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DEVELOPMENT OF CONTINUOUS ISOCYANATES MONITOR

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For Evaluation Purposes by or on Behalf of HHS

EXECUTIVE SUMMARY

This is the Final Report of the SBIR Phase I project entitled "**Development of a Continuous Isocyanates Monitor**", funded under **Grant No. 1 R43 OH02913-01**. This report constitutes the sole deliverable product of the Phase I effort.

The primary objective of the Phase I laboratory program was to demonstrate the technical feasibility of an innovative chemiluminescent technique for the selective detection of isocyanate species in air at levels as low as 0.02 parts per million (ppm).

The proposed analysis technique is based on the generation of a reactive stream of oxygen atoms (by plasma excitation of air or oxygen feed gas) which is then combined with the air stream being sampled to produce activated CNO species from any isocyanates present in the air. The activated CNO species then decay to ground state species with the emission of light (chemiluminescent deactivation) and the light is detected and quantified as a measure of the amount of isocyanate in the original air sample.

The Phase I testwork demonstrated the following aspects of the proposed isocyanates monitoring concept:

- **Toluene diisocyanate in room air could be detected at a level of 0.02 ppm by the chemiluminescent technique.**
- **Aliphatic isocyanates were detected but with detection limits higher than the target 0.02 ppm. Further optimization of the system should extend the detection limits for these materials to the 0.02 ppm level.**
- **The monitor provides nonspecific analysis of isocyanate species and thus serves as a total isocyanates monitor rather than as a monitor of individual isocyanate species in air.**
- **The preferred source of reactive oxygen for the monitor is high purity oxygen, rather than the originally proposed room air. Nitrogen in room air produces chemiluminescent nitrogen oxides in the plasma zone and contributes to high background light levels which interferes with detection of isocyanates at ppm levels.**

- **Chemical interferent effects are minimal for typical organic compounds (aromatic hydrocarbons, alcohols, ketones, etc.) and inorganic species such as atmospheric moisture, carbon dioxide, nitrogen oxides, and ammonia. Organic amines present interferent response in the monitor, but with appreciably lower sensitivity than the isocyanates.**

The technical feasibility of the proposed chemiluminescent isocyanates detection and analysis technique was thus demonstrated, interferent effects were shown to be minimal, and adequate data was collected in the Phase I effort to permit the development of a Phase II workplan to further demonstrate the commercial potential of this innovative isocyanates monitoring technique.

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SCIENTIFIC/TECHNICAL AIMS OF THE PROJECT

BACKGROUND

The application of isocyanates in both manufacturing and public-use operations offers the opportunity for exposure to both immediate users and a relatively wide circle of impacted bystanders. The potential audience for exposure and the highly toxic nature of numerous isocyanates have led to the development of stringent standards of allowable exposure. Consequently, new methodology and instrumentation are required to assure that exposure standards are not exceeded and that appropriate alarms are sounded in real time if excessive isocyanate levels are encountered. The current Threshold Limit Value (TLV) for isocyanate exposure is set at 0.02 ppm.

The previous method for monitoring at the TLV level (colorimetric determination with N-(napthyl)-ethylene diamine) was decertified by NIOSH in 1989. To date no replacement method has been developed and certified to replace this previous technique which had suffered from unproven precision and accuracy, and from sensitivity to non-isocyanate interference due to free aromatic amines. The decertified method also was not well suited to sampling aerosols and aerosol-bound isocyanates for analysis and this is a specific and important issue addressed by the analyzer evaluated in this program.

NIOSH estimates of the population at risk for exposure to isocyanates in the workplace indicate a total of 50,000 to 100,000 persons, and an estimated five percent of this population may be expected to develop adverse respiratory responses as a consequence of these exposures (NIOSH Pub. No. 78-215, 1978). These estimates of at risk population, of course, deal only with workplace exposure and do not include segments of the general population who may suffer exposure in nonwork applications of urethane paints, varnishes, and similar isocyanate containing products.

The majority of isocyanate applications involve the use of one or more of the common isocyanate species: toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), napthalene diisocyanate (NDI), and hexamethylene diisocyanate (HMDI). Toluene diisocyanate is the isocyanate product employed in largest volume and in the broadest range of applications and has been implicated in a number of health studies as a respiratory health hazard and a potent asthma inducer (Fuchs and Valdez, 1951; Butcher, et al., 1977). Pulmonary reactions attributed to TDI include: irritation from high concentrations, asthma, acute pharmacologic airway responses to low concentrations,

chronic deterioration in lung function with low level exposures, and alveolitis (Butcher et al., 1977; Finks et al., 1978: Chester et al., 1979).

The production of urethane foams constitutes a major industrial consumption point of isocyanates. In the production of these foams, polyglycols and isocyanates are reacted to form a polymeric mass. The copolymer of these components may then be reacted with water, in the presence of amines and/or tin catalysts, to undergo further reaction which results in the formation of large amounts of carbon dioxide. The evolving carbon dioxide is entrapped partially in the viscous polymer and produces a foam which may vary in physical properties from highly flexible to quite rigid. Typical applications of these foams range from flexible foam for mattress, cushion, and packing material uses through rigid foam utilization in molded automobile parts such as bumpers and fenders and to rigid foam coatings for polyurethane coated electric wire manufacture.

While the reaction of the isocyanate-polyglycol polymeric resin mix with water will produce urethane foams, the resin composition can also be applied directly to various surfaces as a paint or varnish finish. Upon drying, this resin forms an exceptionally water resistant finish with a high gloss capability and polyurethane paints and varnishes have become increasingly popular in retail paint formulations, in marine paint and varnish applications, and in a wide variety of industrial coatings applications. Among the largest volume appliers of polyurethane finishes is the automotive industry and additional growth is this sector is projected by most industry analysts as the demand for more environmentally resistant finish coats increases.

Exposure to isocyanates in the workplace is most prevalent during the production of the various isocyanates, during the production of urethane foams (NIOSH Pub. No. 78-215, 1978), and during the use of various polyurethane paints and varnishes. Less prevalent exposure incidents include operations in which urethane coated cable may be heated during electronics fabrication and repair, operations in which cable is welded, and operations involving the disposal of polyurethane wastes by incineration. In all cases, the risk of exposure to isocyanates in both vapor and aerosol form exists and thus any reliable sampling and analysis procedure for isocyanates analysis at the 0.02 ppm level should handle both forms of the target isocyanates.

The isocyanate detection and quantification system discussed by ADA Technologies in this document meets the goals of detecting isocyanates at the 0.02 ppm TLV with acceptable precision and accuracy. The system design samples and analyzes both vapor

and aerosol isocyanates and addresses discrimination between isocyanates and typical interferents including the free amine species which the previous method could not eliminate as an interference.

The range of industrial settings in which the successful isocyanates monitor will be applicable is rather wide and includes chemical facilities producing the isocyanate raw materials used in urethane and polyurethane products, the coatings industry producing finished polyurethane paints and varnishes, the urethane foam fabrication, forming, and coating industries, industry segments applying polyurethane coatings, and disposal facilities handling waste urethane materials. At the present time, none of these industries have available to them a suitable real time monitor for isocyanates in the workplace at the required 0.02 ppm level and the proposed system will thus fill a critical monitoring vacuum.

The overall objective of the proposed program was to demonstrate that the chemiluminescent technique is capable of accurately monitoring isocyanates with sufficient sensitivity to detect harmful concentrations in the workplace. The Phase I test plan was designed to demonstrate the technical feasibility of the concept. The Phase I deliverable is this report which describes the monitor geometry, discusses the varying of the instrumental parameters, and presents a plan for the design and testing of a Phase II prototype.

At the completion of Phase I, four important questions about the performance of the instrument are answered.

- **First, what are the optimal physical parameters that govern the chemiluminescence of the reaction of O atoms with isocyanates?**
- **Second, can the instrument be used as a total isocyanate monitor or can it determine individual isocyanates and monitor them simultaneously?**
- **Third, what is the detection limit of the system after it has been optimized.**
- **Fourth, what are the interferences if any?**

The answers to these questions are provided in detail in this Final Report.

The successful completion of the Phase I program serves to justify a Phase II program to design and fabricate a field-worthy prototype. The knowledge gained in Phase

I provides the basis for specifying what geometries, flow rates, vacuum, etc. are required to operate the isocyanate monitor on a continuous basis. A field evaluation can then be conducted at one or more appropriate and typical industrial facilities in Phase II.

The commercialization of the instrument will be the topic of the Phase III effort.

PHASE I TECHNICAL OBJECTIVES AND PROPOSAL

The specific Phase I technical objectives and the workplan proposed to achieve those objectives are excerpted from the Phase I proposal and included here in the Final Report for reference.

PHASE I TECHNICAL OBJECTIVES

Three objectives have been identified for the Phase I technical effort. The first is to optimize the monitor with respect to physical parameters such as cell geometry, flow rates, and pressures. The design of the prototype will hinge on the thorough understanding of how these parameters influence the chemiluminescence of the isocyanate/O atom reaction. The physical parameters will be investigated in a laboratory environment where the conditions can be tightly controlled. A series of initial experiments will be run to determine the optimum operating parameters for detecting TDI.

The second objective is to determine if TDI, MDI, HMDI, and NDI can be identified separately or if the reaction between TDI and O atoms is common for all isocyanates. The reaction of O atoms with TDI may be the only observable reaction and it is important to determine if O atoms react with NDI, HMDI, and MDI. Experiments will be performed to determine if the instrument is a total isocyanate monitor or if the isocyanates can be spectroscopically distinguished from one another resulting in a specific isocyanate monitor. We expect isocyanate to react with O atoms to make NCO free radicals while potential interferents will not form the NCO free radical and thus be spectroscopically distinguishable.

The third objective is to identify and determine if chemical interfering species exist. If interferences do exist, experiments will be conducted to first quantify their effects and then to determine how to either remove or minimize them.

PHASE I WORK PLAN

Six tasks have been defined for the Phase I effort. These address the objectives discussed above, and will provide information needed to optimize the isocyanate monitor such that Phase II prototype can be designed and evaluated. The experiments will be completed on the premises of ADA Technologies, Inc..

Task 1: Define System Parameters

A literature search will be conducted to determine the concentration ranges and health effects of isocyanates in industrial settings. Particular emphasis will be placed on gathering data with respect to the partitioning of isocyanates into the gas and particulate phases. With the aid of an Industrial Hygienist, potential interferences will be identified. This data will aid in the design of all of subsequent experiments.

After completing of literature search and the discussions with the Industrial Hygienist, the Principal Investigator will meet with the appropriate NIOSH or other agency personnel to establish the overall uses and requirements for the isocyanate monitor with respect to current and projected needs. It is important to determine both the physical design constraints as well as the performance criteria so that the design and development of the monitor reflects the needs of the broadest range of potential industry segments which have a need for this instrument.

Task 2: Development of Proof-of-Concept System

A versatile proof-of-concept system will be designed and fabricated for evaluating the chemiluminescent-based isocyanate monitor. One possible configuration of the experimental system is shown in **Figure 1a** and is similar to that used in the preliminary experiments. The reaction chamber (**Figure 1b**) will be made of Teflon with a quartz window at one end and an adjustable plunger at the other end to vary the volume of the chamber. Two Teflon bulkhead unions will be fitted through the plunger. The unions will be drilled out to pass 0.250 inch quartz tubing. This will allow the sample inlet line to be heated up to the last inch and will allow the adjustment of the quartz lines with respect to one another. This configuration will allow the O atoms to mix with the TDI and the chemiluminescence to be monitored by a photodiode array equipped grating monochrometer. This will allow the determination of the spectral structure of the chemiluminescence. The vacuum line will be configured such that the chemiluminescent

reaction takes place in front of the quartz window. All of the data gathered from the experiments will be transferred to computer for analysis and interpretation.

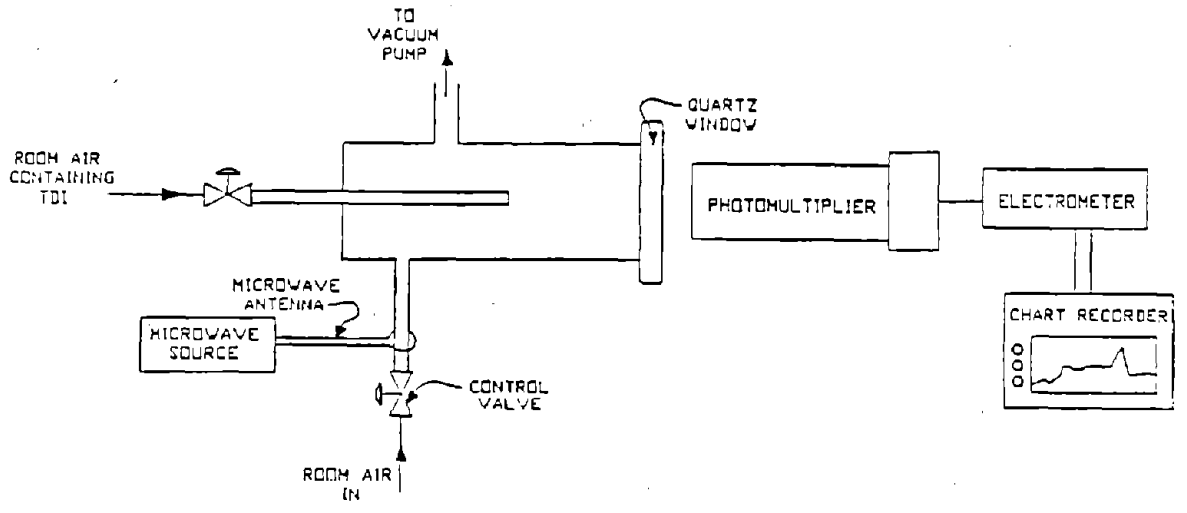

Figure 1a Experimental System Configuration

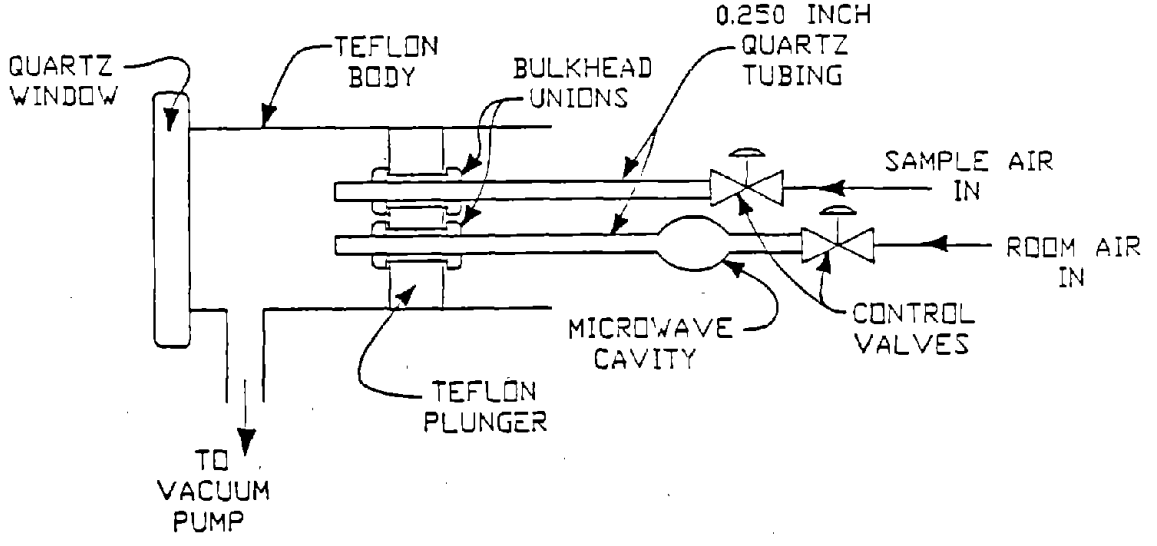

Figure 1b Reaction Chamber

The tentative reactor system design is based on the results of the scoping laboratory tests conducted prior to the Phase I proposal preparation and anticipates the use of materials which will have little tendency to sorb isocyanates. The use of quartz, with its associated risk of breakage, and of Teflon, with poor heat transmission characteristics, may not be optimum for a final prototype instrument. The Phase I work will also address the

use of metallic system components where appropriate in anticipation of their preferred use as robust parts of an eventual commercial instrument.

Task 3: Optimization of Physical Parameters

The parameters that influence the intensity of the chemiluminescence will be investigated. The reaction chamber pressure, O atom and sample air flow rates, and reaction residence times are all interdependent so optimization experiments concerning these parameters will be run one at a time.

By varying the position of the plunger, the volume of the reaction chamber can be changed thus varying the reactants residence time in the chamber. This set of experiments will be done to determine (at given pressures and flow rates) what effect the residence time has on the chemiluminescence of the reaction. It is anticipated that an optimum volume resulting in the largest chemiluminescent signal can be determined.

The effect of changing the vacuum in the reaction chamber will be investigated. The vacuum will be varied from 0.1 to 50 torr by placing a control valve in the vacuum line of the system. By fixing the flow rates of both the sample air and the O atom supply air and by fixing the reactor volume, the effect of varying the vacuum on the chemiluminescent reaction will be determined. The anticipated results are that at a pressure of approximately 50 torr, the microwave cavity will ignite and chemiluminescence resulting from the mixing of the O atom air stream and the sample air stream will be possible. Pressures below approximately 0.1 torr will extinguish the microwave source.

The flow rates of both the sample air and the O atom air stream will be varied to establish the largest chemiluminescent signal. The ratio of the sample flow rate to the O atom source flow rate has been determined to be less then one in the preliminary experiments. This result follows from the fact that the reaction requires a large O atom density to react with the isocyanate. From the previous experiments, it has been shown that the O atom source flow rate has an upper limit of approximately 400 ml/min before the O atom density drops below the level that any chemiluminescence can be observed. The sample flow rate is expected to be approximately 20 ml/min.

A computer will be used to analyze the data from these experiments. Three dimensional plots will be used to determine the interactions between the system pressure, the flow rate ratio, the reaction cell volume, and chemiluminescent response. All

chemiluminescent evaluations will be done using room air that contains TDI concentrations obtained from a calibrated TDI source.

After the system has been optimized, calibration curves will be generated for TDI to determine both the linearity of the monitor and its detection limit at a signal-to-noise ratio of 2 to 1. This data will be used to design the Phase II prototype including any needed changes in the geometry and/or physical parameters to meet the 0.020 ppm TLV.

Task 4: Separate vs Total Isocyanate Species Determination

The ability of the monitor to either detect other isocyanates separately or to be a total isocyanate monitor will be determined. The monitor will be designed to either measure a single wavelength for the chemiluminescence of O atoms with all isocyanates or monitor several wavelengths simultaneously for several isocyanates.

Once the geometry and physical parameters have been optimized for TDI, the other isocyanates of interest, i.e. MDI, HMDI, and NDI will be sampled with the system. One of the advantages of a chemiluminescent device is that it has the potential to respond to particles as well as gases. This is important, since some isocyanates exist in the particulate phase as well as the vapor phase. The MDI, HMDI, and NDI sources will be tested to determine if their vapor pressure as well as fine particles will generate enough chemiluminescent signal for quantification at ppb levels. If the particulate generated chemiluminescent signal is too weak for ppb level quantification, then efforts will be made to heat the sample air line to increase the partial pressure of the isocyanate before it reacts with the O atoms and chemiluminesces.

By using a photodiode equipped grating monochrometer, the spectrum of the chemiluminescence generated by each individual isocyanate can be scanned from 200nm to 1000nm. The results of those scans for each individual isocyanate will determine if the monitor can distinguish between any or all of the isocyanates based upon the emission spectra. If there are regions in the spectra that are unique for each isocyanate, then there is a potential that the monitor can serve as a simultaneous isocyanate monitor for distinct isocyanate species. If there is only a common wavelength for the chemiluminescence associated with all of the isocyanates and if detection limits for each isocyanate are at or below the separate TLV, then the instrument can be developed as total isocyanate monitor. The existing literature on the emission spectra of small energetic molecules, as typified by the recent Doctoral dissertation of Liu (Liu, 1989), does not provide adequate detail in

terms of the relative complexity of organic isocyanates spectra to allow general conclusions on the likelihood of resolvable chemiluminescence band structure.

Calibration curves will be generated for each of the isocyanate species. The results of these experiments will allow comparisons to be made between the individual isocyanate chemiluminescent responses. The various isocyanate concentrations will be generated using mass flow controllers and analyzed isocyanate sources. If the isocyanates only generate one wavelength of chemiluminescence and if photon production is a problem relative to detection by the photodiode array, then a photomultiplier tube will be incorporated into the Phase II prototype design since cooled photomultiplier tubes have a lower detection limit than photodiode arrays by more than 3 orders of magnitude. If several wavelengths are generated and if sufficient signal is available from the chemiluminescent reactions , the diode array will be incorporated into the Phase II prototype design. By using the correct grating in the monochrometer, the photodiode array will allow several hundred nanometers of a spectrum to be analyzed simultaneously. This would allow the simultaneous determination of several isocyanates that generate chemiluminescence at different wavelengths.

Task 5: Evaluation of Chemical Interferences

After the experimental system has been optimized and calibrated for the various isocyanates, a list of the possible interferences will be generated from the literature search and by further conferring with the appropriate agency personnel. Those chemicals that would be found in the same working environments as TDI and other isocyanates will be tested to determine: 1) if they do interfere either positively or negatively and (2) at what concentrations they cause the system to lose sensitivity for the isocyanates. Since a substantial portion of the industrial uses which may expose workers to isocyanate involve the use of formulations containing organic solvents or components, it is anticipated the typically investigated interferents might include hydrocarbons,(both aliphatic and aromatic), ketones, alcohols, glycols, and related compounds. There is a significant volume of reported literature on the chemiluminescence of some of these materials, particularly hydrocarbons, under conditions similar to those proposed in this work and these references will be critically reviewed and relevant data considered. Saturated hydrocarbons and aromatic species are not chemiluminescent; olefinic species exhibit some chemiluminescence but their spectra are expected to be quite distinct.

The concentrations of interferences will be generated using mass flow controllers and either liquid samples of the interferences or certified concentrations in compressed gas cylinders. The response of the instrument to the potential interferences will be documented and tabulated for interpretation.

Any chemical substance that interferes with the system will be dealt with in one of two ways. First, the wavelength of chemiluminescence produced by the interfering species will be determined. If the wavelengths of the isocyanate and interference chemiluminescence are separated by 10 nm or more, it will should be possible to optically filter out the interfering wavelength. If the two wavelengths are within 10 nm of each other, (or is not satisfactorily optically filtered out), the interfering species will have to be either physically removed from the system (filtered from the air stream) or algorithms will be designed that spectrally subtract the interference from the isocyanate spectra. The generation of such a scheme has been successfully demonstrated in ADA laboratories and would be available and applicable to this project.

The laboratory testwork for the proposed isocyanate detection system development will involve the use of limited quantities of the candidate isocyanates and of other organic compounds evaluated as interferents. In the majority of studies, these materials will be used in permeation tube devices or in prepared gas mixtures at considerable dilution thus reducing the risk of exposure to a minimum. In those few instances where handling of pure or concentrated materials is required, the manipulations will be conducted in a laboratory hood and all necessary precautions in the use and disposal of the materials will be observed. High voltage power supplies and photomultiplier tube circuitry will be designed, installed, and operated to eliminate any shock hazard; microwave components for the plasma oxygen atom generation system will be appropriately shielded to eliminate worker exposure to stray radiated energy and appropriate area warning signs will be installed as required.

Task 6: Reporting

At the completion of the project, a Phase I final report will be prepared. The document will present a detailed description of the proof-of-concept isocyanate monitor, discuss the experiments, and analyze the data. Finally, the experiment results will be analyzed relative to the technical feasibility of the instrument.

DISCUSSION OF RESEARCH CONDUCTED

The remainder of the Phase I Final Report will detail the results of the actual tests performed, discuss the data developed, and present conclusions relative to the degree to which the Phase I objectives were met. Details of further work needed to move the project to the Phase II prototype demonstration stage and ultimate Phase III commercialization of the isocyanate monitor are also provided.

DESCRIPTION OF TEST WORK

The Phase I project was carried out in basically the format set forth in the tasks presenteed in the preceding section of this Final Report. Significant departures from the original proposal were confined primarily to the design of the chemiluminescence cell and to the quantification of the chemiluminescent light output. Both of these areas are discussed in detail in the appropriate parts of the report sections which follow.

Literature Information on Isocyanates and Interferent Species

The literature searched to support the Phase I effort included both that pertinent to isocyanates exposure in the workplace and to the likely interferent species which might be present in environments where isocyanate monitoring was a goal. Ideally, the isocyanate monitor would be totally specific to the species of interest and thus not be susceptible to producing false positive indications of isocyanate from any other chemical species. In fact, the likelihood of such absolute specificity is relatively low and thus the definition of probable interferent species and some definition of their effect on the isocyanate detection system is important.

In searching for information relative to isocyanates applications and exposure risk, references on future trends in isocyanates use were also of interest since these trends may serve to define the specific isocyanates which will be necessary to monitor for in the next five to ten years. In this regard, the increasing interest in aliphatic isocyanates as replacements for aromatic isocyanates in outdoor coatings usage is an important factor to consider.

The references identified in the literature search are listed in the Reference section of this Final Report. Based on the information obtained from these references, the

following specific conclusions were arrived at which aided in the definition of the Phase I laboratory tests.

- **The presence of isocyanate species in workplace air is likely to be accompanied by oxygenated organics, aromatic hydrocarbons, and trace levels of organic amines deriving from the raw materials used to produce the isocyanates. The isocyanate monitor will have to accommodate these interferent species by sample handling, spectral specificity, or a combination of these approaches.**

- **The physical form of isocyanate species in the workplace air is dependent largely on the specific operation (coatings application, foam production, etc.) and includes both vapor and aerosol forms of the active species. There is no clear reason to attempt to differentiate between vapor and aerosol forms of the isocyanate based on the reported toxicity and epidemiological studies of these materials.**

- **Isocyanates exhibit significant tendency to sorb to surfaces and the industrially significant compounds have relatively low vapor pressures at ambient temperature. Both factors suggest that sampling probes or sampling lines be of minimum length and be equipped with heating where practical.**

  The tendency to lose isocyanates by sorption does compromise the likely effectiveness of any attempt to selectively sorb interferents from the air stream being sampled. This same sorptive tendency presents a risk of "memory" in sampling probes or lines, a factor which needs to be considered when evaluating the ability of the monitoring technique to respond to episodic isocyanate presences in the workplace environment.

- **The kinetics of the reaction of active oxygen with isocyanates to yield chemiluminscent reaction products is fast and thus the sample volume of the reaction cell can be kept small. The use of a small reaction cell coupled with a high flow rate for both the sampled gas stream and the active oxygen stream means that the monitor should be intrinsically fast-responding to isocyanate appearances in the atmosphere being sampled.**

The following section describes the laboratory system which was constructed to test the basic technical feasibility of the proposed chemiluminescent reaction for the detection and quantitation of isocyanates in air.

Laboratory Test Apparatus Set Up

The basic laboratory test system was configured around the use of a microwave plasma to generate a stream of active oxygen which was then mixed with a stream of room air containing controlled amounts of isocyanate or other species of interest. The two gas streams were mixed in a reaction volume which was in the field of view of a photomultiplier tube which could detect light from the chemiluminescent reactions taking place. The light intensity was related to the amount of isocyanate or other reactive species in the room air being sampled and thus provided a means to quantify the concentration of these materials in the air. Output data from the photomultiplier tube and associated electronics was recorded on a strip chart to provide a permanent record of the system response to both isocyanates and interferents.

Figure 2 presents a schematic of the laboratory system as it was initially set up for the Phase I tests.

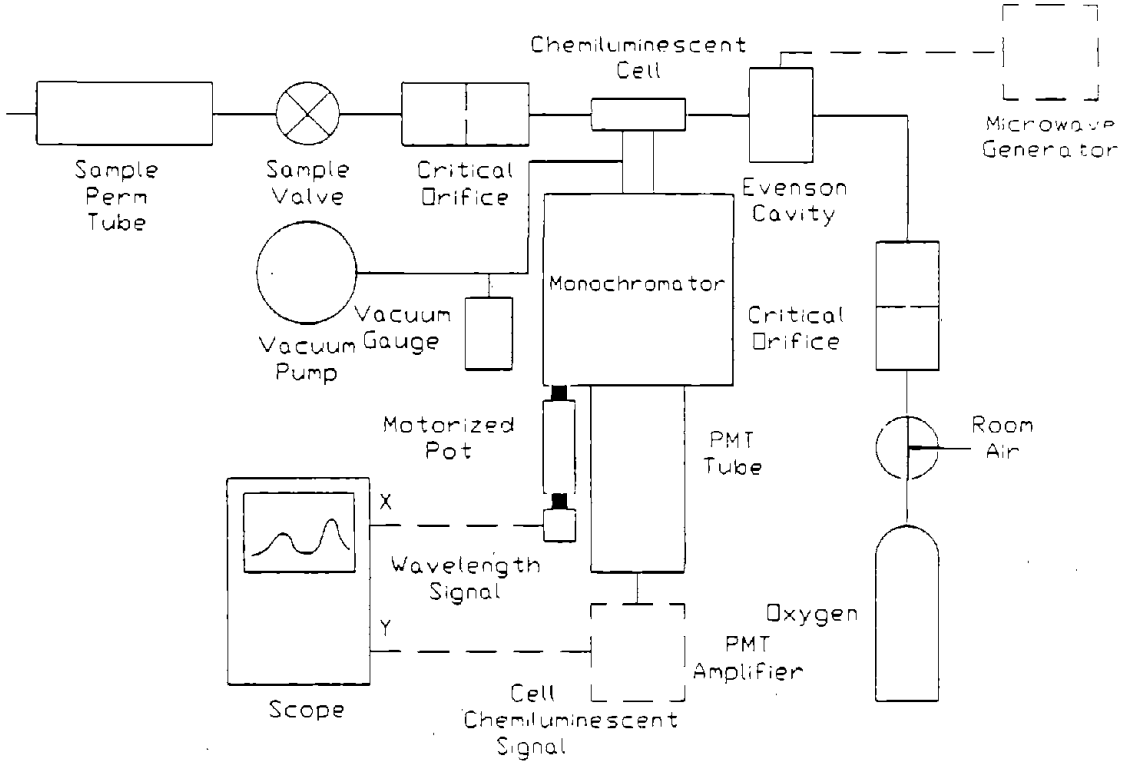

Figure 2 Laboratory Test Set-Up for Phase I Tests

The original proposal had envisioned using room air as a feed for the microwave generator to produce active oxygen. The initial tests with the system configured to use air, however, confirmed the presence of high chemiluminescent background from nitrogen oxides produced in the plasma. This high background light level would effectively mask the light output from low levels of isocyanates (on the order of the desired 0.02 ppm detection limit) reacting with active oxygen from the plasma generator.

The detail of the nitrogen oxides chemiluminescent background was then investigated further prior to detailed work with isocyanates to determine whether the spectral makeup of this light was amenable to selective filtering at a wavelength which would not impact light arising from the isocyanates-active oxygen reaction. If such selective filtering, through the use of bandpass filters or possibly with a monochromator, was not an option, then the Phase I monitor system would operate with pure oxygen gas feed to the plasma in order to eliminate chemiluminescent nitrogen oxides formation.

Figure 3 presents the spectral trace of the chemiluminescent light detected in producing active oxygen in the microwave plasma cavity with room air as feed to the plasma cavity. The spectrum of chemiluminescence arising from injecting toluene diisocyanate (TDI) into the reaction cell, with pure oxygen serving as a source gas for the plasma generator, is also presented.

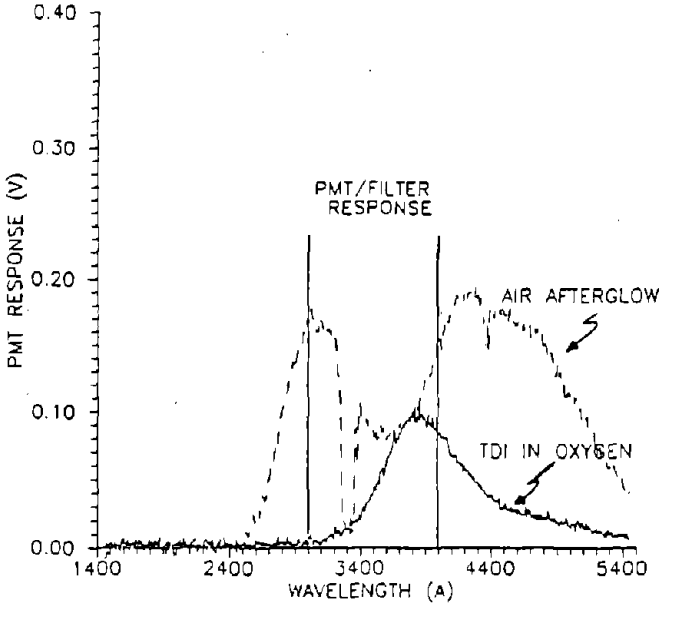

Figure 3 Spectra of Chemiluminescent Species in Feeding Air or Pure Oxygen to the Isocyanate Monitor System

These spectra show that the chemiluminescence due to nitrogen oxides produced in the air-fed plasma is relatively broad banded and occurs above about 300 nM. The broad banded light emission observed from about 240 to 340 nM is attributed to scattered light from the plasma zone itself. These observations led to the conclusions that: (1) the isocyanates monitor would best be configured with a pure oxygen feed to the plasma cavity in order to reduce any nitrogen oxide background to a minimum and (2) that the rejection of stray light from the plasma zone was in fact critical design consideration for eventual system design.

If the subsequent tests with isocyanates detection led to the conclusion that adequate sensitivity was present to allow the light loss attendant on using either filters or a monochromator, then use of room air feed to the plasma along with these elements (in place of pure oxygen feed to the plasma) would be an option to consider. Given the very close overlap and the relatively high light intensity from the nitrogen oxides chemiluminescence, the likelihood of such a direct solution to the interference problem seemed slight.

The nitrogen oxides chemiluminescent overlap with the chemiluminescent signal deriving from the isocyanate-active oxygen reaction was dealt with in Phase I by using pure oxygen as a plasma feed gas to wholly avoid formation of NO_x in the plasma zone. Rejection of the shorter wavelength scattered light from the plasma was achieved by modifying the inlet to the chemiluminescent cell as described later in this report. In a prototype (Phase II) system design, more extensive testing of light trap incorporation can be appropriately included to assure maximum rejection of this light background.

Figure 4 presents a diagram of the laboratory isocyanate monitor system configured to use pure oxygen as a source of gas for the microwave plasma generator. The filter employed in the system was a colored glass bandpass filter with a spectral pass of 320-400 nM. The choice of this range was made to eliminate the UV component of the plasma and also a significant portion of the visible stray light component entering from the plasma zone or from external room light entering through the walls of the quartz plasma containment tube.

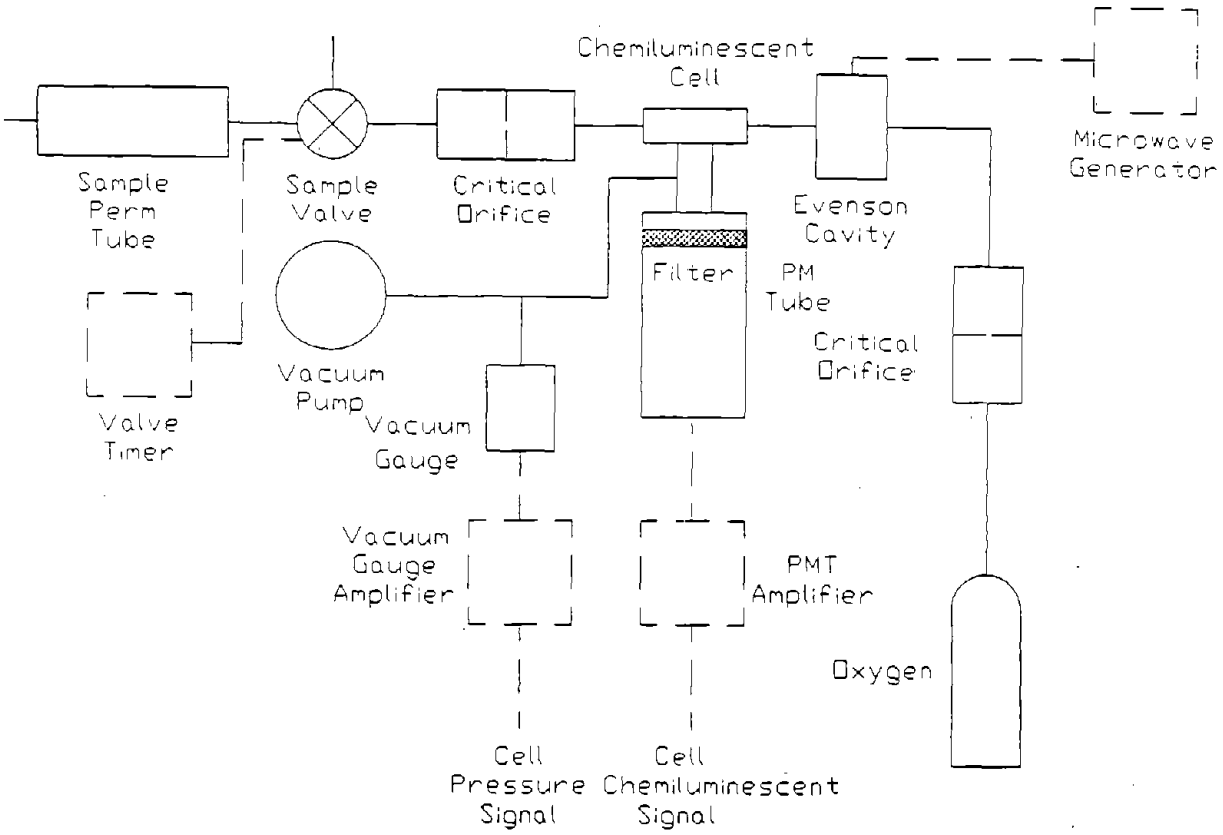

Figure 4 Laboratory System Configured with Pure Oxygen Feed to the Microwave Plasma Generator

This system configuration was used to demonstrate the technical feasibility of the isocyanates chemiluminescent detection concept in the tests described in subsequent sections of this report.

Isocyanates and Interferent Compounds Tested

The compounds selected for testing were chosen on the basis of their frequency of use in the workplace, their likely reactivity with active oxygen to produce chemiluminescent products, and/or references to their being specific interferents in isocyanate monitoring in the (now disqualified) method for isocyanates detection and measurement in air.

In the case of isocyanates, toluene diisocyanate (TDI) and hexamethylene diisocyanate (HMDI) and methyl isocyanate (MIC) were chosen for use. The first two materials are widely used in industrial operations for both foam production and coatings application and thus are of direct interest from an industrial hygiene exposure risk

standpoint. The last compound, while not as widely used as the first two, does represent the most volatile member of the isocyanates family of compounds and is the simplest of the family of aliphatic isocyanates which are of growing use in the industry. These compounds represent aromatic and aliphatic isocyanate families of materials and this is important since the proposed monitor should respond well to both classes of compound. The current emphasis is on the use of aromatic isocyanates but aliphatic isocyanates are rapidly gaining popularity and their use and potential for worker exposure is a near future occurrence of significant importance. All three isocyanate species were available in certified permeation tube devices which allowed known quantities or concentrations of the materials to be introduced into inlet room air samples in a safe and exactly controlled manner.

Because of the limited time constraints of a Phase I program, it was necessary to limit the number of potential interferents to be examined. Selection was made on the basis of likely presence of a class of compounds in the same work environment as the isocyanates and on similar reaction chemistry of the interferent molecule with active oxygen to produce chemiluminescence.

Thus, oxygenated organics were chosen for study since the production of foams and the application of coatings may involve polyglycol species in addition to isocyanates. For the purposes of the Phase I work, ethanol, methanol, and acetone were used as oxygenated compound representatives because of the greater ease of introduction of these compounds into the chemiluminescent cell compared to the low volatility polyglycols.

Since aromatic solvents may be used in the coatings industry along with isocyanate compounds, and since there are some literature reports of chemiluminescent reactions of aromatics with active oxygen, this class of compounds was also examined for interferent potential. The aromatics chosen for testing were benzene, toluene, and p-xylene, all of which were available in certified permeation tube devices.

The chemiluminescent species underlying the detection of isocyanates upon reaction with active oxygen is the activated isocyanate NCO^* species which decays with the emission of energy in the form of visible light. The formation of this species can also be hypothesized when active oxygen reacts with other organics having a carbon-nitrogen functionality in their structure. With this possible source of interference with isocyanate detection as proposed in Phase I, several other potential interferents were also included in the test matrix. Specifically, acetonitrile, trimethyl amine, and aniline were selected as compounds with pertinent structural features and with at least a potential for widespread

enough industrial use to present a risk of significant presence along with isocyanates in some work environments.

The above system and suite of chemicals for detection and/or interferent studies served as the basis for the specific Phase I tests described in the next section of the Final Report.

Specific Tests and Test Procedures Performed

Laboratory System Set-Up and Initial Operation

The laboratory system was initially operated without the introduction of any organics in order to determine the stable operating conditions for the active oxygen plasma. In conducting these initial tests of plasma stability and behavior, the details of the reaction cell design were also defined.

Initial plans had been to employ a quartz and Teflon reaction cell into which the active oxygen and sampled room air streams would be mixed in the field of view of the photomultiplier tube. In working with these materials of construction, and in attempting to minimize the surfaces upon which isocyanate could be removed by sorption, it became evident that an alternative cell configuration with better incident and plasma light rejection and with much less surface area was desirable. Thus, the reaction cell was redesigned and constructed from stainless steel and polymer parts and was sized and configured to provide high levels of incident light rejection and a small internal volume.

In redesigning the reaction cell, it became apparent that a simple and minimum-size inlet probe was necessary to avoid isocyanates loss by sorption ahead of the reaction cell. The best design element to minimize the probe wall area was found to be to replace the probe completely with a fixed orifice sample inlet which fed directly to the reaction cell. The sample rate of the inlet can then be fixed and reproduced by simply specifying the orifice diameter. Furthermore, since the sampled air stream expands into the reaction cell which is at a vacuum (of about 1 to 10 torr) immediately after passing through the orifice, there is no significant opportunity for deposition of aerosols on the sample inlet. In fact, given the reduced pressure in the cell, flash vaporization of any high boiling isocyanate (e.g. HMDI) species can be expected with little or no heating of the cell above ambient temperature.

The use of the room air sampling orifice, in place of the traditional probe through which air might be sampled to the analysis cell, provides an effective means of assuring accurate sampling and analysis of total vapor and aerosol isocyanates species. This was an important Phase I design objective.

The material of construction for the reaction cell was also an issue which required some testing prior to deciding on a stainless steel and aluminum material combination as the cell material of choice. The use of a quartz reaction cell was appealing from the standpoint of nonreactivity but the poor ambient light exclusion and risk of breakage of this material were detrimental qualities. A structural polymer, black Delrin, was also tested and found to have excellent incident light rejection potential but it was rapidly attacked by species in the oxygen stream from the plasma and failed by cracking. Aluminum was tested as a reaction cell but was found to exhibit unacceptable sorption of isocyanate and/or reactive oxygen species and thus to inhibit chemiluminescent reactions.

Figure 5 shows the redesigned chemiluminescent cell which was fabricated and used in the Phase I tests.

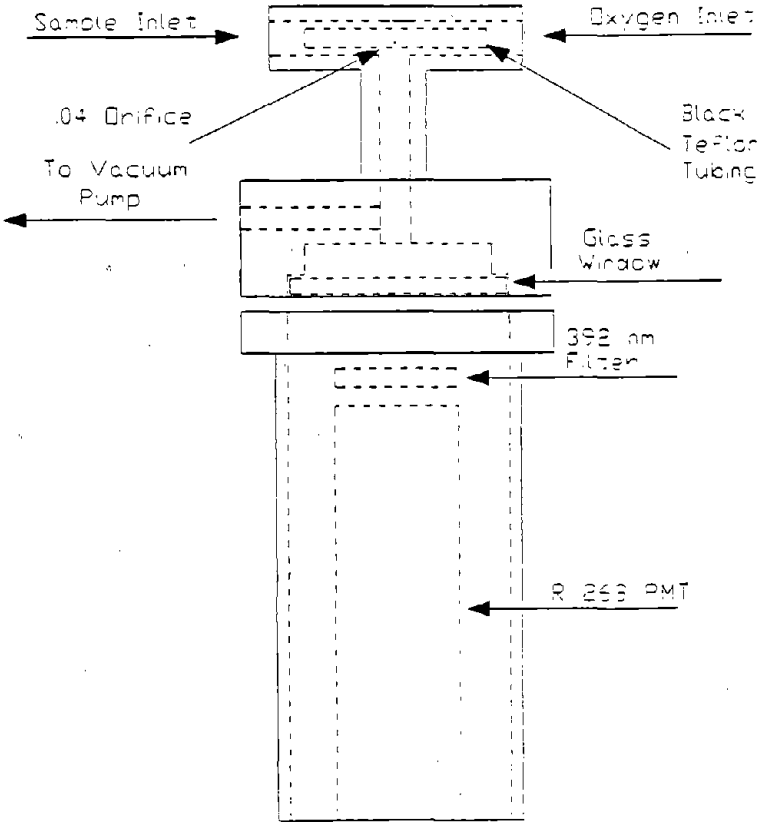

Figure 5 Chemiluminescent Reaction Cell Design

The reaction cell was coupled to the quartz microwave plasma containment vessel with standard threaded and o-ring sealed fittings. The feed to the plasma generator was controlled with a fixed orifice and variable pressure regulator on the oxygen cylinder; flow to the plasma was then changed by simply increasing or decreasing the pressure delivered to the orifice.

The overall vacuum in the system was monitored with a thermocouple gauge and controlled by varying the inlet rate of sampled room air and of oxygen fed to the plasma. The vacuum in the system was recorded on one of the two channels on the strip chart recorder also used to monitor signals from the system photomultipler tube detector.

The inlet to the reaction cell orifice was connected to a three way, electrically actuated, solenoid valve which allowed the selective sampling of clean room air or of room air which had been "doped" with isocyanate or interferent from permeation tubes. Control of perm tube temperature and the rate of air flow past the perm tube assured the production of a known and stable composition gas stream (simulating bulk room air with that level of contaminant) for the monitor to sample. In all cases, the flow of air past the perm tube exceeded the inlet flow rate to the monitor to assure that no dilution air was drawn into the reaction cell along with the gas of interest. The use of the switching valve allowed basically unattended sample introduction over extended periods of time to allow evaluation of system response time, reproducibility of response, and overall system stability or drift.

The intensity of light produced in the chemiluminescent reaction cell was monitored continuously with a Hamamatsu R268 photomultiplier tube (PMT). The optical filter with bandpass of 320 to 400 nM was placed between the PMT and the reaction cell to exclude light background not arising from the chemiluminescent reactions taking place in the cell. Output of the PMT was processed with standard circuitry to produce a voltage output proportional to incident light on the PMT and this voltage signal was continuously recorded on a strip chart recorder.

Optimization of Oxygen Plasma Operating Parameters

The operating conditions for production of a stable microwave plasma were first determined by systematically varying the input microwave power and oxygen flow (system pressure) while observing variations in coupling efficiency for the plasma. For these tests, a

flowmeter (tube rotameter type) was installed in the oxygen line to the microwave cavity so that actual gas flowrates for the feed gas could be defined.

The production of reactive oxygen atoms in the microwave plasma cavity is directly related to the coupled microwave energy input to the cavity and to the mass flow rate of feed oxygen to the plasma. Since the plasma is produced and maintained under vacuum conditions (pressures less than 10 torr in the present case), the mass flow rate of feed oxygen which can be delivered is also a function of pumping capacity for the vacuum pump and thus is practically constrained by the size of pump and its pumping characteristics.

Plasma stability tests with the Phase I system showed that a stable oxygen plasma could be maintained in the 13 mm o.d. quartz plasma confinement tube at system pressures of 1 to 6 torr. This pressure range corresponded to oxygen feed rates, at that pressure, of 10 to 200 cm^3/min. At pressures outside of this range, the plasma exhibited visible flicker instability or was self extinguishing in a very short time. These operating limits were used in subsequent monitor response tests.

In all tests, the microwave power input to the cavity was adjusted to give maximum coupling and to minimize reflected power loss. Under typical operating conditions with about 100 watts of forward microwave power to the plasma confinement tube, reflected power readings of 10 to 20 percent were achieved. While tuning the power generator and Evenson cavity, it was found that the production of a stable plasma, with minimum flicker, was more important to stable operation of the isocyanates detection instrument than was the use of maximum input power to the cavity. Any significant instability in the plasma translated to substantially increased noise levels in the PMT output and thus compromised the detection limit for isocyanates.

RESULTS AND THEIR SIGNIFICANCE IN MEETING PROJECT AIMS

Having established the operational parameters to use in the oxygen plasma the next tests in the Phase I effort were directed at defining the system response to isocyanates and potential interferent species. Results of these tests are presented in the following sections.

Test Data and Interpretation

Toluene diisocyanate was introduced from a perm tube (at 70°C) into the room air stream being sampled by the instrument and the initial response tests for the

chemiluminescent detection concept were carried out with this compound as a typical isocyanate target for analysis..

Response as a Function of Sampled Air to Oxygen Plasma Feed Rate

In developing the Phase I chemiluminescent analyzer, it was next necessary to define the optimum practical sample rate for the room air being analyzed. The sensitivity of the analyzer, based on the fundamental equation describing the relationship of chemiluminescent intensity and analyte concentration, shows that response is directly dependent upon mass flow of analyte to the reaction zone. The limit on mass flow, however, is also impacted by the overall pressure necessary in the system to sustain a stable oxygen plasma and on the pumping requirements necessary to maintain that pressure against the inflow of both oxygen from the plasma and room air from the sample orifice. Thus, the initial experiments in this part of the Phase I testwork investigated the effects of varying TDI-doped room air sampling rate within a narrow range of oxygen flow rates to the plasma (60-100 cm^3/min).

Figure 6 presents a graphic summary of the effect of changing the sample air inlet rate to oxygen feed rate ratio on the chemiluminescent intensity. In these tests, the inlet rate of 0.6 ppm TDI in room air was held constant (at 60 cm^3/min) and oxygen feed rate to the plasma was varied from about 15 to 100 cm^3/min.

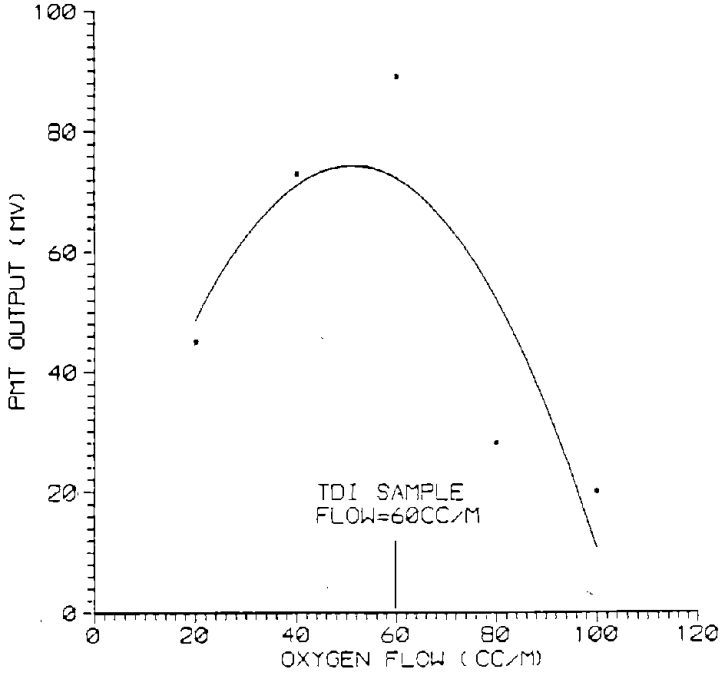

Figure 6 Chemiluminescent Reaction Intensity as a Function of Varied Air Sample Rate to Oxygen Feed Rate to Plasma

The test data indicate that the system produces a maximum sensitivity (maximum light intensity for a given inlet level of TDI in air) at an approximately 1:1 flow ratio of sampled room air to oxygen feed to the plasma. Since the actual mass flow to the system will be constrained by the capacity of the pump and its ability to maintain the desired vacuum of about 1-10 torr, the use of a flow ratio rather than definition of a specific volumetric flow rate for air sample is a pertinent design criterion for the monitor. Using this factor, and knowing the capacity of the vacuum pump, it is then possible to define the specific orifice sizes for both the room air sample inlet rate and for the oxygen inlet rate to the plasma. Use of fixed orifices in both sample and feed lines, rather than control valves, substantially simplifies the monitor design and eliminates a potential leak point at valve stem packing glands.

The optimum sensitivity of the isocyanates monitor is achieved at an approximately 1:1 volumetric flowrate ratio for oxygen feed to the plasma and room air sampled to the chemiluminescent cell.

Response Time for TDI in Room Air

In functioning as a real time analyzer for isocyanates in room air, the proposed instrument should have a rapid response time to an increase in analyte species in the incoming air sample. The response time of the Phase I instrument was thus tested using 0.6 ppm TDI in air as an inlet sample to determine the response time with a constant sampled air inlet rate (60 cm^3/min) and a varied oxygen flowrate to the plasma.

Figure 7 presents summary data for the response time tests.

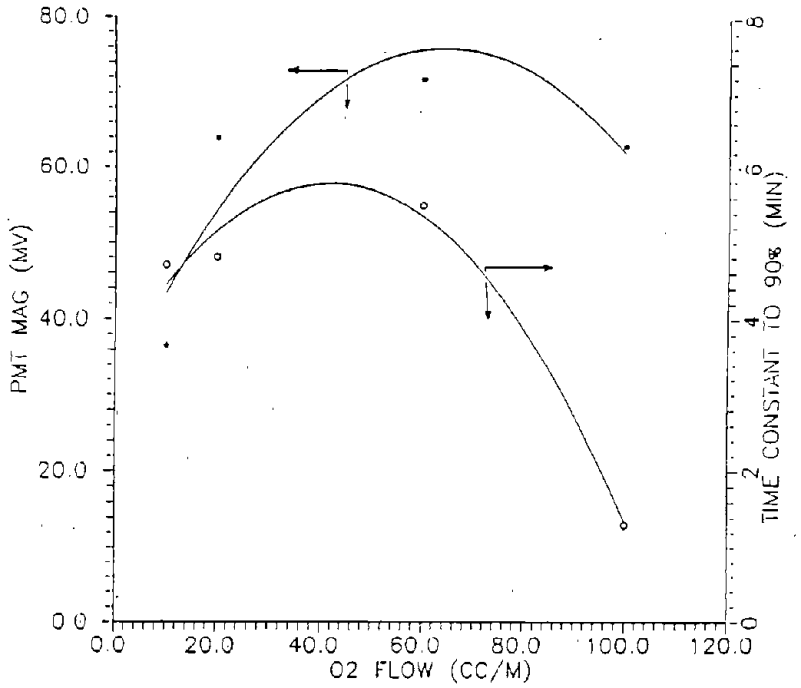

Figure 7 Response Time and Sensitivity for Chemiluminescent Detection of 0.6 ppm TDI in Room Air

While higher oxygen flowrates are shown to provide more rapid monitor response, the tradeoff in decreased light intensity (lower PMT voltages) is also evident at these higher flowrates. In designing the monitor, then, compromise must be reached between maximum response speed and acceptable sensitivity to isocyanates. In the Phase I system, this compromise amounts to operating with about 60-100 cm^3/min of both oxygen feed to the plasma and room air sample feed to the detection cell.

Further optimization of oxygen input rate, sampled room air inlet rate, and the attendant compromises on total gas feed to the system along with desired vacuum to maintain and the size and cost of the vacuum pump to achieve these goals is a legitimate part of the Phase II portion of this instrument development effort.

Response as a Function of TDI Concentration and Detection Limit for TDI in Room Air

The isocyanates monitor was next tested to determine the response of the system, at the optimum air sampling rate, to TDI as a function of the TDI concentration in the inlet air. The concentration of isocyanate in the inlet air stream was controlled by varying the flowrate of air over the perm tube while the tube was maintained at constant temperature. Using this technique, and operating at flow rates over the perm tube which always

exceeded the sampling rate of the monitor, it was possible to produce air streams containing TDI at levels as low as 0.02 ppm (20 ppb) for direct sampling to the monitor.

Figure 8 presents data showing the response of the monitor to TDI concentrations of 0.02 to 0.64 ppm in room air.

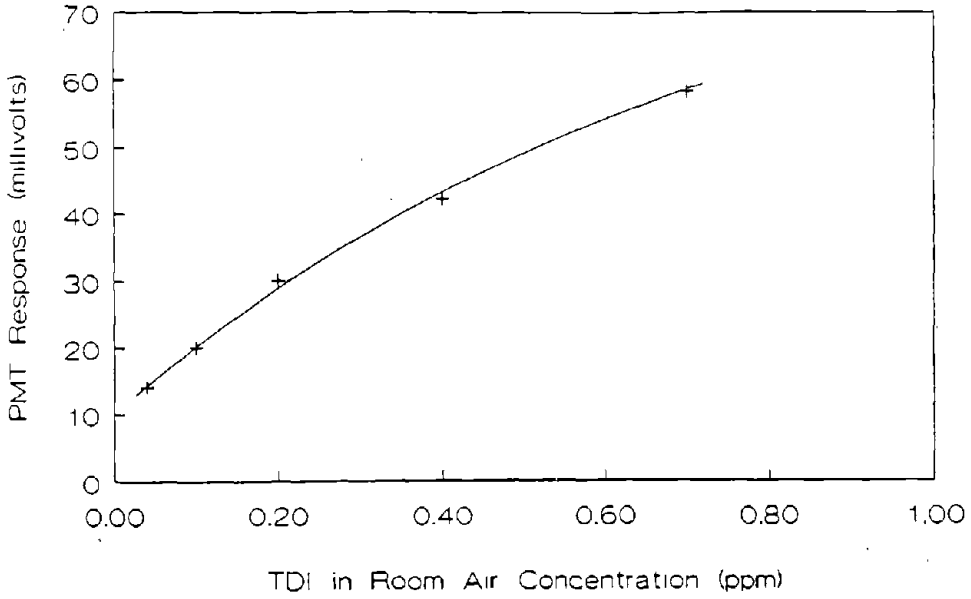

Figure 8 Monitor Response as a Function of TDI Concentration

Based on this response plot, the isocyanates monitor was demonstrated to have a reproducible and nearly linear response to TDI in air over a concentration range of 0.02 to 0.70 ppm.

These data confirm the technical feasibility of using the proposed chemiluminescent analysis concept to detect TDI at a detection limit of 0.02 ppm in air. The signal to noise (S/N) ratio for the PMT output at 0.02 ppm TDI is approximately 3:1 with the measurement conditions and parameters used in the Phase I tests.

Sensitivity as a Function of Isocyanate Species

The range of isocyanates employed in industrially significant quantities, and thus the range of compounds of concern from an industrial hygiene standpoint, includes both aliphatic and aromatic isocyanate species. While toluene diisocyanate is widely used in both foam and coatings applications at present, there is increasing interest in using aliphatic isocyanates and in fact recent announcements by Mobay and other manufacturers

specifically address the increased demand for aliphatic isocyanates in the near future (Chemical & Engineering News, 1991; Reisch, 1991).

Since the one of the goals of the proposed isocyanates monitor is to detect a suite of isocyanates, with potential for differentiating among individual species, the next laboratory tests in Phase I addressed the sensitivity of the instrument to other isocyanate species. For the purposes of these tests, hexamethylene diisocyanate (HMDI) and methyl isocyanate (MIC) were chosen for test compounds. Both are aliphatic isocyanate species and they represent a wide range of volatility, with HMDI having a boiling point of 255 °C compared to a boiling point of 39 °C for MIC.

Room air containing known concentrations of each of these isocyanate compounds was introduced to the chemiluminescent instrument and responses were compared to that for TDI under the same instrument operating parameters. **Figure 9** presents comparative response data for these isocyanate compounds along with comparative response sensitivity for TDI as a reference point.

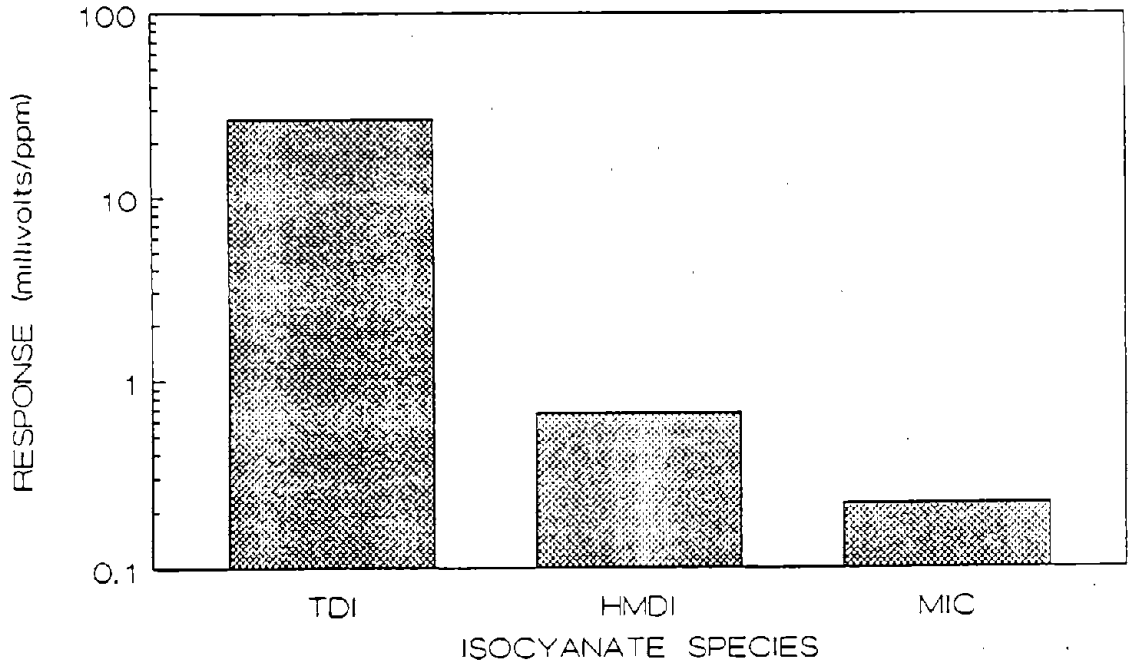

Figure 9 Comparative Sensitivity of the Chemiluminescent Detector for Aliphatic Isocyanates and for TDI

A review of this data indicates that there is in fact a significant difference in the sensitivity of the chemiluminescent detector for the aliphatic and aromatic isocyanate compounds. The primary reason for this variation in sensitivity probably is a different rate

constant for the reaction of active oxygen with the aliphatic and aromatic isocyanates arising from varied reaction mechanisms. Some additional chemiluminescence from the aromatic ring in the TDI undergoing chemiluminescent reaction with the atomic oxygen from the microwave plasma may also be a factor with respect to enhanced sensitivity for the aromatic isocyanate species. If that light output (from active oxygen-aromatic ring reactions) falls in the same spectral range as that from the CNO^* derived from all isocyanates, then an apparent higher sensitivity for TDI (and other aromatic isocyanates) would result.

The response of the system to TDI had, of course, been optimized during the course of the Phase I tests but the time constraints of the program did not permit similar optimization for each of the other isocyanate compounds. Based on the level of sensitivity increase achieved for TDI, however, it is not unreasonable to expect that similar parameter optimization for the aliphatic isocyanates (in Phase II) would result in improved detection limits by factors of an order of magnitude. Improvements of this size would result in detection limits for these aliphatic isocyanates very similar to those reported here for TDI.

The variable sensitivity of the chemiluminescent detection concept to aliphatic and aromatic isocyanates is an area that will require further evaluation and quantification in Phase II in order to demonstrate wide ranging applicability of the instrument to different isocyanate generating sources. Additional optimization will be required to achieve a detection limit of 0.02 ppm isocyanates in air for the aliphatic isocyanates expected to be of commercial importance.

Effect of Trace Air Leakage into the Plasma Feed Gas

During the course of the Phase I tests, the problems associated with nitrogen oxides chemiluminescence was noted and the subsequent need to operate the oxygen atom plasma with pure oxygen rather than with room air as a feed gas has been discussed above. In working with the laboratory system in the various tests detailed above, however, the test data showed reproducible variability which could be correlated with air in-leakage to the system upstream of the microwave plasma.

An analysis of the data from these tests further suggested that low levels of nitrogen oxides (formed in the plasma reaction zone by reaction of atmospheric nitrogen brought in with trace air leaks and active oxygen being produced in the plasma) might actually enhance isocyanate chemiluminescence in the reaction cell. Air leakages corresponding to

additions of about 10-50 ppm air into the oxygen plasma feed gas resulted in increased TDI chemiluminescent signals by multipliers of 3 to 5 fold. There is a nominal increase in noise associated with the plasma as air inleakage increases and this offsets to a degree the gain in apparent TDI sensitivity.

While no extensive tests were performed to further investigate this effect in Phase I, the results presented above do suggest that trace amounts of nitrogen oxides in the reaction cell may impact sensitivity of the instrument for TDI monitoring. A recent paper presented at the Spring 1992 American Chemical Society Annual Meeting (Brown and Garay, 1992) reporting on modeling of the selective reduction of NO_x by HNCO (the simplest of isocyanate species) may be pertinent to the reaction chemistry underlying this apparent sensitization.

The effect of trace nitrogen oxide species in the oxygen atom plasma should be further investigated in Phase II as it relates to ultimate system sensitivity for isocyanates monitoring and to system design considerations to assure complete exclusion of air or intentional addition of controlled amounts of air if this improves system detection limits or stability.

Chemiluminescent Isocyanates Monitor Response to Chemical Interferences

Having developed the isocyanates monitor and demonstrated its ability to detect and quantify isocyanates as described above, the next tests in Phase I addressed the response of the system to a suite of possible interferents. In these tests, the instrument was operated under conditions which had been found to be optimum for detection of TDI so that a relative sensitivity to interferents under known and practical operating conditions could be derived.

In the interferent tests, the isocyanate permeation tube in the sampled room air line was replaced with permeation tubes containing the chosen interferents. The temperature and flow rate through the permeation tube enclosure was then adjusted to give the desired concentration of interferent in the air stream being sampled by the chemiluminescent detector. Relative responses of the PMT to each interferent were then recorded and compared with the response of the system to TDI at the detection limit (0.02 ppm). Using this comparison approach, the data could then be employed to project what level of interferent would be adequate to give a false positive response equivalent to that produced by 0.02 ppm TDI in room air.

The tested interferents exhibited a substantial range of responses in the chemiluminescent detection system. **Figure 10** presents a graphic summary of the relative responses to selected materials in room air relative to 0.02 ppm TDI in room air.

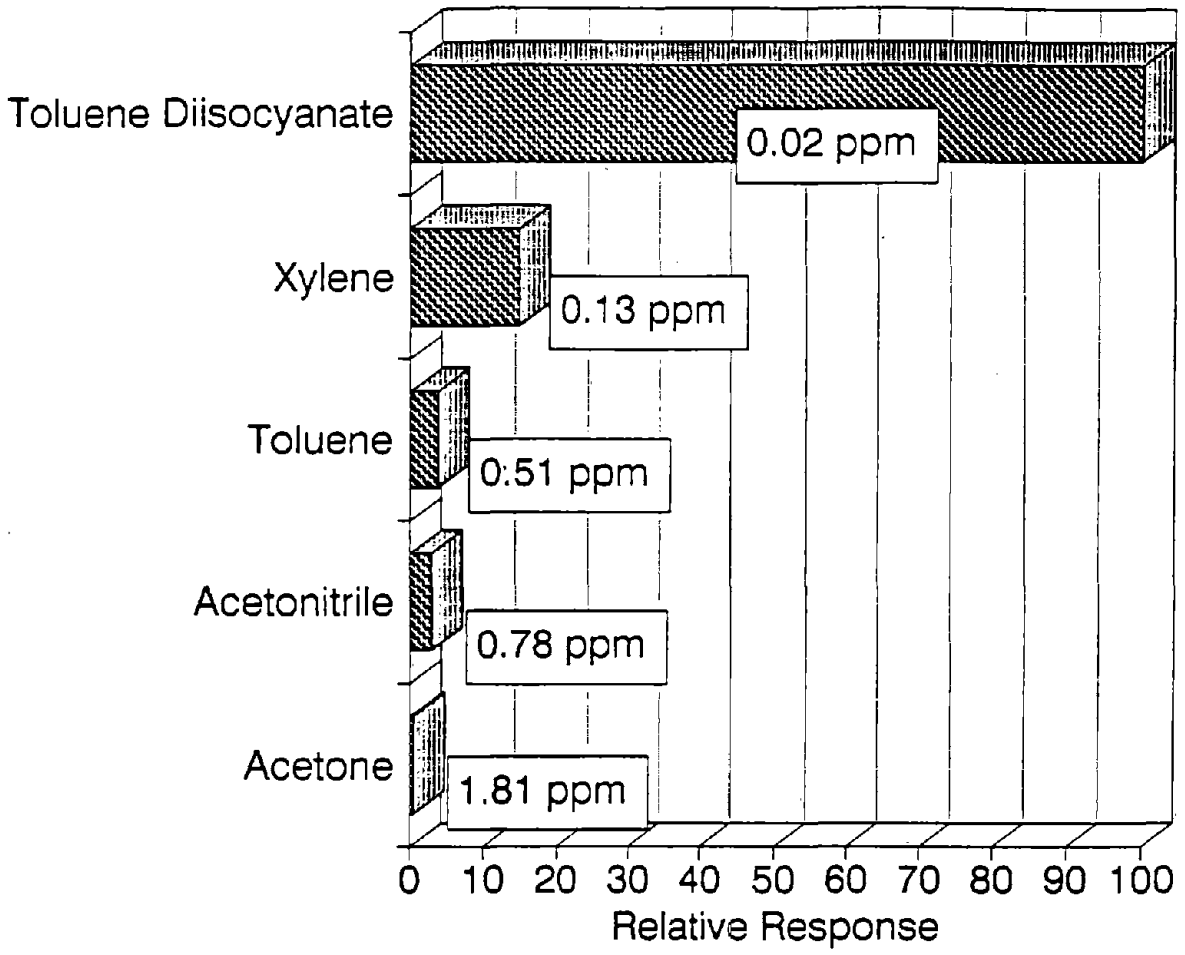

Figure 10 Relative Response Factors for Interferents and for 0.02 ppm TDI in Room Air

Based on the results of the interferents testing, it is concluded that the chemiluminescent monitor will have minimal sensitivity to species other than isocyanates because its sensitivity for isocyanates is significantly higher than that for any of the interferents tested when levels of isocyanate and interferent are comparable.

The interferent sensitivity of the monitor appears most directly related to the presence of carbon-nitrogen functionalities in the molecules to which it is most sensitive, a finding consistent with the proposed mechanism for chemiluminescence arising from CNO^* species. Among compounds with the C-N functionality, the alkyl amines (for example dimethyl amine and trimethyl amine) and aromatic amines (e.g. aniline) exhibit the highest

response with detection limits approaching that of TDI. While the chemiluminescent method developed in Phase I is thus sensitive to interference from amines, the impact of the sensitivity is mitigated by the fact that free amines are not typically present in workplace environments, in significant concentrations, in combinations with the common isocyanate species. If free amines are present at trace levels in the isocyanate products being used (as residual raw materials from the isocyanate manufacture), then their concentrations will much lower than that of the isocyanates and thus interferent effects will be negligible.

Nominal levels of interference from aromatic hydrocarbons reacting with active oxygen to produce chemiluminescence can most probably be minimized or eliminated by the choice of filters and exact wavelength of light monitored in the Phase II instrument. Literature reports (Krieger, et al, 1978; Houpt and Langeweg, 1981) on the reactivity of substituted benzenes indicate that the reactivity and thus chemiluminescent light output from these reactions is related to the ionization potential of the hydrocarbon molecule. The substituted benzene species have lower ionization potentials than the parent benzene molecule and thus exhibit higher reactivity and light output on an equimolar basis.

The activated CNO species can be envisioned as forming from direct decomposition of isocyanates, which contain this group, or from oxidation reactions involving active oxygen with amines, nitriles, and other compounds which contain only the C-N linkage in their structure. Reduction of interference from these materials will most probably not be reduced by the use of narrower bandpass filters in the monitor or by the use of a monochromator to more fully isolate the CNO^{*} emission wavelength. It is possible, however, that further adjustment in the ratio of active oxygen to sampled room air and/or modification of the residence time of sample in the chemiluminescence cell may allow increased sensitivity for isocyanates relative to amines.

Inorganic nitrogen compounds (ammonia) and oxygenated organics (alcohols, ketones, etc.) show little or no significant interferent impact as would be expected on the basis of the absence of C-N structural features in these compounds. As in the case of the aromatic hydrocarbon interferents, added spectral filtering of the chemiluminescent light reaching the PMT will aid in reducing the impact of these compounds as interferents in isocyanates monitoring.

The conclusion of the interferents tests is that the chemiluminescent isocyanates monitor is most susceptible to positive interference from other organic species containing the C-N linkage in their structure. The monitor is less sensitive to these compounds than it is to isocyanates, by a significant margin. Interferences from species other than those with C-N bonds in the molecules can be handled by spectral filtering techniques and the optimization of this filter selection is an appropriate task in the Phase II effort.

PROBLEM AREAS ENCOUNTERED

Based on the results of the Phase I testwork, the overall technical feasibility of using the chemiluminescent technique for detecting isocyanates in room air at a target level of 0.02 ppm has been demonstrated. However, there are several specific response features of the system which will require further testwork and design optimization in the Phase II effort in order to produce a prototype instrument for testing and validation in actual workplace environments as an isocyanates monitor. These areas for future investigation are discussed below.

Noise Sources and Instrument Drift Associated with Plasma

In operating the chemiluminescent monitor during the Phase I tests, it was noted that the oxygen plasma developed instability and that background noise from the plasma increased as the quartz tube containing the plasma aged. While no visible etching of the plasma containment tube was evident, the replacement of the tube with a new quartz unit reduced this noise and plasma instability in all instances.

Recent literature reports of the etching and aging effects observed in plasma generators used for emission spectroscopic analyses of both solution and gaseous samples also note this problem with tube etching and its negative effect on performance of the plasma as an emission source (Bolainez, et al, 1992).

The long term stability of the chemiluminescent monitor was not a specific item tested in the Phase I effort, but observation of the baseline stability of the monitor (when operating with only the trace chemiluminescence from the nitrogen (5-10 ppm) and subsequent NO_x arising from the pure oxygen feed to the plasma) suggested that some "zero drift" in PMT output could be expected on a timescale of 1-4 hours.

Additional testwork and design modification of the monitor in Phase II will better quantify the plasma tube aging phenomenon, propose remedial or corrective steps, and provide for electronic or calibration protocols to correct for the long term zero drift of the monitor. Alternative plasma confinement materials (such as alumina) may also be investigated in this regard.

DL a Function of Structure of Isocyanate

The chemiluminescent isocyanates monitor as developed and tested in Phase I shows a significant variation in sensitivity to different isocyanate species in room air.

The data on TDI, HMDI, and MIC suggest that the sensitivity of the monitor may be intrinsically higher for aromatic isocyanate species than it is for aliphatic isocyanates. The current exposure risk from aromatic isocyanates is probably higher than that from aliphatics because of the historical prevalence of aromatics in industrial applications. However, future trends appear to favor increased use of aliphatic isocyanates, particularly in coatings applications for severe outdoor service environments, and thus the issue of increased sensitivity to aliphatic isocyanates is an important one to address in the Phase II effort.

Increased sensitivity for the detection of aliphatic isocyanates by design changes in the Phase I monitor, including possible changes in sample rate of air to the monitor, alterations in the ratio of air sample to oxygen feed rate to the plasma, and similar factors should be a goal of the Phase II workplan.

Need to use Oxygen Instead of Air for Plasma Feed

The need to use oxygen, rather than room air itself, as the feed gas to the oxygen plasma is due to the substantial background chemiluminescence of NO_x formed in the plasma if any nitrogen is present. The spectral characteristics of this NO_x chemiluminescence is such that it cannot be effectively enough filtered from the CNO^* chemiluminescence to permit detection of isocyanates at the target 0.02 ppm level.

The need to use oxygen rather than air as the feed gas to the plasma generator is a feature of the monitor which impacts the overall size and design of the system, impacts the cost of operation as cylinder gas is required, but does not impact the overall feasibility of the monitor as an isocyanate monitor with adequate sensitivity to detect isocyanate species in room air at 0.02 ppm levels.

At a feed rate of about 60 cm^3/min, a standard oxygen cylinder would have adequate capacity to supply a continuous gas feed to the system for approximately 60 days. This does not represent an unreasonable system constraint from the standpoint of cylinder changeout frequency or cost of operating oxygen for the instrument.

Inability to Perform Compound-Specific Analyses

The Phase I proposal had envisioned using the chemiluminescent monitor as a compound-specific isocyanates monitor which would differentiate among various aliphatic or aromatic isocyanate species in air by virtue of spectral details or fingerprints in their chemiluminescent emission spectra.

Testwork in Phase I, as described above, led to the conclusion that the intensity of the chemiluminescent light from reaction of isocyanates with active oxygen was insufficient to permit spectral resolution as a means of differentiating among specific isocyanates.

DEGREE OF DEMONSTRATION OF TECHNICAL FEASIBILITY

The chemiluminescent isocyanate monitor designed, constructed, and tested in the Phase I effort has demonstrated the overall technical feasibility of the proposed concept for the real time analysis of isocyanate species in room air at sub-ppm levels. More specific details of the degree to which the technical feasibility has been demonstrated in several areas of monitor performance are cataloged below.

Meeting DL Goals

The Phase I instrument was capable of detecting toluene diisocyanate in room air at a concentration of 0.02 ppm with a signal to noise (S/N) ratio of approximately 3:1. Thus, for this industrially significant isocyanate compound, the DL goal was achieved.

The detection limit for aliphatic isocyanates (including hexamethylenediisocyanate and methyl isocyanate) was higher than the target 0.02 ppm limit with the monitor as constructed for the Phase I tests. Design and operational modifications to the monitor in Phase II may allow attainment of the DL goal for these and other aliphatic isocyanates.

Ability to Discriminate Among Isocyanates

The Phase I monitor was not able to provide discrimination among various isocyanate species on the basis of the spectral details in the chemiluminescent emission of products from reaction of the target isocyanates with plasma-generated active oxygen.

While the feasibility of the monitoring concept was demonstrated for total isocyanates in room air, the feasibility of using the monitor as a compound-differentiating instrument for multiple isocyanates at sub-ppm levels was not demonstrated.

Freedom from Interferences

The chemiluminescent monitor was shown to exhibit very little interference from organics likely to be present in workplace air along with isocyanates except for those organics which contained a carbon-nitrogen functional group in their structure. Thus, aliphatic and aromatic hydrocarbons, alcohols, and ketones (all potentially likely classes of interferents with potential industrial solvent usage) showed little or no significant chemiluminescent interference. In cases such as toluene or xylene where some low level chemiluminescence was observed, the emission is in a spectral region which can be isolated from the isocyanates emission by simple bandpass filters.

The Phase I monitor does respond positively to aliphatic and aromatic amines in room air and in some cases responds with sensitivity approaching that for isocyanates. The response to amines is probably due to formation of intermediate CNO species and their subsequent chemiluminescence reactions with the active oxygen from the plasma. The monitor is less sensitive to carbon-nitrogen species such as acetonitrile (CH_3CN) which have a carbon to nitrogen multiple bond in their structure.

The positive interference of amines in the Phase I isocyanate monitor is mitigated by the typical absence of significant levels of amine air contamination in the work environment that is being monitored for isocyanate exposure.

System Design for Phase II

The positive results of the Phase I effort have demonstrated the fundamental technical feasibility of the proposed technology for real time monitoring of isocyanates in room air at 0.02 ppm levels. Based on these test results, specific features to be addressed in the Phase II isocyanates monitor are presented below.

- The air sampling inlet to the chemiluminescent cell may be equipped with a three way switching valve to permit sequential sampling of room air and of a reference zero gas. By employing this modulated sample profile, the drift in the monitor associated with plasma drift and DC drift in the PMT circuits can be continuously compensated for.

- Additional design work on the oxygen plasma containment tube should focus on reducing plasma instability or noise resulting from etching or other reaction with the containment vessel.

- The alternative of using an RF coupled plasma in place of the microwave plasma employed in Phase I should be addressed since the electronic circuitry and costs for the RF source may be significantly lower than that for the microwave source.

- The specific style and size of vacuum pump to be incorporated into the Phase II monitor must be considered in light of the cost, maintenance requirements, and potential increase in sensitivity associated with transport of maximum quantities of both active oxygen and sampled room air into the chemiluminescent analysis cell.

- Optimization of the PMT type and of the electronics for amplification of the PMT output signal may lead to lower detection limits and higher sensitivity of the Phase II instrument for all isocyanates. This may be a primary approach to achieving higher sensitivity and lower detection limits for the aliphatic isocyanates.

- If sufficient increases in sensitivity can be made in the PMT portion of the Phase II instrument, then it may yet be possible to use a monochromator or other emitted light dispersion system to provide compound-specific analyses of isocyanates based on observed emission fingerprints. While the data from the Phase I tests suggest that this is an unlikely technical objective to meet, the great desireability of having isocyanate speciation in the monitor nevertheless suggests that this potential be explored to the maximum extent practical in Phase II.

- Improved detection sensitivity might also permit greater freedom from interference, even from aromatic or aliphatic amines, if enough amine-specific spectral data can be isolated to permit correction algorithm to be used in the spectral analysis.
- A more complete investigation of the possible enhancement of isocyanates chemiluminescence in the presence of trace nitrogen oxide species is germane to the issue of achieving lower detection limits for all isocyanate species.
- Additional design modification and optimization should result in a Phase II instrument with response to real time fluctuations in room air isocyanate concentrations faster than the 2 to 5 minute response time in the Phase I instrument.
- Finally, the incorporation of microprocessor capability in the Phase II instrument should yield a unit with improved ability to perform unattended sampling, analysis, data logging, and alarm functions with minimal routine maintenance.

PUBLICATIONS

No publication of results other than that in this Phase I Final Report has resulted from the conduct of this testwork.

INVENTIONS

The novelty and utility of the chemiluminescent technique for monitoring isocyanates in air is under continuing investigation with respect to potential filing for patent protection.

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15. Supplementary Notes

16. Abstract (Limit: 200 words) The main purpose of this project was to demonstrate the technical feasibility of an innovative chemiluminescent technique for the selective detection of isocyanate species in air at levels as low as 0.02 parts per million (ppm). The analysis was based on the generation of a reactive stream of oxygen atoms which is then combined with the air stream being sampled to produce activated CNO species from any isocyanates present. The activated CNO species then decay to ground state species with the emission of light which is detected and quantified as a measure of the amount of isocyanate in the original air sample. Using this approach, toluene-diisocyanate (584849) could be detected in room air at a level of 0.02 parts per million (ppm) by the chemiluminescent technique. Aliphatic isocyanates were detected but with detection limits higher than the target 0.02ppm. Further optimization of the system should extend the detection limits for these materials to the 0.02ppm level. The monitor provided nonspecific analysis of isocyanate species and therefore served as a total isocyanates monitor rather than as a monitor of individual isocyanate species in air. The preferred source of reactive oxygen for the monitor was high purity oxygen, rather than the originally proposed room air. Chemical interferant effects were minimal for typical organic compounds including aromatic hydrocarbons, alcohols, and ketones and inorganic species.

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