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BACKGROUND

Recent increased use of Personal (diffusive) Monitors by industrial hygienists is due to their *efficiency versus other methods*. The need for efficiency has been driven by a growing realization of the *need to acquire adequate statistical data demonstrating compliance with PELs and STELs*.

Personal Monitoring devices for chemicals can be divided into two groups:
(a) "Reactive" Monitors which form a non-volatile derivative from the collected chemical, and
(b) "Sorbent" Monitors which "sorb" the analyte but do not modify it chemically.

"Reactive" Personal Monitors which sample by diffusion and "trap" the analyte chemically work well in a variety of situations and are widely accepted because they avoid reverse diffusion (analogous to "breakthrough" in tube sampling) by forming a non-volatile derivative in the Monitor. Aldehydes, being reactive, can be collected on a variety of media which has been impregnated with a reagent system.

DESIGN CONSIDERATIONS FOR AN ALDEHYDE MONITOR

Below are listed the Design Goals for the Aldehyde Monitor and how each has been addressed in the development of the ChemDisk™ Aldehyde Monitor.

Sampling Grid provides fixed Diffusion Layer to provide reliable Sampling Rate... The Sampling Grid previously designed for the Organic Vapor Monitor (and known to provide unit-to-unit variation of better than 3%) has been employed. This Grid, of injection-molded polypropylene, has been shown to be dimensionally reproducible, non-contaminating, inert, and non-sorbing with respect to a variety of organics. See also *Demonstration of Sampling Rate and Performance.*

Reagent System reacts completely with Sample to form a single Aldehyde Derivative ...
2,4-dinitrophenyl hydrazine (DNPH) has been shown to react stoichiometrically with aldehydes to form 2,4-dinitrophenylhydrazone derivatives which have been used for decades as a method of characterizing a large number of aldehydes.

Aldehyde Derivative can be analyzed to provide accurate method of analysis... More recently, the DNPH-aldehyde reaction has formed the basis of two regulatory analytical methods, *EPA TO-11* for carbonyl compounds and *OSHA Method 64* for glutaraldehyde. Besides excellent reaction properties with virtually all aldehydes, DNPH forms yellow derivatives with high UV-visible absorption in the 355 nm region which can be readily separated via High Performance Liquid Chromatography (HPLC) systems and quantitated via a UV-visible detector.

The Technology Leader in Personal Monitoring
for Chemicals in the Workplace

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Low Background Blank for System and Reagent to enable low detection limits... Ultimate sensitivity in an analytical system is a product of the *quantity of sample collected* and the *inherent sensitivity of the analytical method* used. The high sensitivity of the HPLC analysis with UV-visible detector in the vicinity of 355 nm balances the moderate sampling rates available with diffusive samplers and, overall, provides a method capable of detecting *less than 0.1 ppm-hr of most aldehydes.*

Special Process Controls to Obtain Low Background Blank... Since formaldehyde is ubiquitous in the environment, every laboratory has experienced problems with high formaldehyde blanks arising from the presence of formaldehyde in air, water, building materials, paper, plastics, shampoo, etc.

Accordingly, each material in contact with product inside the hermetically-sealed pouch (*including the pouch itself*) has been tested for its contribution to the background blank. In addition, key components are heat-treated during manufacture to further minimize any aldehyde accumulation.

The reagent-treated wafer on which formaldehyde is collected has been prepared from an inert fiberglass shown to be superior to paper with respect to both its inertness and its lower formaldehyde content.

To minimize formaldehyde and enhance shelf life, the process of treating and packaging the wafers has been designed to be carried out entirely in an inert gas environment which serves to minimize pickup of ambient formaldehyde and to preserve the reagent system from oxidation.

SAMPLE CAPACITY OF CHEM DISK™ MONITOR

Sample capacity is determined largely by the quantity of DNPH Reagent System present in the reagent-treated Wafer which collects the aldehyde sample. A quantity of DNPH Reagent per Monitor is present which is capable of reacting with more than 3 μmoles of aldehyde (e.g. equivalent to more than 100 μg of formaldehyde). Taking the Sampling Rate for formaldehyde into account, the Monitor has the capacity to sample a formaldehyde exposure in excess of 80 ppm-hour (equivalent to 10 ppm for an 8-hr sampling time). A Linear Relationship between Formaldehyde Exposure Level (*ppm*) and formaldehyde (*μg*) collected has been shown for formaldehyde levels in the range of 0.1-30 ppm-hr (See also *Demonstration of Sampling Rate and Performance.*)

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VALIDATION SCHEME - Sampling Rate Determination & Post-Exposure Challenge

Each Analyte (chemical) to be qualified for sampling by the ChemDisk™ Aldehyde Monitor is subject to a battery of tests including Sampling Rate and Performance Determination, De-Sorption Efficiency, Reverse Diffusion Challenge, and Humidity Challenge.

DEMONSTRATION OF SAMPLING RATE AND PERFORMANCE - FORMALDEHYDE

Exposures were performed as described in the Aldehyde Exposure Challenge Lab Method. In this method, aldehyde levels were continuously generated in an inert chamber in which the environment was continuously re-circulated through a Sampling Tunnel containing Monitors to be tested. Air Samples were drawn continuously from the vicinity of the Monitors and conveyed to external twin impingers which were subsequently analyzed for formaldehyde via NIOSH 3500 (chromotropic acid method).

Similar methodology was employed by the Wisconsin Occupational Health Service in its independent study for which results are also included in this report.

Linear Regression Plots of four distinct studies performed during 1992-1993 at Assay Technology and at the Wisconsin Occupational Health Service (Madison, WI) are included in this report. A summary of these results is given below.

(1) *Formaldehyde levels ranging from 0.1 to 13 ppm* with *exposure times ranging from 15 min to 24 hours* were monitored with all values in the four studies clustering around a single regression line.

(2) The linear response of the monitor over a wide dynamic range with low background demonstrates Dosimetric Performance capable of effectively monitoring 15-minutes STELs (0.2-5ppm), 8-hr TWAs (0.01-3ppm), or 24-hr Indoor Air Quality tests (below 0.01 ppm).

(3) The Sampling Rate was determined from Least Squares Linear Regression analysis of all the exposure data. The Slope of the plot of **Formaldehyde Exposure** in *ppm-hr* (referenced to the NIOSH 3500 Method) *versus* **Formaldehyde Found** (μg) in the Monitor yielded the Sampling Rate when the Slope was multiplied by the molar volume, divided by the molecular weight, and appropriate unit conversion factors were applied.

(4) A formal Sampling Rate value was taken from data of studies performed in 1993 representing the most current manufacturing and analytical methodology. When the 1993 regression line was compared to 1992 data (including the Wisconsin Study) (see Figures), no significant differences were observed indicating that the Sampling Rate is stable with respect to manufacturing variables.

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DEMONSTRATION OF SAMPLING RATE AND PERFORMANCE - GLUTARALDEHYDE

Exposures were performed as described in the Aldehyde Exposure Challenge Lab Method. In this method, aldehyde levels were continuously generated in an inert chamber in which the environment was continuously re-circulated through a Sampling Tunnel containing Monitors to be tested. Air Samples were drawn continuously from the vicinity of the Monitors and conveyed to external twin samplers which incorporated filters treated with 2,4-dinitrophenylhydrazine. Samplers were collected and analyzed as indicated in OSHA Method 64.

Independent studies were also conducted at two technically-competent companies in the chemical industry. In these studies a known glutaraldehyde environment was generated by continuous flash vaporization of a glutaraldehyde solution of known concentration with generated vapor continuously flowing through an exposure an inert exposure chamber containing the monitors.

Results from the independent studies was correlated with in-house data to compute a grand average Sampling Rate. Data from the thrid-party studies are currently under internal review at the respective companies and will become available presently. A summary of validation results is given below.

(1) *Glutaraldehyde levels ranging from 0.01 to 0.5 ppm* with *exposure times ranging from 15 min to 4 hours* were monitored with all values clustering around a single regression line.

(2) The linear response of the monitor over a wide dynamic range with low background demonstrates dosimetric performance capable of effectively monitoring 15-minutes STELs (0.01-0.2ppm) or exposures of longer duration.

(3) The Sampling Rate was determined from Least Squares Linear Regression analysis of the data.

The Slope of the plot of **Glutaraldehyde Exposure** in *ppm-hr* (referenced to the OSHA Method 64) *versus* **Glutaraldehyde Found** (μg) in the Monitor yielded the Sampling Rate when the Slope was multiplied by the molar volume, divided by the molecular weight, and appropriate unit conversion factors were applied.

(4) A formal Sampling Rate value was taken from data of studies performed in 1993 and 1994 representing current manufacturing and analytical methodology combined with data from independent outside studies performed at Abbott Labs and Union carbide.

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DE-SORPTION EFFICIENCY

Forward Method - A DNPH-impregnated wafer from a ChemDisk™ Monitor was spiked with a known quantity of Aldehyde using a microsyringe, then placed into a glass vial which was sealed. After equilibration, a measured volume of solvent (acetonitrile) was added. A control containing an identical quantity of Analyte in Acetonitrile was treated in a parallel manner.

Calculation of De-Sorption Efficiency - De-Sorption Efficiency (DE) was calculated as follows regardless of equilibration method employed.

$$\text{De-Sorption Efficiency (DE)} = \frac{[\text{Analyte Found } (\mu g), \text{ DNPH Wafer}]}{[\text{Analyte Found } (\mu g), \text{ Control }]}$$

De-sorption efficiency (i.e., % recovery) in the range 98-102% were found in all studies.

REVERSE DIFFUSION CHALLENGE TEST

A specific test was developed by Assay Technology in 1984 to evaluate its first products, ChemChip™ monitors to ensure that sample was not lost during or after sampling. This test has been applied to ChemDisk™ Monitors to provide a challenge to determine whether practical sampling capacity has been exceeded in a particular application.

In this test, Monitors are exposed at a level **equivalent to exposure at the PEL for eight hours**, then allowed to stand under ambient conditions (as if sampling) in an environment containing no analyte.

Under such conditions, reverse diffusion experienced if practical sampling capacity is exceeded would be detected as loss of analyte when the quantity of analyte recovered by a Monitor subjected to this challenge is compared to the quantity recovered from a "control".

To pass the Reverse Diffusion challenge, the quantity of Analyte recovered from the "challenge" samples exposed at the PEL must not be more than 10% less than the quantity recovered from controls when experimental error has been taken into account.

Monitors challenged with one day of post-exposure standing in open air (zero formaldehyde level) met the requirements of this test and showed negligible loss of formaldehyde.

Monitors which had been re-packaged for return to the lab and challenged for one week also met the requirements of negligible loss of formaldehyde.

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HUMIDITY CHALLENGE TEST

Diffusion rates and sampling rates of vapors in air have been shown in previous studies to be unaffected by humidity variation provided that moisture levels encountered do not create aerosols or react chemically with the analyte. However, potential humidity effects can arise in diffusive samplers if the capacity (the capability of the collection medium to absorb or retain analytes) were adversely affected by moisture.

To test this possibility with the most rigorous challenge, Monitors were equilibrated at a variety of relative humidities in the range 15-85%. Sampling rates for Monitors pre-conditioned at a specific relative humidity were compared to sampling rates for Monitors pre-conditioned at 40-60% relative humidity to determine if any humidity effects would be observed. In controlled exposure studies, statistically significant differences were not observed between Monitors pre-conditioned at 15-20% versus Monitors pre-conditioned at 40-60% RH. Similarly, no significant difference was found between Monitors pre-conditioned at 80-85% RH versus Monitors pre-conditioned 40-60% RH.

It is concluded that sampling rates of ChemDisk™ Aldehyde Monitors are not adversely affected by humidity variations typically encountered under field conditions.

SUMMARY COMMENTS

The ChemDisk™ Aldehyde Monitor has been designed to provide accurate monitoring of aldehydes via a combination of a reliable design, a selective and sensitive derivative chemistry, and utmost care exercised in the design and manufacture of monitors so as to ensure (to the extent possible) a formaldehyde-free monitor with very low background.

Appropriate tests have been carried out at Assay Technology and elsewhere to ensure that the design goals have been met.

A continuous program of quality control and quality improvement (including *quality testing of each lot of Monitors manufactured*)is maintained by Assay Technology.
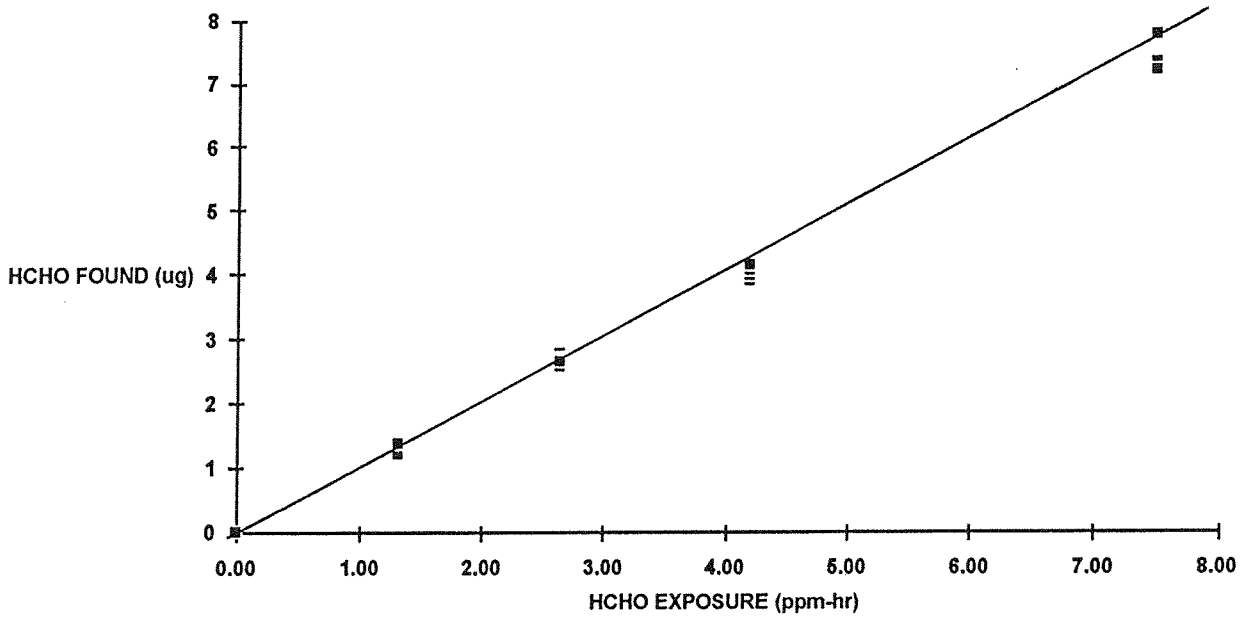
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MASS COLLECTED vs FORMALDEHYDE LEVEL (Oct 92)

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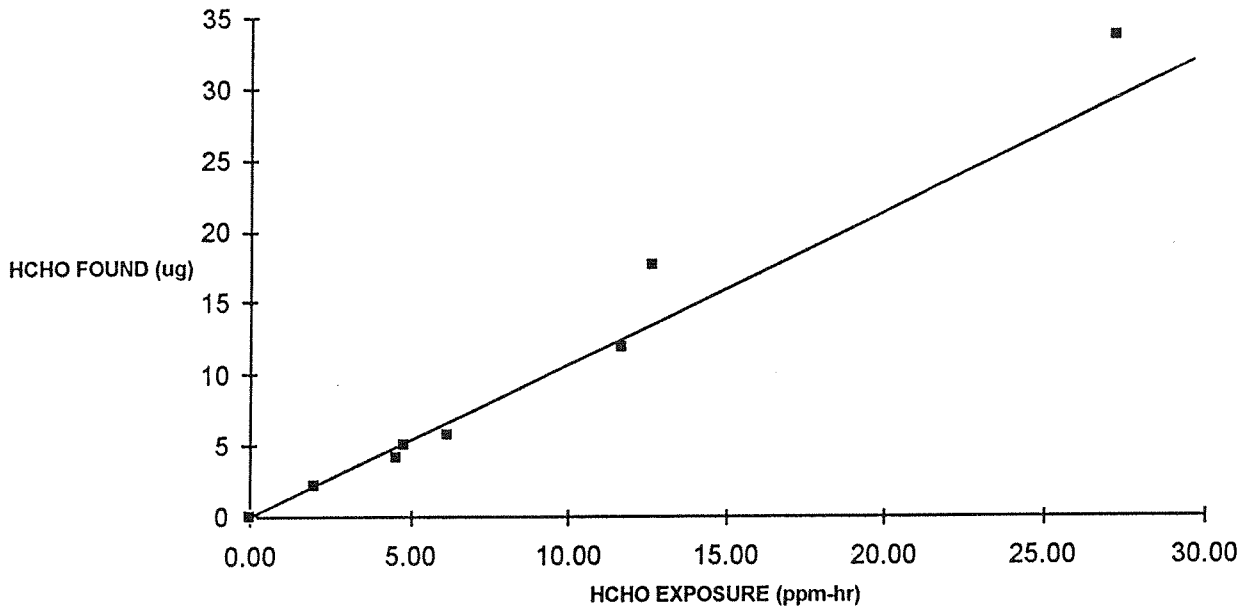
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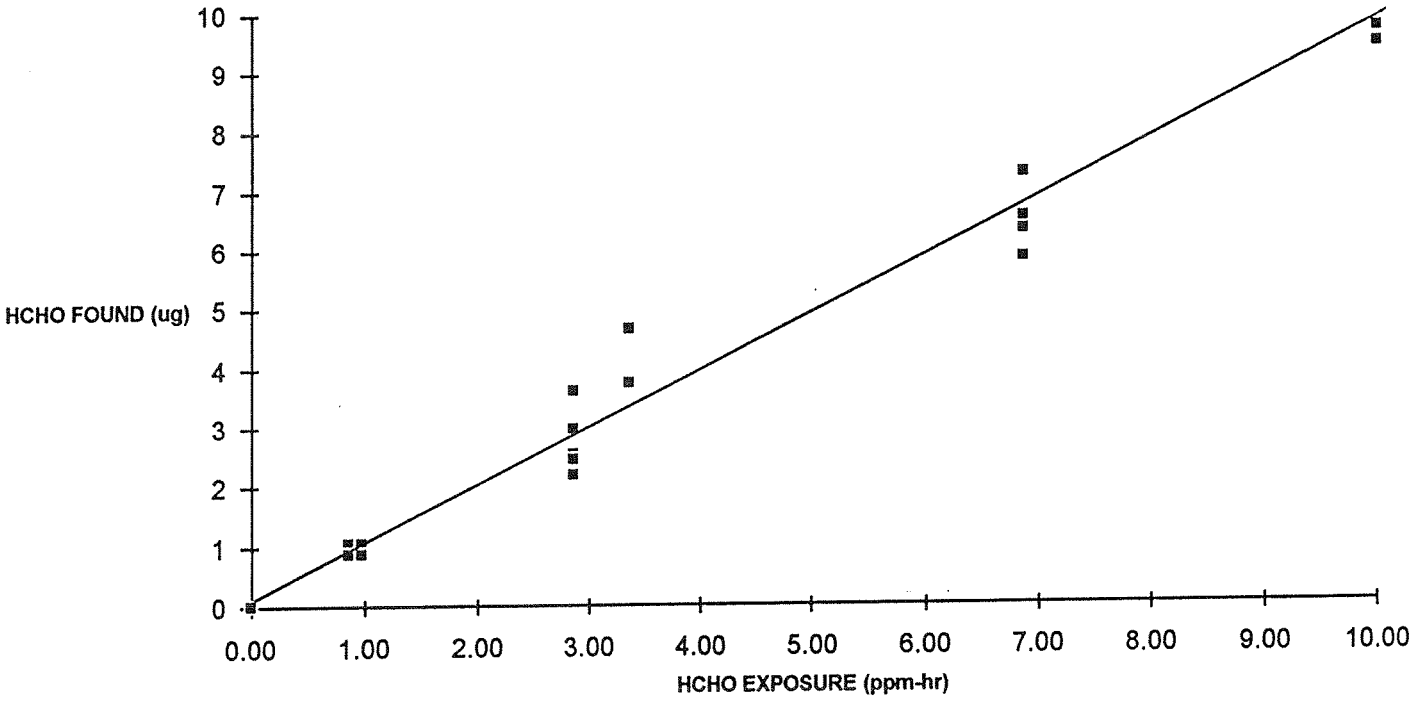
MASS COLLECTED vs FORMALDEHYDE LEVEL (Jul 93)

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MASS COLLECTED vs FORMALDEHYDE LEVEL (Sep 93)

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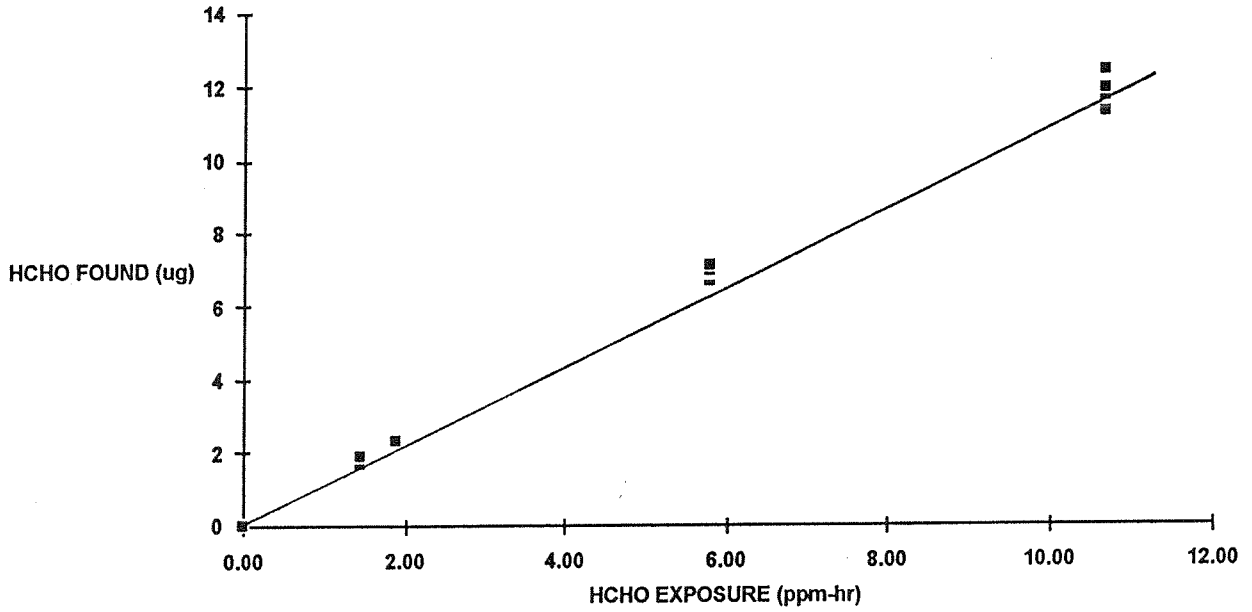
MASS COLLECTED vs FORMALDEHYDE LEVEL (1993 Data)

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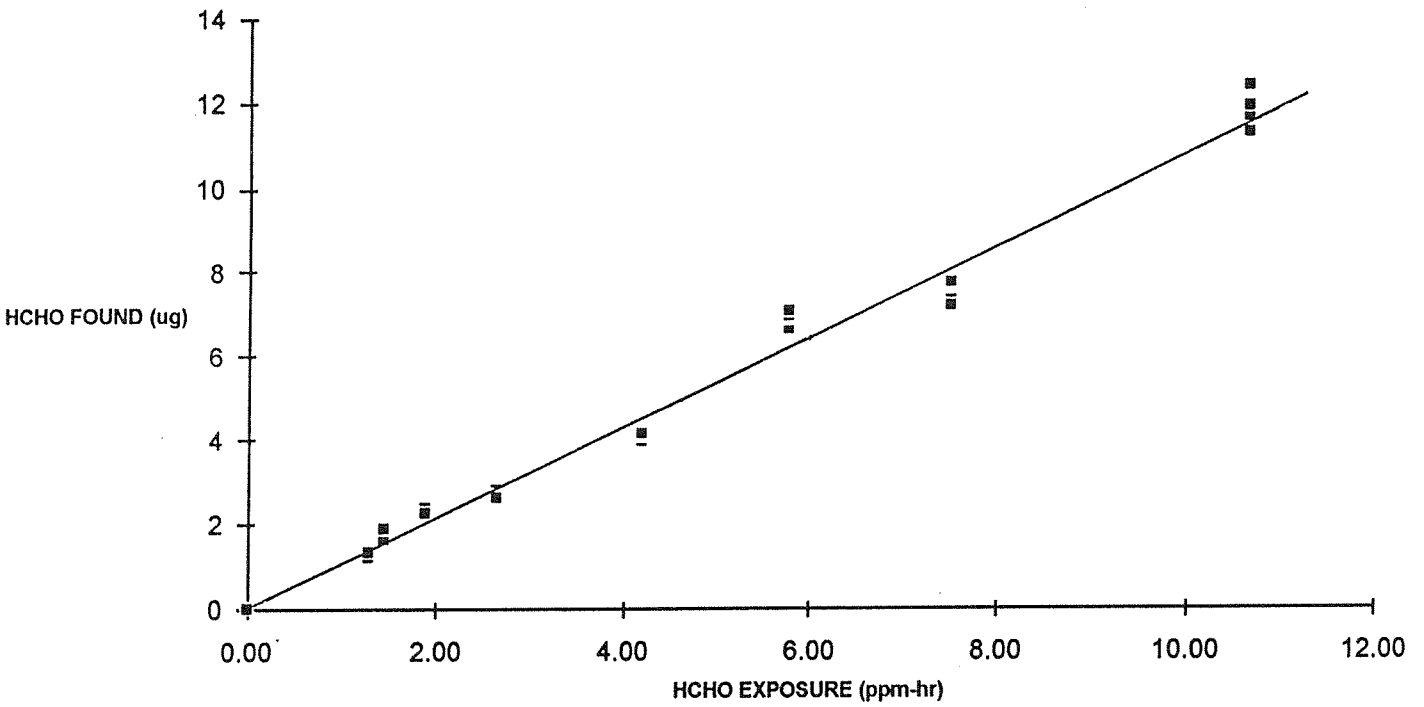
MASS COLLECTED vs FORMALDEHYDE LEVEL (All Data)