A REVIEW OF HYDRAZINE SENSORS
THE STATE OF THE ART

by

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ABSTRACT

Several types of sensors have been developed over the past few years that quantify the vapor concentrations of the hydrazines. These sensors are able to detect concentrations as low as 10 parts per billion (ppb) up to several parts per million (ppm). The scope of this review will be focused on those sensors that are most current in the marketplace as either leak detectors or personnel monitors. Some technical information on the theory of operations of each hydrazine detector will also be included. The review will highlight current operations that utilize hydrazine sensors including the Kennedy Space Center (KSC), the United States Air Force (USAF) at Cape Canaveral Air Station (CCAS), USAF F-16 facilities. The orientation of the review will be towards giving users usable practical information on hydrazine sensors.

INTRODUCTION

The National Aeronautics and Space Administration (NASA) and the United States Air Force (USAF) currently utilize "hydrazine", a hypergolic propellant, as rocket fuel. In the case of NASA and the shuttle program, this propellant may be found either as hydrazine (HZ) or monomethylhydrazine (MMH), depending on the applicable orbiter system. In comparison, the USAF uses HZ and MMH in various satellite programs and unsymmetrical dimethylhydrazine (UDMH) or AEROZINE-50 (50/50 mix of HZ and UDMH) in the Titan and Delta launch programs. The current Threshold Limit Value (TLV) for HZ, MMH, or UDMH is 10 ppb. This value, recently established by the American Conference of Governmental Industrial Hygienists (ACGIH), lowered the allowable level of exposure by a factor of 10 from the previous level of 100 ppb. Several sensors now exist that are able to monitor for potential toxic vapor concentrations as low as 10 ppb. This report briefly describes the detection techniques used by these sensors, followed by a review of these sensors and their operational use. In addition, sensors are reviewed that cannot meet the new 10 ppb ACGIH level but may be acceptable as area monitors capable of adequately quantifying higher vapor concentrations.

DETECTION TECHNIQUES

COLORIMETRIC

The principle of operation of a colorimetric sensor is the development of a color on a chemically impregnated sensor due to a reaction between the substrate impregnated on the sensor and any reactant chemical present in the air passing by the sensor. The intensity of the color is directly proportional to the concentration of the contaminant of interest in the sample. The determination of a concentration or dose value can be determined by manual comparison of the observed color to a "calibrated reference wheel" or electronic comparison of the color intensity to a calibrated color reader.

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* This work was performed under contract No. NAS10-98001 with NASA, John F.Kennedy Space Center, Florida. Approved for public release; distribution is unlimited.

CONDUCTIVE

The operation of a conductive sensor is based on the observed changes in the conductivity (resistance) of the sensor over time as the sensor is exposed to toxic vapors such as HZ, MMH, or UDMH. The changes in the conductivity (resistance) are caused by the adsorption of toxic vapors onto the surface of the sensor.

ELECTROCHEMICAL

In the case of hydrazine electrochemical sensors, the measured current is generated by the oxidation of HZ, MMH, or UDMH in an electrolytic cell. The output current of the detector is directly proportional to the concentration of the "hydrazine" vapors that pass by a sensing electrode. The specificity of the electrochemical system can be provided, in principle, by properly selecting the sensing electrode, supporting electrolyte, and the potential difference between the reference and sensing electrodes. Some electrochemical systems employ a third, or counterelectrode, to provide added stability.

INFRARED (IR)

An IR detector measures the amount of energy absorbed by molecules such as HZ, MMH, and UDMH. Diatomic molecules such as oxygen, nitrogen, and hydrogen to not absorb in the mid-IR region of the electromagnetic spectrum. IR spectroscopy is the measurement of the wavelength and intensity of the absorption of mid-infrared light by a sample. Mid-infrared light (2.5 - 50 μm, 4000 - 200cm-1) is energetic enough to excite molecular vibrations to higher energy levels. A Nichrome filament is commonly used as a source of IR radiation. The wavelength of IR absorption bands are characteristic of specific types of chemical bonds, and IR spectroscopy finds its greatest utility for identification of organic and organometallic molecules.

CHEMILUMINESCENCE

The term "chemiluminescence" refers to the emission of light from a chemical reaction. In its simplest form several reactants form an excited state intermediate. The decay of the intermediate results in a product and the emission of light. This reaction can occur in the gas, liquid and solid phases. The light emitted from chemiluminescent reactions has differing degrees of intensity, lifetime and wavelength. The wavelength can extend across the spectrum from near ultraviolet, through the visible and into the near infrared. Solution phase chemiluminescent reactions which have found analytical application often produce light in the visible region.

PHOTOACOUSTIC

In PhotoAcoustic Spectroscopy (PAS) the gas to be measured is irradiated by intermittent light of a pre-selected wavelength. If the frequency of the light is coincidental with an absorption band of the gas, the gas will absorb part of the light. The heat generated by the absorbed light causes the gas to expand and results in a pressure rise. By chopping the light the pressure alternately increases and decreases and generates an acoustical signal. This signal is subsequently detected by a microphone.

ION MOBILITY

A small portion of an air sample that is drawn over the surface of a semi-permeable membrane is transferred to the detector side of the membrane through solution, diffusion and evaporation mechanisms. The materials that have passed through the membrane are transferred to an ionization region and mixed with a secondary sample of air containing a dopant. A radioactive source generates high energy particles that cause the formation of positively and negatively charged ion clusters. These ions are eventually separated, collected and quantified using "time of flight" principles from mass spectroscopy

SENSORS

PERSONAL

Colorimetric (Dosimeter Badges)

At present, a two-spot passive dosimeter badge developed and tested by the Naval Research Laboratory (NRL) and Geo-Centers, is extensively used at Kennedy Space Center (KSC) for personnel monitoring of HZ and MMH. This badge, manufactured by Bacharach/GMD, utilizes two chemistries: para-N,N-dimethylaminobenzaldehyde (PDAB) and vanillin, to quantify either HZ or MMH and assure that no false positives occur. A color must be observed on both spots of the badge as verification of the presence of toxic vapors. In the case of both HZ and MMH, the PDAB spot turns orange, while the vanillin turns yellow. There is no observable color when the badge is exposed to UDMH vapors. The minimum detectable doses of HZ and MMH for this badge are 25 ppb-hr and 50 ppb-hr, respectively. Relative humidity had little effect on the response of the badges. The badges are good for 3 to 4 days if unexposed to sunlight or any HZ/MMH. Tobacco smoke is a minor interferent for the vanillin chemistry, generating a pink/purple coloration. A holder is available consisting of a black, plastic molded housing fitted with a Lumar polyester sheet that eliminates the effects of sunlight.

Unlike HZ and MMH, there is no reaction between UDMH and vanillin. In comparison, UDMH reacts with 2,4-dinitrobenzaldehyde (DNB) to form a yellow color, but HZ and MMH produce little to no color. Utilizing this non-reactivity a two-spot passive badge was developed by NRL and manufactured by Bacharach/GMD that positively identifies the presence of UDMH while making sure the presence of only HZ or MMH does not interfere. The minimum detectable dose of UDMH for this badge is 40 ppb-hr. The DNB does not respond to ammonia, nitrogen dioxide, alcohols, or amines and is not effected by changes in the relative humidity. The DNB spot on the badge can be covered with an UV-absorbing window to prevent any sunlight effects.

The K and M Environmental Corporation has developed a simple, direct-read one-spot passive badge for all of the hydrazines (HZ, MMH, and UDMH). The badge operates on the same principle of diffusion employed by the GMD 2-spot badge. The presence of HZ, MMH, or UDMH is indicated by the formation of a color change in the shape of an exclamation mark inside a triangle on the front of the badge. Unlike the GMD/NRL badges, that are constructed from impregnated filter paper, the K&M sensors are fabricated from a uniformly coated indicator layer placed on an inert surface. This alternative construction causes the sensor to be more sensitive and consistent in its' color formation. The minimum detectable levels (MDL) for HZ, MMH, and UDMH are 4.5, 6 and 10 ppb-hr, respectively. Unlike the GMD/NRL badges, testing at a variety of humidities ranging from 20 to 85 % indicate that the best results were obtained when the Relative Humidity (RH) is greater than 55%. The effects of cross interferences including 25 ppm ammonia, alcohols, aromatic hydrocarbons, aromatic amines, halogenated hydrocarbons, aldehydes, carbon monoxide, and nitrogen dioxide were tested. None of these chemicals showed any effect on the performance of the badges. The HZ/MMH sensor is ten times more sensitive to HZ and MMH than to UDMH. In comparison, the UDMH badge is ten times more sensitive to UDMH than to either HZ or MMH.

Modifications of the passive 2-spot dosimeter badge to incorporate an active pumping system have led to decreasing the amount of time needed to ascertain the presence/absence of a potentially toxic vapors. In the case of UDMH, a 1-spot dosimeter badge, manufactured by Bacharach/GMD, that utilizes DNB chemistry, has an MDL of less than 50 ppb-L. At the 10 ppb level and a pumping rate of 1 standard liter per minute (sLpm) a discernible color would be visible after 5 minutes.

The Interim Active Vanillin Sampler (IAVS), developed by the Applied Chemistry Lab (ACL) at KSC, consists of an intrinsically safe sample pump (GILLIAN) that draws ambient air through a single-spot dosimeter badge (GMD Sure-Spot) treated with vanillin and phosphoric acid. Laboratory testing has shown that the badge shows a yellow color after sampling 10 ppb HZ or MMH vapors for 3 minutes at a rate of 2 sLpm. These vapor concentrations may be determined either by comparison to a calibrated vanillin color wheel or reading with a commercially available color analyzer such as the Minolta Chromameter.

Conductive (Polymer-based dosimeter)

The Spire Corp. and Spectral Sciences, Inc. initially developed a conductive polymer-based dosimeter using poly(3-hexyl) thiophene-based sensing elements. The rights to this sensor have recently been transferred to the Physical Sciences Corp. The original sensor demonstrated a minimum detectable dose of approximately 1 ppb- hr and a saturation dose of approximately 250 ppb-hr as measured in dry conditions. Although this result offered sufficient coverage of the TLV limit of 80 ppb-hr, testing in a humidified environment with greater than 60% RH indicated increased sensor reactivity and a reduced saturation dose of only 30 ppb-hr. In addition to the observed problems with humidity, the sensor seemed to off-gas starting material (HZ or UDMH), even when neither of these chemicals was present. The sensor has undergone refinements in both the software and sensor itself, in an effort to minimize the effects of humidity. The off-gassing has not been confirmed and the issue is being revisited through an additional series of tests. A later version of the sensor has been fabricated with a thicker polymer film that may raise the saturating dose and allow for a broader dynamic range for the sensor. Testing of the refined sensors is currently on-going.

PORTABLE

Colorimetric (Paper Tape)

The AutoStep Plus, a portable sensor manufactured by Bacharach/GMD, quantifies the amount of chemical contaminant (HZ/MMH/UDMH) by measuring a specific color reaction on a paper tape cassette using light reflectance. The amount of reflected light and incoming concentration of the chemical contaminant are inversely proportional; i.e. a more intense color detected on the paper tape is interpreted as the presence of a higher concentration in the vapor sample; less light is reflected back to the detector. The advertised ranges for all the hydrazines are: 0 to 550 ppb (low) and 0 to 1000 ppb (high). This sensor has been tested by the ACL at KSC and found unable to quantify vapor concentrations of HZ, MMH, or UDMH at the advertised 10 ppb level. Work is in progress by Bacharach/GMD to develop paper tape that will be insensitive to changes in humidity and also able to quantify vapors at the 10 ppb level.

The ChemKey TLD and SPM monitors, both manufactured by Zellweger Analytics (formerly MDA Scientific), are portable gas sensors that utilizes an exclusive Chemcassette® to monitor for toxic chemicals. Both the TLD and SPM run on batteries with continuous run times of 4 and 8 hours, respectively. The SPM can be fabricated with a Z-purge package to allow placement of the analyzer into a hazardous environment. In this mode, the SPM is line powered only. The phosphomolybdic acid (PMA) impregnated tape utilized in both the TLD and SPM develops a stain upon exposure to UDMH, MMH, or HZ. The intensity of the stain is measure of the concentration of gas present. The Chemcassette® is continually advanced to prevent poisoning the sensor. The standard ranges available for MMH, HZ, and UDMH are 21 to 600, 20 to 300, and 53 to 1500 ppb. The low ranges available are 3 to 30 ppb for MMH, 2 to 30 ppb for HZ, and 5 to 30 ppb for UDMH.

Electrochemical

The Interscan series 4000 2-electrode electrochemical monitor is cable of detecting MMH and HZ vapor concentrations at the 10 ppb level. This analyzer is somewhat high in maintenance since it requires the periodic addition of water to the electrochemical cell. The depletion of the water from the cell is due to the evaporation of supporting electrolyte as sample air is pumped across the surface of the sensing electrode. The overall life of the cell is decreased due to the intrusion of CO_2 into the cell (300 ppm in air) and the subsequent formation of carbonic acid. This acid neutralizes the basic cell electrolyte forming carbonates in the process. Although the formation of carbonate cannot be stopped, the substitution of cesium hydroxide (CsOH) for potassium hydroxide (KOH) has led to a more soluble carbonate species and helped to prevent plugging of the sensor membrane. The minimum detectable level (MDL) of MMH or HZ using the Interscan 10 ppb analyzer is 2 ppb. Work is currently being done in an attempt to lower the 90% Full Scale (FS) response time to less than 10 minutes. Additional work is being done to increase the calibration cycle from 30 to 45 or 60 days. The current specifications for the 10 ppb sensors require that the 50% FS response time be 2 minutes or less.

GINER, Inc. has developed a lightweight compact 3-electrode electrochemical sensor capable of detecting HZ, MMH, or UDMH at the 10 ppb level. The solid polymer electrolyte-based sensor has a response time of 3-4 minutes (90% FS) for low ppb levels of UDMH. Response times for both MMH and HZ are considerably higher. The linear range of the sensors is from 10 to about 100 ppb. The noise exhibited by this sensor is less than 0.5 ppb, and the drift was less than 0.5 ppb over a 4 hour period of zero air sampling (no HZ, MMH, or UDMH present). In comparison, the response of the sensor drifted less than 0.5 ppb over a 4 hour period of sampling a stable ppb level of UDMH. The response accuracy of the sensor was not affected by RH changes between 20 and 80%. A rejection ratio of more than 200:1 was noted for a 50 ppm ammonia vapor sample. There are no changes in the electrolyte concentration during operation. Carbonation of the electrolyte does not effect the response of the sensor. For maintenance, the sensor only requires the addition of 5 to 10 cc of water every 3 to 5 days, based on 6 to 8 hours of usage per day. The sensor contains an on-board microprocessor that continuously collects sensor output for subsequent downloading to a PC. The MDL of any of the three hydrazines is 2 ppb. Work is currently being done on evaluating improved sensors with shortened response times for both MMH and HZ. These sensors are not yet commercially available.

Ion Mobility

A modified hand-held ion mobility spectrometer (IMS) manufactured by <u>Graseby Ionics</u> has been evaluated as a field analyzer for MMH and HZ. During initial testing the MDL for MMH was found to be 6 ppb with a 0 to 1 ppm total analytical range and an insensitivity to humidity change, acetone and selected chlorofluorocarbons. The initial observed ammonia interference was decreased by changing the internal dopant to 5-nonanone from acetone. As a further test of the IMS for space flight use, the spectrometer was flown on two Space Shuttle missions: STS-37 and STS-49. The usefulness of the monitor was emphasized on the first mission. In comparison, the second mission focused on the development of operational procedures. Calibration of the monitor was performed before and after STS-37 at ambient pressure to concentrations of HZ and MMH ranging from 40 to 615 ppb. In addition, the humidity was varied from 0 to 80 % RH at 100 ppb to access instrument stability. Testing before and after STS-49 was done at 10.2 pounds per square inch (psia) to simulate Extravehicular Activity (EVA). The published spectra of HZ, MMH, and ammonia show that separation and quantification of the individual hydrazines can be accomplished under EVA conditions. Response times (90% FS) varied from a low of 2 to 3 minutes at 500 ppb to a high of 4 to 5 minutes at 55 ppb. Recovery times were observed as long as 35 minutes (296 ppb).

In an effort to develop an instrument capable of monitoring at the 10 ppb level <u>Graseby Ionics</u> incorporated some of the features of the hand-held unit into a larger "transportable" analyzer. The 5-nonanone dopant was retained, but the sample inlet system was modified to reduce any potential surfaces that could react with HZ, or MMH, prior to introduction into the Ionization Region of the IMS. In addition, the dopant container was protected from evaporation by means of a closed-loop pneumatic system containing a diffusion source of the dopant. During tests at the Toxic Vapor Detection Laboratory (TVDL) the IMS was never able to quantify HZ or MMH concentrations any lower than 20 to 30 ppb despite repeated service calls by Graseby Ionics personnel.

Chemiluminescence

Several chemiluminescent detectors have been fabricated and tested by <u>NRL</u> for their ability to monitor low ppb levels of HZ in air. Initial work centered on using luminol and platinum to generate a signal from the catalytic oxidation of HZ. A sample of air containing the HZ is simultaneously pumped down a Teflon tube containing the luminol solution. A photomultiplier tube (PMT) is used for detection of the liquid. The linear range of this system is 10 to 2000 ppb with a maximum response achieved in less than 2 minutes. Using a ruthenium complex as the chemiluminescent reagent sub-ppb detection limits have been observed for HZ, MMH, and UDMH. This sensor is very pH dependent due to the effect on the reagent as well as reactivity HZ, MMH, and UDMH. Further work on the ruthenium complex sensor has incorporated a three electrode electrochemical cell. This cell is used to continually regenerate the active reagent. The sensitivity order of the hydrazines have been found to be HZ >> MMH > UDMH. The response times for analysis range from seconds to several minutes depending on the analyte.

IR

The <u>MIRAN SapphIRe</u> , manufactured by the <u>FOXBORO Corporation</u>, is a portable ambient air analyzer capable of analyzing for over 100 individual chemicals. Using an optical filter and a variable pathlength gas cell (0.5 to 12.5 meters) the SapphIRe can measure both ppb and ppm concentrations of chemical vapors. The MDL for a specific compound depends on its' IR absorption characteristics. Up to 5 compounds can be measured simultaneously in the presence of 5 additional compounds. In the case of HZ, the measurement range is 0 to 50 ppm, with an MDL of approximately 500 ppb.

FIXED

Colorimetric (Paper Tape)

The MDA 7100, manufactured by Zellweger Analytics (formerly MDA Scientific), is a fixed single point gas sensor that utilizes the same Chemcassette® as the portable TLD and SPM sensors to monitor for toxic chemicals. The standard ranges available for MMH, HZ, and UDMH are 10 to 2000, 10 to 1000, and 10 to 5000 ppb, respectively. Low range calibrations are also available for MMH (5 to 100 ppb), HZ (2 to 1000 ppb), and UDMH (3 to 100 ppb). Tests by the Naval Research Lab (NRL) indicate that the UDMH MDL is 26 ± 6 ppb with the HZ and MMH MDL values likely to be even higher. This analyzer is designed to work for a single sample point.

The Remote Intelligent Sensor (RIS), a Bacharach/GMD product, is housed in an environmentally sealed, intrinsically safe package. It has internal battery back-up that enables the RIS to operate for up to eight hours in case of a power outage. The sensor for this instrument is the same paper tape system the portable AutoStep Plus employs. The detection range available for both HZ and MMH is 0 to 2 ppm with an MDL of 20 ppb. The Communications and Networking Package option available with the RIS makes it possible to network as many as 120 units.

Electrochemical

The Applied Chemistry Lab (ACL) at KSC has field-tested a Hydrazine Vapor Area Monitor (HVAM) designed as a continuous ambient air monitoring system. The HVAM incorporates the Zellweger Analytics/Polymetron HZ Analyzer as the core detector. This detector is a three-electrode liquid analyzer typically used in boiler feed-water applications. A dual-phase sample collection/transport method is utilized that simultaneously pulls ambient air samples containing HZ and a very dilute sulfuric acid solution (0.0001M) down a length of ¼ inch outside diameter (o.d.) tubing from a remote site to the analyzer. The remote site can be as far as 60 feet away from the core detector. The dilute acid is separated from the air and adjusted in pH to a value greater than 10.2 prior to analysis. The dilute acid and base solutions are continuously generated during the operation of the analyzer by mixing small metered volumes of more concentrated acid/base with dilution water. A set of Barnstead ion-exchange cartridges purifies all of the wastewater for reuse. The pumping of all liquids within the analyzer is accomplished using a single pump motor fitted with a mix of peristaltic pump heads. Adding a stirrer in the liquid cell has enhanced the signal/noise (S/N) ratio of the analyzer. The onboard microprocessor continuously monitors liquid levels, sample vacuum, and liquid leak sensors. The overall response of the system can be checked periodically by capturing the analyzer response to a known amount of calibration standard that is injected into the dilute acid line. The ppb output of the analyzer is adjusted based on the measured response from the internal calibration standard. Changes in the peristaltic pump rate due to aging of the tubing are compensated for using this methodology. This analyzer is designed to operate for 90 days unattended. At the end of this operational period, a Line Replaceable Unit (LRU) is taken out of the analyzer, pump tubing replaced, fresh acid, base, and calibration solutions prepared, and the core detector recalibrated. The downtime of the analyzer system can be minimized by using a second LRU as a backup. The MDL for the HVAM is 2-3 ppb. The analyzer can be calibrated for HZ, MMH, or UDMH with response factors of 1.0, 0.75, and 0.3, respectively. The analyzer can quantify vapor concentrations for 2 ranges: 0 to 1000 ppb, or 0 to 10 parts per million (ppm). The response time for a 10 ppb sample is 10 to 12 minutes (90% FS) with a large cell of approximately 25 cubic centimeters (cc) in volume. A small prototype cell (5- 10 cc) has been tested and shown to have a response time (90% FS) of approximately 3 minutes. The analyzer is currently single point. Future modifications to the system include the addition of multi-point (6) capability.

The ENMET Corporation manufactures several sensors that can sense HZ, MMH, or UDMH in the ppm range. The EN-GUARD system can be configured for up to 10 sensors all operating in the range of 0 to 1 ppm. The sensor that comprises the core analyzer is a disposable amperometric two electrode sensor with a life expectancy of 9 to 12 months. The ability of this system to quantify vapor concentrations at the 10 ppb level has not been determined. A second fixed monitoring system, the TG-Series, is available with a measurement range of 0 to 10 ppm. The TG-Series, like the EN-GUARD, can be configured with up to 10 sensors. The TG-Series sensor utilizes a cylinder filled with electrolyte that can be refilled periodically as needed. The CTX 2042 series, a more advanced version of the TG-Series, has interchangeable sensors, is precalibrated for the gas of choice, and includes the sensor and transmitter in one housing. The Smart Block Sensors® used in the CTX analyzers are utilized by ENMET for most of their portable analyzers.

The Drager Corporation manufactures an electrochemical three electrode sensor for the continuous real-time monitoring of HZ, MMH, an UDMH. The sensor is used together with the Polytron 2 transmitter. The default measuring range for the sensor is 0 to 1 ppm with a projected lower detection limit of 0.02 ppm (20 ppb). The expected sensor life is > 12 months.

Photoacoustic

The Bruel & Kaer INNOVA 1312 multi-gas monitor can quantitatively analyze up to 5 components and water vapor. The analyzer makes use of optical filters to monitor for a specific gas. Samples can be collected from points as far as 200 feet away. With the addition of a Multipoint Sampler air samples from up to 12 locations can be analyzed. Using a 5 second sample integration time the MDL for HZ is 100 to 200 ppb. If the sample integration time is increased to 50 seconds the MDL drops to a range of 15 to 30 ppb. In comparison to standard IR analyzers the photoacoustic analyzer is generally considered to be more stable. For example, zero point drift is almost non-existent as zero is always reached when there is no gas present.

IR

A MIDAC Fourier Transform Infrared (FTIR) spectrometer has been incorporated into an intrinsically safe, purged enclosure as part of prototype replacement Hypergolic Vapor Detection System (HVDS) at KSC. The analyzer was acoustically isolated from the vibrations produced by the shuttle as it leaves the launch pad. The FTIR and associated hardware remained operational through 2 shuttle launches. The prototype system was capable of analyzing 6 sample points at a rate of 1 sample point/minute. The maximum sample line length was 200 feet. The MDL for MMH was determined to be 500 ppb.

RESULTS AND CONCLUSIONS

The data presented in Table 1 summarizes the "hydrazine" sensors presented in the body of this report. There are very few sensors available that can measure vapor concentrations at the ACGIH level of 10 ppb. Most sensors can easily measure at the ppm level. Since the 10 ppb level of measurement has been mandated by the ACGIH for personnel monitors it is imperative that programs continue to be funded towards this end.

ACKNOWLEDGEMENTS

The author wishes to thank all those who contributed to this paper through their efforts at evaluating instrumentation and continuing to explore better ways to monitor for toxic chemicals such as HZ, MMH, and UDMH.

Table 1. Hydrazine Sensors (Summary)

Sensor	Type	Manufacturer	MDL	HZ/MMH/UDMH	Comments	COTS
Colorimetric	Personal/Dosimeter	Bacharach/GMD	25, 50 ppb-hr	HZ, MMH	2-spot (PDAB/Vanillin)	Yes
Colorimetric	Personal/Dosimeter	Bacharach/GMD	40 ppb-hr	UDMH	2-spot (DNB/Vanillin)	No
Colorimetric	Personal/Dosimeter	K and M	4.5, 6, 10 ppb-hr	HZ, MMH, UDMH	1-spot, exclamation point	Yes
Colorimetric	Personal/Dosimeter	Bacharach/GMD	50 ppb-hr	UDMH	1-spot	No
Colorimetric	Personal/Dosimeter	Bacharach/GMD/ACL	30 ppb-min	HZ, MMH	1-spot, IAVS	Yes
Conductive Polymer	Personal/Dosimeter	Physical Sciences Corp.	(1)	HZ, UDMH	Problems with humidity	No
Colorimetric	Portable	Bacharach/GMD	10 ppb (2)	HZ, MMH, UDMH	Auto-Step Plus	Yes
Colorimetric	Portable	Zellweger Analytics	2,3,5 ppb (2)	HZ, MMH, UDMH	Chem Key TLD/SPM	Yes
Electrochemical	Portable	Interscan	2 ppb	HZ, MMH	Series 4000	Yes
Electrochemical	Portable	GINER	2 ppb	HZ, MMH, UDMH	Linear to approx 100 ppb	No
Ion Mobility	Portable	Graseby Ionics	10 ppb (2)	HZ, MMH	Used on shuttle	Yes
Ion Mobility	Transportable	Graseby Ionics	20 to 30 ppb	HZ, MMH	Can't see 10 ppb	No
Chemiluminescence	Portable	NRL	Sub-ppb	HZ, MMH, UDMH	pH dependent	No
IR	Portable	Foxboro	500 ppb	HZ	Worn on shoulder	Yes
Colorimetric	Fixed	Zellweger Analytics	25 ppb (UDMH)	HZ, MMH, UDMH	HZ, MMH MDLs higher (?)	Yes
Colorimetric	Fixed	Bacharach/GMD	20 ppb (2)	HZ, MMH	Questionable MDL	Yes
Electrochemical	Fixed	ACL	10 ppb	HZ	Prototype	No
Electrochemical	Fixed	ENMET	100 ppb (2)	HZ, MMH, UDMH	EN-GUARD (0 to 1 ppm)	Yes
Electrochemical	Fixed	ENMET	100 ppb (2)	HZ, MMH, UDMH	TG-Series (0 to 10 ppm)	Yes
Electrochemical	Fixed	ENMET	(1)	HZ, MMH, UDMH	CTX 2042 (0 to 1 ppm)	Yes
Electrochemical	Fixed	Drager	20 ppb	HZ, MMH, UDMH	PAC-3 MDL 10 ppb	Yes
Photoacoustic	Fixed	Bruel & Kaer INNOVA	15 to 30 ppb	HZ	50 sec sample integration	Yes
IR	Fixed	MIDAC	500 ppb	MMH	Tested on shuttle pad (KCS)	Yes

NOTES:
(1) No data available
(2) Questionable value

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- Background
- Detection Techniques
- Sensors
- Summary

BACKGROUND

- Hypergols (HZ, MMH, UDMH) used by NASA and USAF
- Old TLV of 100 ppb lowered to 10 ppb by ACGIH
- User need for reliable sensors

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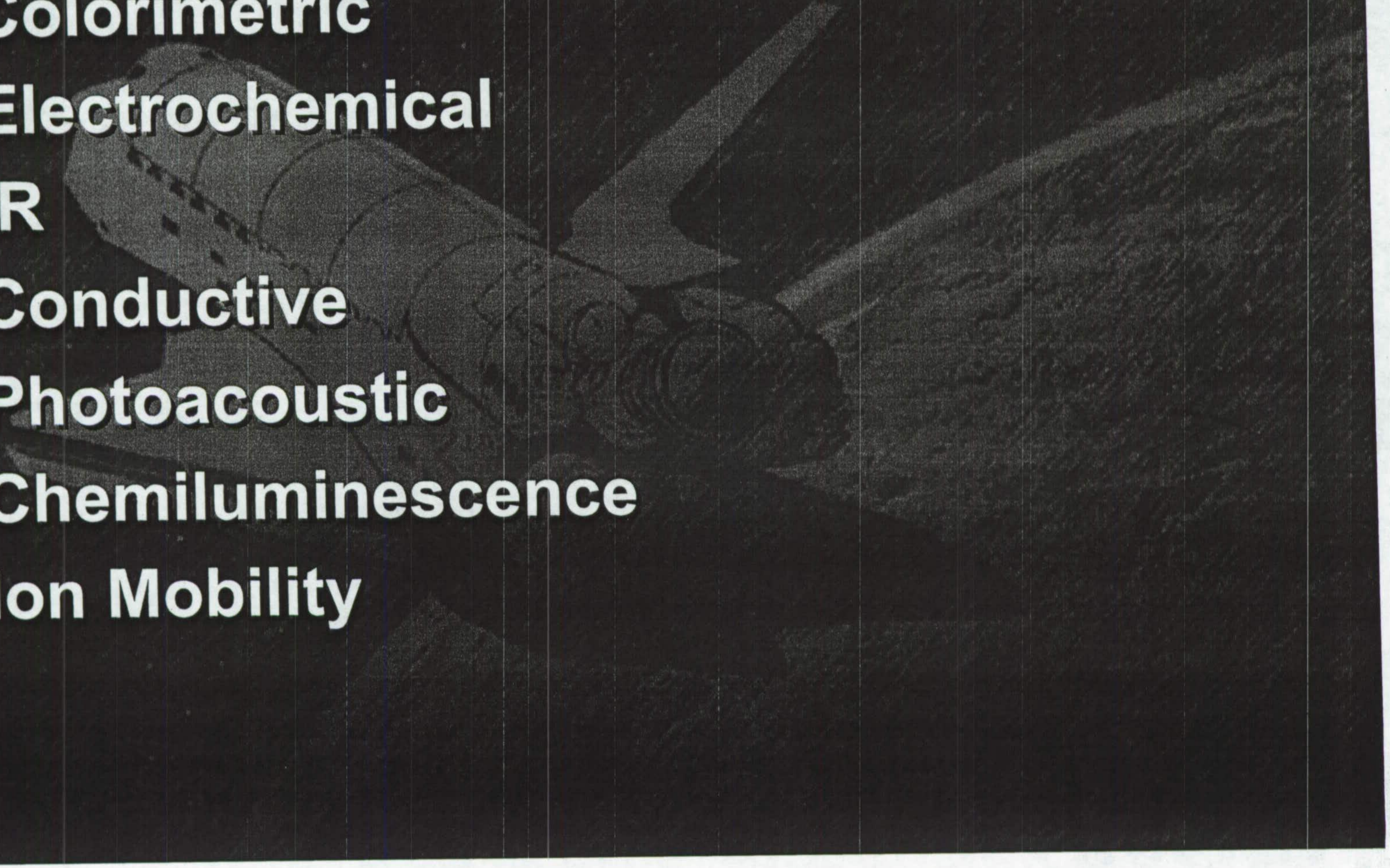
DETECTION TECHNIQUES



- Colorimetric
- Electrochemical
- IR
- Conductive
- Photoacoustic
- Chemiluminescence
- Ion Mobility

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SENSORS

Personal

- Dosimeter Badge (Colorimetric)
  - 2 spot Passive (Bacharach/GMD) (COTS)
    - MDL HZ/MMH (20 to 50 ppb-hr)
  - 1 spot Passive (K&M Environmental) (COTS)
    - MDL HZ/MMH/UDMH (4.5, 6, 10 ppb-hr)
  - 1 spot Active (Bacharach/GMD)
    - MDL HZ/MMH (30 ppb-min)

SENSORS

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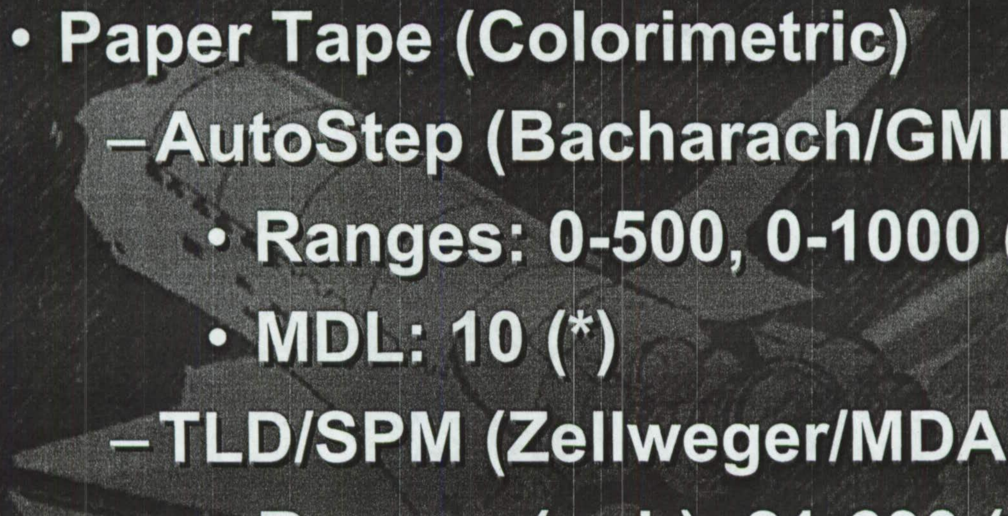
Personal

- Dosimeter Badge (Conductive)
  - Polymer Sensor
    - MDL (250 ppb-hr)
  - In Test with new coatings and software to compensate for humidity and off-gassing effects

SENSORS



Portable

- Paper Tape (Colorimetric)
  - AutoStep (Bacharach/GMD) (COTS)
    - Ranges: 0-500, 0-1000 (All)
    - MDL: 10 (*)
  - TLD/SPM (Zellweger/MDA) (COTS)
    - Ranges (ppb): 21-600 (3-30) MMH 20-300 (2 to 30) HZ; 53 to 1500 (5-30) UDMH
    - MDL: 10 (*)

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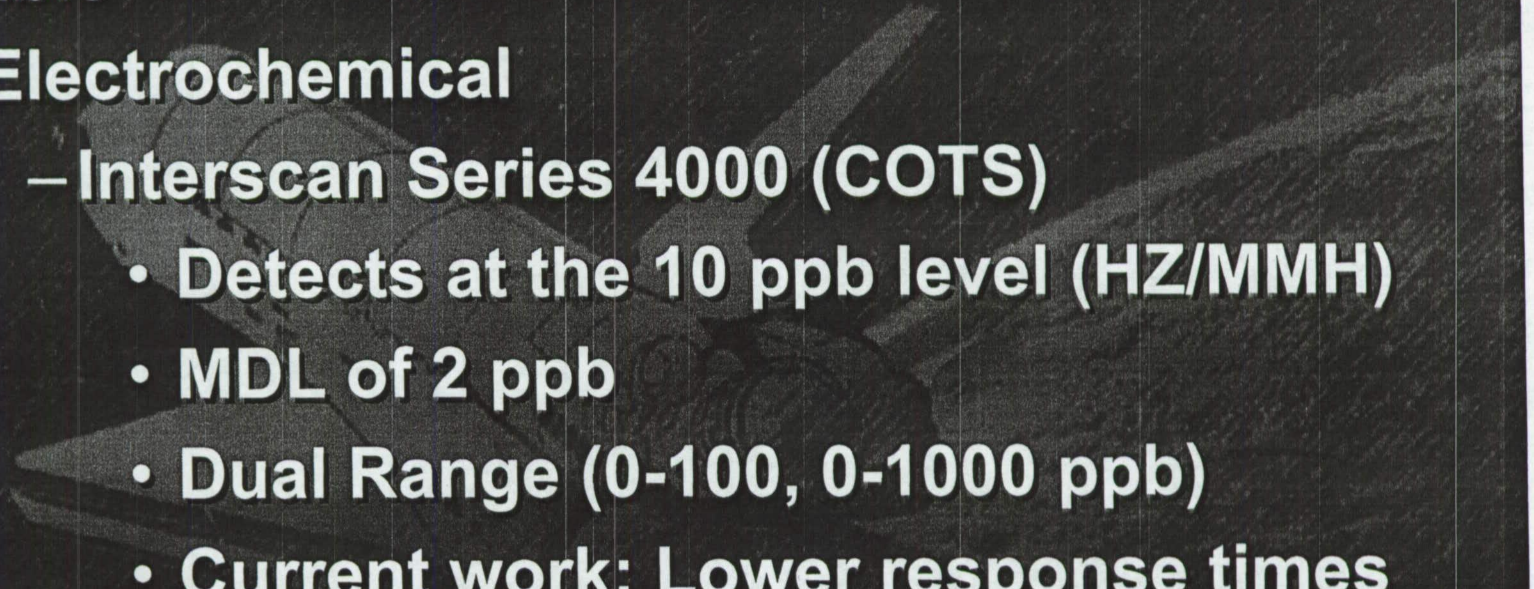
SENSORS



Portable

- Electrochemical
  - –Interscan Series 4000 (COTS)
    - Detects at the 10 ppb level (HZ/MMH)
    - MDL of 2 ppb
    - Dual Range (0-100, 0-1000 ppb)
    - Current work: Lower response times and increase calibration cycles

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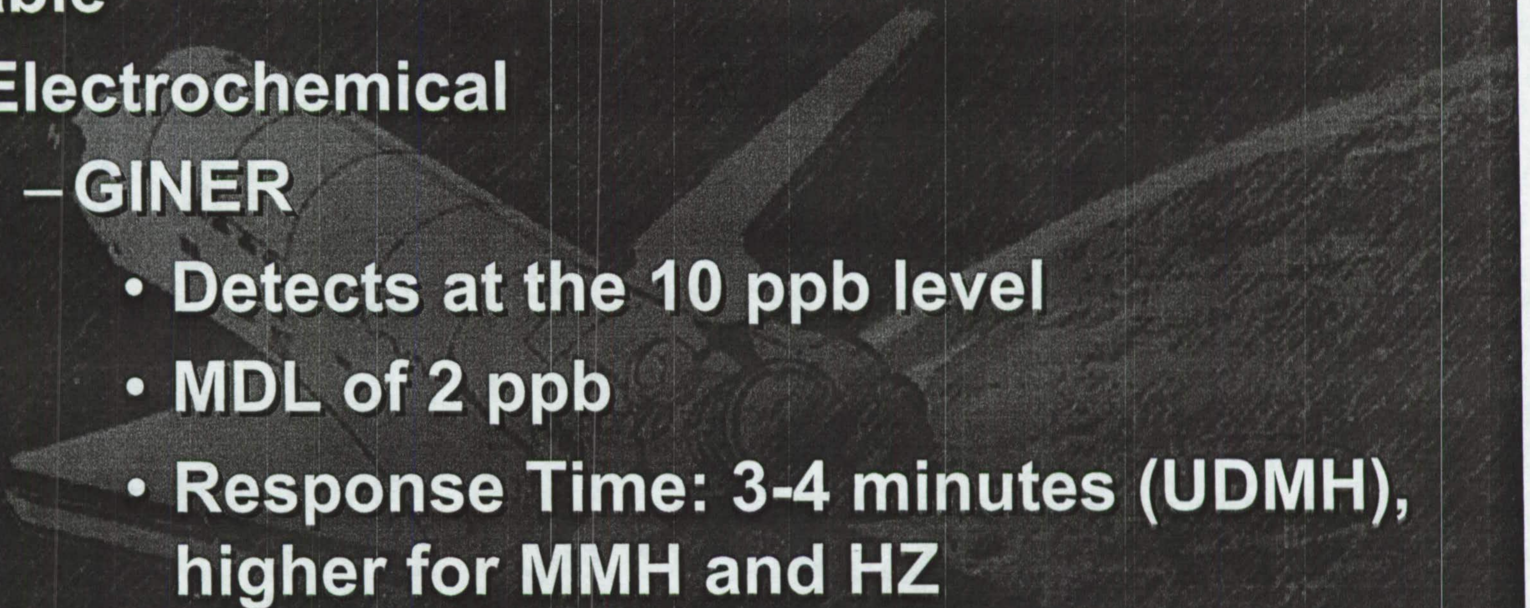
CORPORATION

SENSORS



Portable

- Electrochemical
  - GINER
    - Detects at the 10 ppb level
    - MDL of 2 ppb
    - Response Time: 3-4 minutes (UDMH), higher for MMH and HZ
    - Current work: Lower response times

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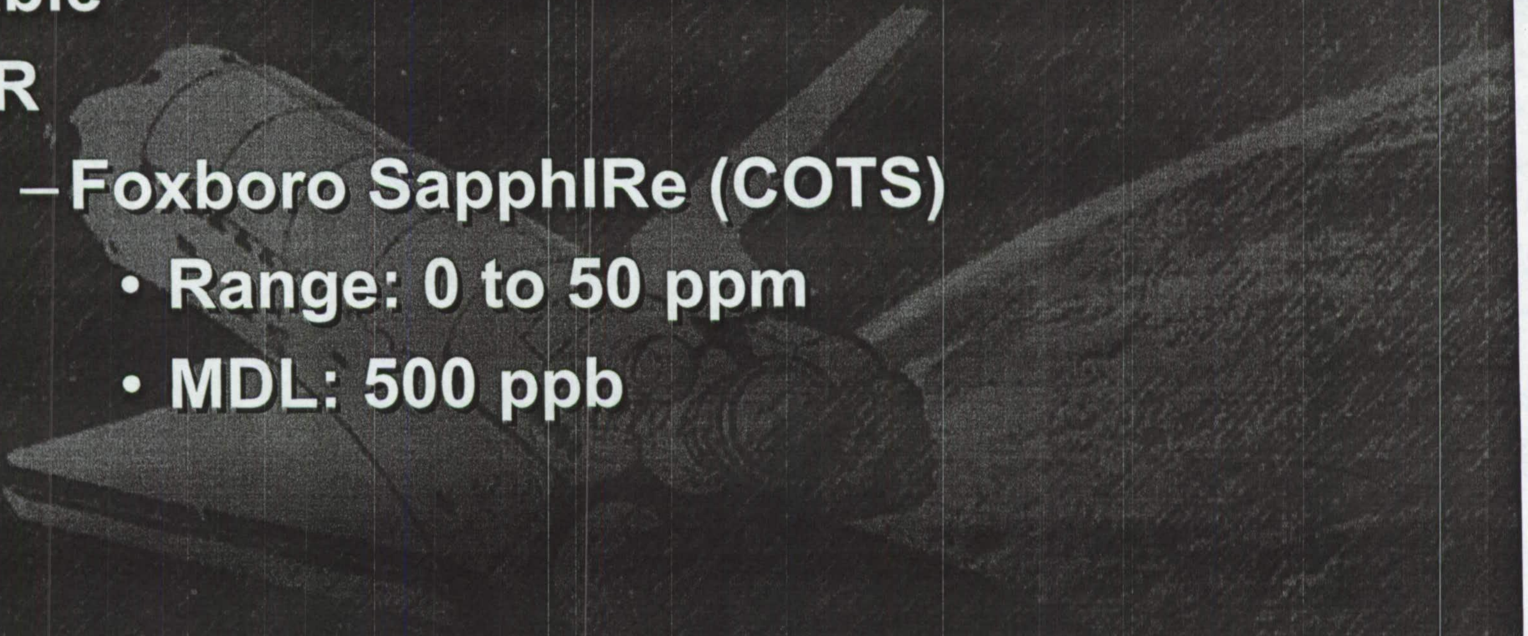
SENSORS

Portable

- ION Mobility
  - Graseby
    - Cannot detect at the 10 ppb level
- Chemiluminescence
  - NRL Developed
    - MDL: sub-ppb levels
    - pH dependent

SENSORS



Portable
- IR
  - –Foxboro SapphIRe (COTS)
    - Range: 0 to 50 ppm
    - MDL: 500 ppb

SENSORS

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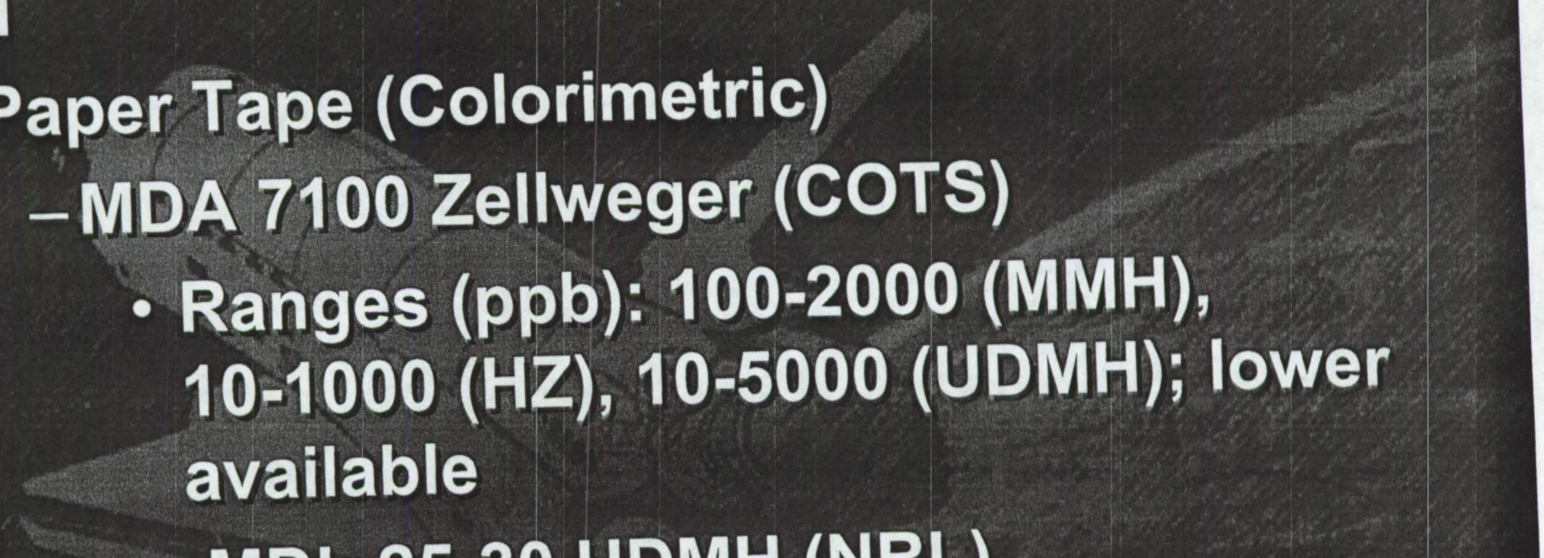
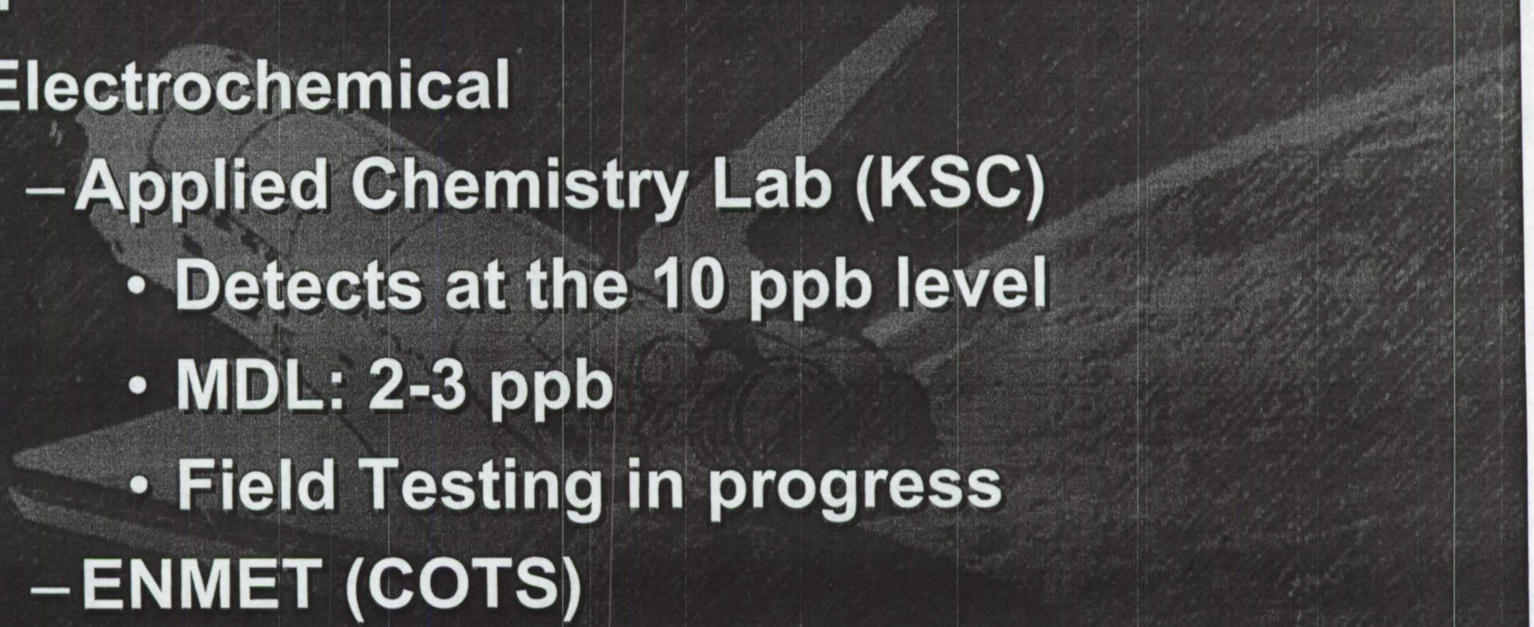


Fixed

- Paper Tape (Colorimetric)
  - MDA 7100 Zellweger (COTS)
    - Ranges (ppb): 100-2000 (MMH), 10-1000 (HZ), 10-5000 (UDMH); lower available
    - MDL 25-30 UDMH (NRL)
  - RIS (Bacharach/GMD) (COTS)
    - 0 to 2 ppm
    - MDL: 20-30 ppb

SENSORS



Fixed

- Electrochemical
  - Applied Chemistry Lab (KSC)
    - Detects at the 10 ppb level
    - MDL: 2-3 ppb
    - Field Testing in progress
  - ENMET (COTS)
    - EN-Guard, CTX 2042 (0 to 1 ppm)
    - TG-Series (0 to 10 ppm)

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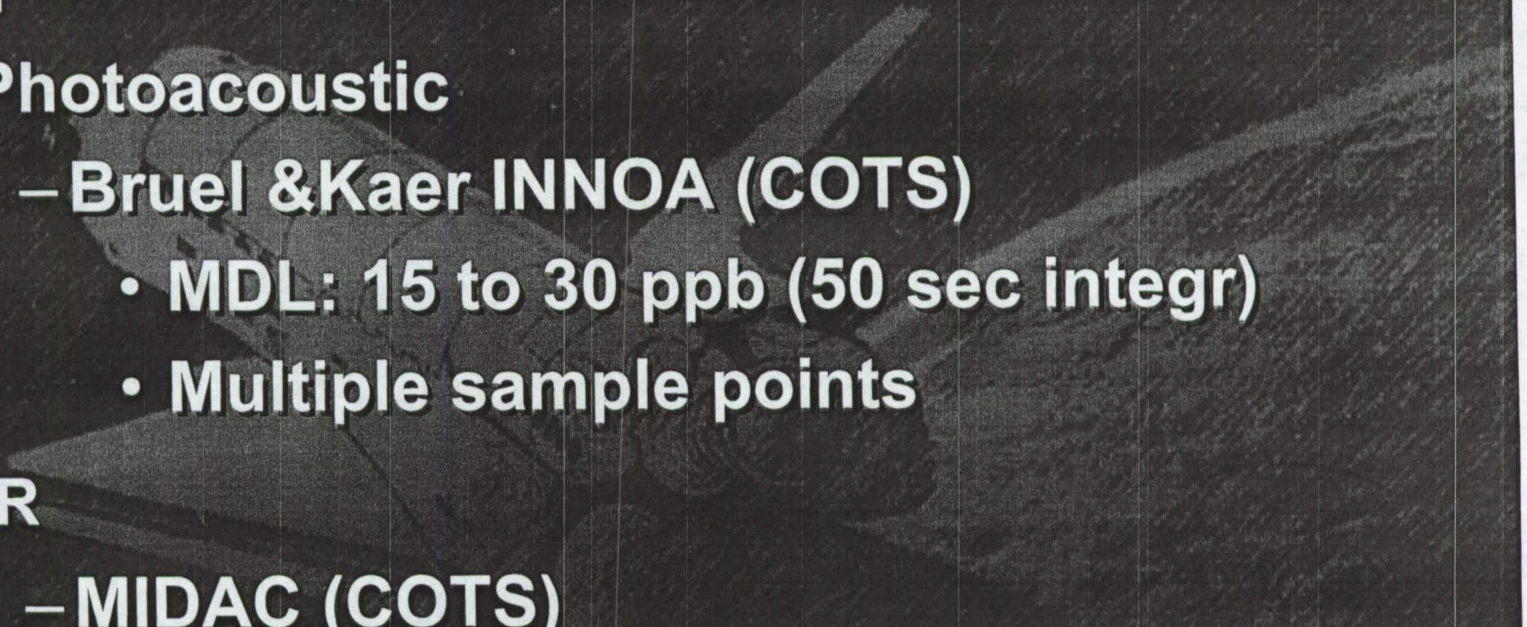
SENSORS



Fixed

- Photoacoustic
  - Bruel &Kaer INNOA (COTS)
    - MDL: 15 to 30 ppb (50 sec integr)
    - Multiple sample points
- IR
  - MIDAC (COTS)
    - MDL: 1ppm on single scan (500 ppb)
    - Range: 1 to 100 ppm

SENSORS

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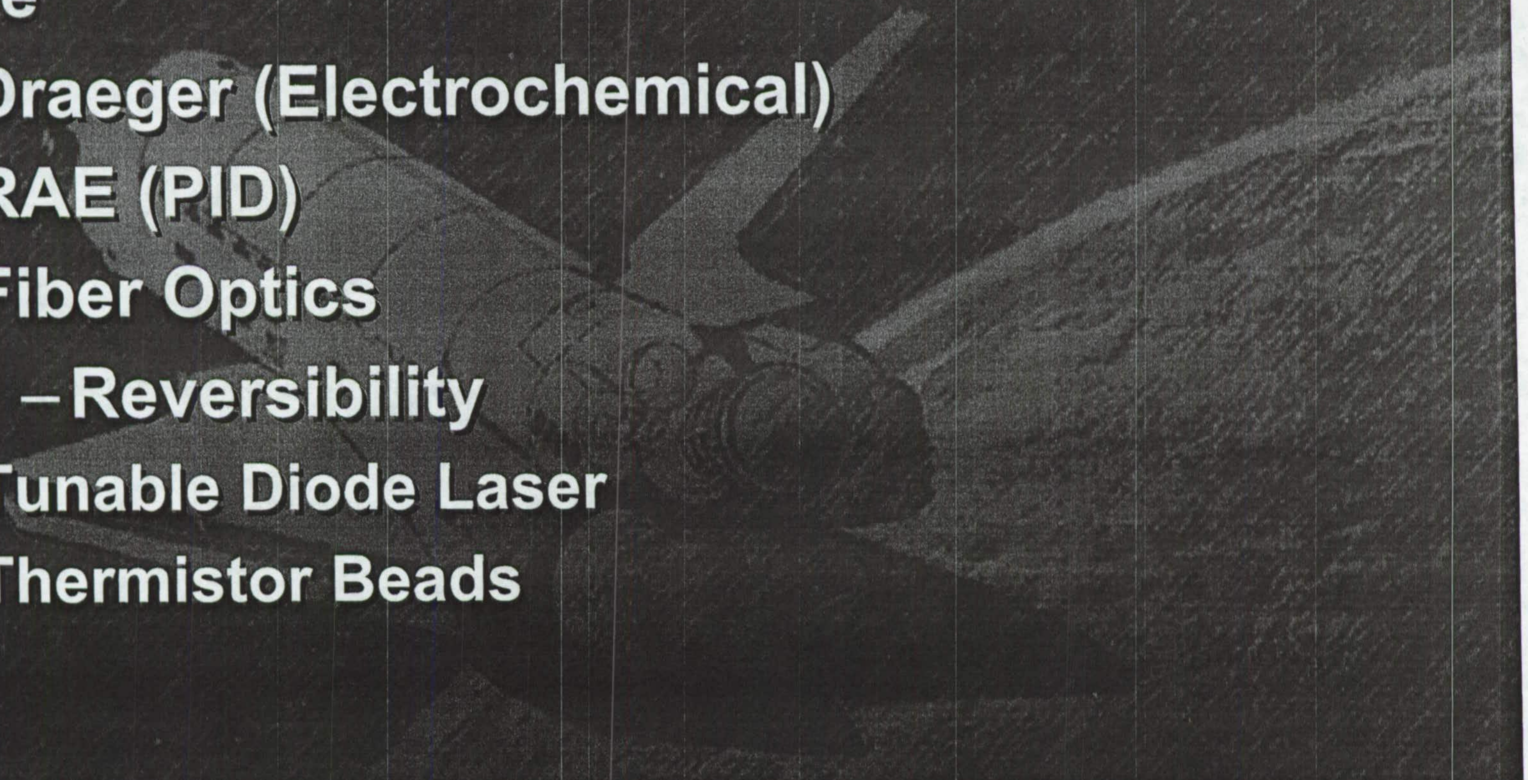
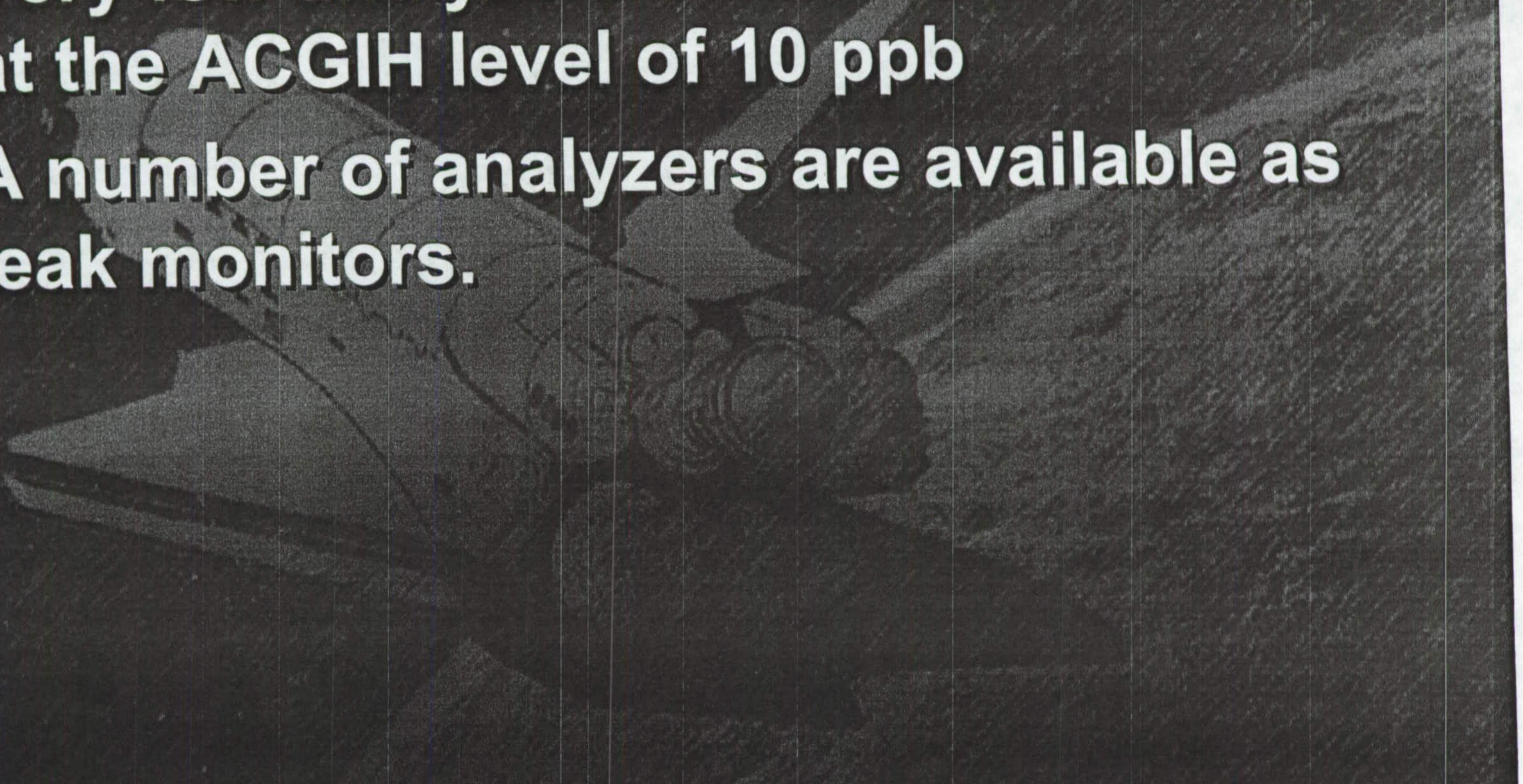


Future

- Draeger (Electrochemical)
- RAE (PID)
- Fiber Optics
  - Reversibility
- Tunable Diode Laser
- Thermistor Beads

SUMMARY



- Very few analyzers available to monitor at the ACGIH level of 10 ppb
- A number of analyzers are available as leak monitors.

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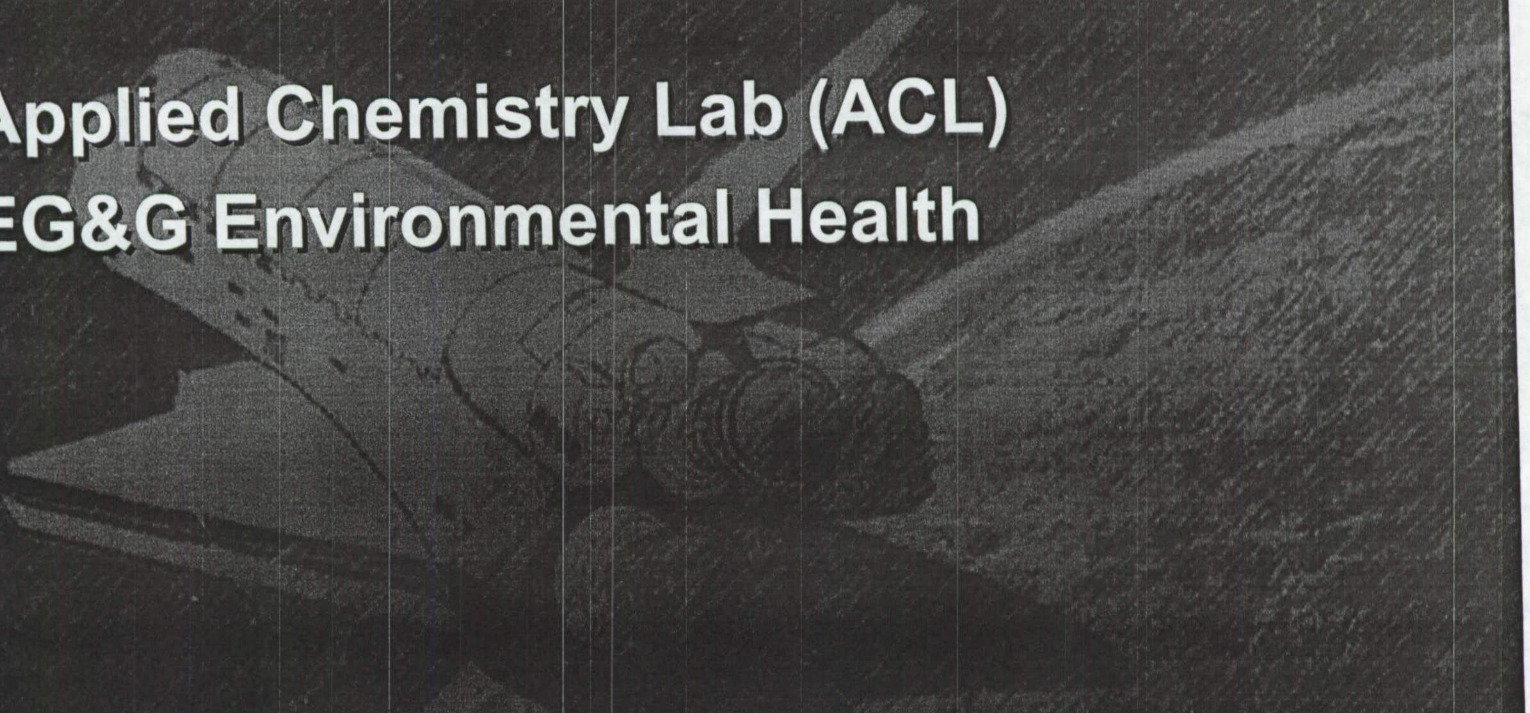
ACKNOWLEDGEMENTS



- Applied Chemistry Lab (ACL)
- EG&G Environmental Health