3	
char/ignition test		0	1	2	3	
iodine crystal test (gasoline, oil, diesel)		0	1	2	3	
ammonia test		0	1	2	3	
cyanide test		0	1	2	3	

If a portable, lightweight device that could carry out all of these tests (evaporation, combustibility, oxidizer peroxide, water reaction, pH, charring, iodine crystal, ammonia, cyanide) were available in the price ranges listed below, would it be useful to your district? If your response is a 0 or 1, please indicate why this device wouldn't be useful (e.g. too expensive, don't need tests, liability issues, etc.)

Price range	Usefulness				Comments
	not useful	0	1	2	3 very useful
\$500 - \$1000		0	1	2	3
\$1000 - \$5000		0	1	2	3
\$5000 - \$10,000		0	1	2	3
\$10,000 - \$20,000		0	1	2	3

Tests for the following substances were suggested in the November 4th meeting. Please indicate the importance of each, and add any additional tests you would like to see on the RLAB:

	not important	0	1	2	3	very important
Test for cement		0	1	2	3	
Test for fertilizer		0	1	2	3	
Test for lime		0	1	2	3	
Test for arsenic		0	1	2	3	
Test for sulphur		0	1	2	3	
Test for asbestos		0	1	2	3	
Test for pesticides		0	1	2	3	
		0	1	2	3	
		0	1	2	3	
		0	1	2	3	
		0	1	2	3	
		0	1	2	3	

III Automated Testing Technology

It may be possible to modify analytical laboratory equipment for use in the field. The resulting Automated Testing Technology (ATT) would either be used in combination with the RLAB or in a stand-alone application. The ATT system could perhaps be precalibrated for a specific district to allow substances that are frequently spilled in that district to be identified more quickly.

What substances would you want such a system to be precalibrated for in your district?

If a portable ATT system capable of duplicating the results of a HasCat analysis existed in the price ranges listed below, would it be useful to your district? If your response is a 0 or 1, please indicate why this device wouldn't be useful (e.g. too expensive, don't need tests, liability issues, etc.).

Price range	Usefulness				Comments
	not useful	0	1	2	3 very useful
\$5000 - \$10,000		0	1	2	3
\$10,000 - \$15,000		0	1	2	3
\$15,000 - \$25,000		0	1	2	3
\$25,000 - \$50,000		0	1	2	3
\$50,000 - \$75,000		0	1	2	3

If a portable ATT system existed that was capable of carrying out a qualitative analysis (i.e. results indicate chemicals are in substance, but not how much of each), would it be useful to your district? If your response is a 0 or 1, please indicate why this device wouldn't be useful (e.g. too expensive, don't need tests, liability issues, etc.).

Price range	Usefulness				Comments
	not useful	0	1	2 3 very useful	
\$5000 - \$10,000	0	1	2	3	
\$10,000 - \$15,000	0	1	2	3	
\$15,000 - \$25,000	0	1	2	3	
\$25,000 - \$50,000	0	1	2	3	
\$50,000 - \$75,000	0	1	2	3	

If a portable ATT system existed that could carry out a quantitative analysis (i.e. results indicate what chemicals are present and how much of them is present), would it be useful to your district? If your response is a 0 or 1, please indicate why this device wouldn't be useful (e.g. too expensive, don't need tests, liability issues, etc.).

Price range	Usefulness				Comments
	not useful	0	1	2 3 very useful	
\$5000 - \$10,000	0	1	2	3	
\$10,000 - \$15,000	0	1	2	3	
\$15,000 - \$25,000	0	1	2	3	
\$25,000 - \$50,000	0	1	2	3	
\$50,000 - \$75,000	0	1	2	3	

APPENDIX B
QUESTIONNAIRE RESULTS

**Identification of Unknown Spills:
Survey of Caltrans' Needs**

This survey is a follow-up to the presentation on the RLAB project by Laura Demsetz at the Hazardous Material Coordinators meeting on November 4. The RLAB project is investigating a range of technologies to aid in the identification of unknown spills. We are currently designing a portable lab that allows screen tests to be controlled remotely. In addition, we are developing a "wish list" of specifications for an automated testing system based technologies currently used in the laboratory. To ensure that the results of this project are of use to Caltrans, we hope you will take a few minutes to complete this survey. Further comments on this project are welcome at any time; contact Laura Demsetz (phone: 510 642-1927; fax: 510 643-5264). The survey is self addressed; after completing it, please fold and staple. Thank you for your time.

Your name (optional): _____

Your position (optional): _____

Your district (optional): 11, 5, 1, 9, 12, 4, 10, 6, 3, 2

Please use the space below for any additional comments you have after completing the survey.

district 9 - strong support for project;

if it worked it would be great, but would have to be cheaper than current method; these things tend to get expensive - ask Mimi)

1. CURRENT PRACTICE

Who is typically first to arrive at the scene of a spill?

*closest supervisor
highway maintenance supervisor or superintendent
field personnel
caltrans supervisor
chp
caltrans, chp, fire
maintenance supervisor or superintendent
highway patrol or caltrans personnel
for caltrans, the FRO trained super or supt
caltrans maintenance worker or caltrans highway worker*

Who typically carries out the on-site identification of an unknown?

*local county health dept. hazmat team
local county health inspector or fire dept. hazmat team
district hazmat manager
district hazardous materials specialist via a contractor
spill clean-up contractor
fire, health, contractor
county health or OES if available; if not, we call a spill contractor
designated contractor
a prequalified clean-up contractor
caltrans district 2 spill team or a spill contractor*

How long after the spill is reported does this person arrive at the scene?

*0.5 to 1.5 hours
0.5 to 1.0 hours
sometimes 4+ hours
1-4 hours
1 hour
fire-fast; health- medium; contractor-slow
various, say 1 hour
1-2 hours
2-3 hours
caltrans - 1-2 hours
contractor 4-9 hours*

What method is used for on-site identification (e.g. HazCat, HeinzCat, etc.)

*hazcat (5)
heinzcat
hazcat through a contractor
both
haz-cat for most spills
heinzcat -1- hazcat -2*

How long does the on-site identification take?

15-30 minutes

15-20 minutes

30+ minutes

1 hour

1/2 - 1 hour (2)

10 minutes

1/2 hour

10-15 minutes

1-2 hours including suit up

What is the end result of the on-site identification (e.g. specific chemical composition, chemical group,

class of unknown, hazard level, etc.)

general hazard level

specific chemical group

hazard category

categorization of unknown (flammable, corrosive, etc)

hazardous waste manifest and other reports completed; contractor removes spilled material

depends on what it is

if any doubt we call a contractor to clean up the spill

chemical group and hazard level

chemical group and class

pH, chemical group, hazard class, specific composition

For what percent of unknowns is off-site lab analysis required prior to clean up?

1-5%

0% (2)

<10%

2%

none (2)

very few

pchs on pavement 5%

normally none, confirmation of unknowns maybe 5%

Who carries out clean-up?

spiller, caltrans, contractor

state contractor or contractor hired by spiller

caltrans crews and contractors

contractors

spill contractor

fire, contractor, caltrans

if not hazardous, caltrans; if hazardous, spill contractor

designated contractor

caltrans oversees, contractor on big spills, small spills of TPB we clean up in-house

small cleanups - caltrans, large cleanups - contractor

How long after the spill is reported does this person arrive at the scene?

0.5 - 2 hours

1-2 hours (3)

caltrans: 1/2-1 hour; contractor 4-12 hours

1 - 6 hours

1 hour

(no answer)

2 hours

avg 4-6 hours, some up to 48 hours

caltrans: 1/2 - 2- hours; contractor: 4-9 hours

How long does the clean-up take?

1-4 hours

1 hour - several days

1-6 hours

1 -4 hours

1 or more hours

20 minutes - 12 hours

1/2 hour - weeks

depends on size, an overturned truck approx 6 hours

1/2 hour to several hours to several days

What is Caltrans' role in identification and clean-up in your district?

basic container, label, shipping papers, placards, MSDs

use local government agencies for identification and statewide contractors to do the clean up categorization& cleanup if < 50 gal where caltrans has code of safe operations for spilled material

isolate, make notifications, administrate contract, assure compliance

call out spill contractor

FRO - non has

responsible - we become the generator

initiates ID and cleanup through local contractors working with health dept. and other agencies

FRO/2 spec/spill contractors

district 2 team does ID and small cleanup depending on spill; contractor call for approx 70% of cleanups

What are the most frequently spilled substances in your district? How often are these substances

"unknown" at the time of the spill?

petroleum products (diesel) 70%, unknown 20%

liquids, 30% unknown

petroleum, <15%

fuels (diesel, gasoline), 90%

diesel fuel, various oils, etc., 10-15%

gas/diesel, 50%

diesel - not very often, usually truck is still on location of spill

diesel fuel, lime, cement; they are almost always known

diesel and oils, seldom

hydrocarbons, petroleum products, diesel 70% of the time - misc the rest - Roy Collins in HQ has specifics

What percent of the spills in your district are of a sludge rather than a pure compound?

20%

30%

20%

40%

25%

neither

5%

50%

90%

85% (once chemical hits the ground and mixes with dirt)

Additional comments on current practice (good points, bad points, problems):

all field employees now trained to FRA or FRO levels

some employees still want to remove caps and smell the products to confirm what they suspect it is

PPE not always available; contractor travel time >8 hours

saves resources (good point); roads could be closed and people and environment exposed for lengthy time

traffic congestion is a problem

over 400 spills/year, I don't have time to go out to each; other qualified non-ct people, but I'm only qualified ct

questions worded so that answers are only guesstimates

we usually achieve clean-up in a reasonably short time; good responses from all agencies

we use a portable robot to collect samples; would be great if robot could dig into the soil and make liquid

samples without starting a fire

II. SCREEN TESTS

In our current design, the RLAB does not attempt to carry out a definitive analysis. Rather, it allows a group of screen tests to be carried out remotely. The information from these screen tests should be of use in planning spill response.

Please indicate the importance of each of these tests in determining spill response:

Mounted on next generation ROV:

	not important	0	1	2	3	very important
radiation meter		0	1(4)	2(1)	3(4)	no answer (1)
organic and inorganic gas meters		0	1	2(2)	3(7)	no answer (1)
combustibility meter		0	1	2	3(10)	
pH meter		0	1(2)	2(2)	3(8)	

Included in RLAB:

	not important	0	1	2	3	very important
evaporation test		0(1)	1(3)	2(3)	3(3)	
combustibility test		0(1)	1	2	3(9)	
oxidizer test		0(1)	1	2(1)	3(8)	
peroxide test		0(1)	1(1)	2(1)	3(7)	
water reaction test		0(1)	1	2(3)	3(6)	
pH test		0(1)	1	2(1)	3(8)	
char/ignition test		0(1)	1	2(5)	3(4)	
iodine crystal test (gasoline, oil, diesel)		0(1)	1	2(3)	3(6)	
ammonia test		0(1)	1(1)	2(2)	3(6)	
cyanide test		0(1)	1(1)	2(1)	3(7)	

If a portable, lightweight device that could carry out all of these tests (evaporation, combustibility, oxidizer peroxide, water reaction, pH, char/ignition, iodine crystal, ammonia, cyanide) were available in the price ranges listed below, would it be useful to your district? If your response is a 0 or 1, please indicate why this device wouldn't be useful (e.g. too expensive, don't need tests, liability issues, etc.)

Price range	Usefulness				Comments
	not useful	0	1	2	3 very useful
					circled 3 at this level
\$500 - \$1000	0(1)	1	2(1)	3(7)	too expensive (1); don't need (1)
\$1000 - \$5000	0(1)	1	2(4)	3(4)	too expensive (1); don't need (1)
\$5000 - \$10,000	0(2)	1(3)	2	3(4)	too expensive (3)
\$10,000 - \$20,000	0(3)	1(2)	2(1)	3(3)	too expensive (3)
<i>would depend on what management wants - they want everything but don't want to pay for it</i>					

Tests for the following substances were suggested in the November 4th meeting. Please indicate the importance of each, and add any additional tests you would like to see on the RLAB:

	not important	0	1	2	3	very important
Test for cement	0	1(1)	2(3)	3(6)		
Test for fertilizer	0	1(1)	2(3)	3(6)		
Test for lime	0	1(1)	2(3)	3(6)		
Test for arsenic	0	1	2(5)	3(5)		
Test for sulphur	0	1(2)	2(3)	3(5)		
Test for asbestos	0	1(2)	2(3)	3(5)		
Test for pesticides	0	1	2(2)	3(7)		
<u>drug lab materials</u>	0	1	2	3(1)		
<u>mining materials</u>	0	1	2(1)	3		
<u>waste oil</u>	0	1	2	3(1)		
<u>waste antifreeze</u>	0	1	2	3(1)		
<u>chlorinated solvents</u>	0	1	2	3(1)		

(these are all normal spill materials; a quick test would be great)

III Automated Testing Technology

It may be possible to modify analytical laboratory equipment for use in the field. The resulting Automated Testing Technology (ATT) would either be used in combination with the RLAB or in a stand-alone application. The ATT system could perhaps be precalibrated for a specific district to allow substances that are frequently spilled in that district to be identified more quickly.

What substances would you want such a system to be precalibrated for in your district?
gasoline, diesel, asbestos, druglab materials, mining materials
as much as possible
gasoline, diesel, acids, chlorine
none
unknown
pesticides or poisons
all in previous list
diesel in soil; gasoline in soil; cement; fertilizer; sulfur; silicates; pesticides

If a portable ATT system capable of duplicating the results of a HazCat analysis existed in the price ranges listed below, would it be useful to your district? If your response is a 0 or 1, please indicate why this device wouldn't be useful (e.g. too expensive, don't need tests, liability issues, etc.).

Price range	Usefulness				Comments
	not useful	0	1	2	3 very useful
					(circled 2 at this level)
\$5000 - \$10,000	0(1)	1	2(1)	3(7)	cost (1); don't need (1)
\$10,000 - \$15,000	0(2)	1(1)	2(3)	3(3)	cost (2); don't need (1)
\$15,000 - \$25,000	0(3)	1(2)	2(1)	3(3)	cost (4); don't need (1)
\$25,000 - \$50,000	0(5)	1(1)	2	3(3)	cost (5); don't need (1)
\$50,000 - \$75,000	0(5)	1(1)	2	3(3)	cost (5); don't need (1)
<i>(we spend much more than this on analyzing by contractors, when we could do the analyzing ourselves and keep the roads open)</i>					
<i>(these are just my opinions; if keeping the road open is important they may also be management's opinions; I've been told interstate commerce on I-5 loses approx. \$1 million an hour when highway is closed)</i>					

If a portable ATT system existed that was capable of carrying out a qualitative analysis (i.e. results indicate chemicals are in substance, but not how much of each), would it be useful to your district? If your response is a 0 or 1, please indicate why this device wouldn't be useful (e.g. too expensive, don't need tests, liability issues, etc.).

Price range	Usefulness				Comments
	not useful	0	1	2	3 very useful
					circled 2 at this level
					circled 1 at this level (usually not important to us how much of a substance or chemical is contained in spilled material).
\$5000 - \$10,000	0(1)	1	2	3(6)	cost (1); don't need (1); no answer (1)
\$10,000 - \$15,000	0(1)	1(1)	2(1)	3(4)	cost (1); don't need (1); no answer (1)
\$15,000 - \$25,000	0(3)	1(1)	2(1)	3(3)	cost (4); don't need (1)
\$25,000 - \$50,000	0(4)	1(1)	2	3(3)	cost (5); don't need (1)
\$50,000 - \$75,000	0(4)	1(1)	2	3(3)	cost (5); don't need (1)

(again, management decision)

If a portable ATT system existed that could carry out a quantitative analysis (i.e. results indicate what chemicals are present and how much of them is present), would it be useful to your district? If your response is a 0 or 1, please indicate why this device wouldn't be useful (e.g. too expensive, don't need tests, liability issues, etc.).

Price range	Usefulness				Comments
	not useful	0	1	2	3 very useful
no answer to this question (1)					
\$5000 - \$10,000	0(2)	1	2	3(6)	still need lab certificationfor disposal (1) too expensive (1); don't need (1)
\$10,000 - \$15,000	0(2)	1(1)	2	3(5)	still need lab certificationfor disposal (1) too expensive (1); don't need (1)
\$15,000 - \$25,000	0(3)	1	2(2)	3(3)	too expensive (2); don't need (1) still need lab certificationfor disposal (1)
\$25,000 - \$50,000	0(4)	1(1)	2	3(3)	too expensive (4); don't need (1) still need lab certificationfor disposal (1)
\$50,000 - \$75,000	0(4)	1(1)	2	3(3)	too expensive (4); don't need (1) still need lab certificationfor disposal (1)