Formaldehyde
(that long forgotten irritating friend)

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Formaldehyde

- Chemical name: formaldehyde
- Synonyms: formic aldehyde, methanal, methyl aldehyde, methylene oxide
- Chemical Abstract Number: 50-00-0
- Chemical formula: CH_2O
- Registered Trade Names for 37% aqueous Solution: Formalin, Formol, Morbicid, Veracur

Formaldehyde – Physical and Chemical Properties

- Molecular weight = 30.03
- Color: colorless
- Physical state: Gas
- Melting point: -92°C
- Boiling Point: -21°C
- Odor: pungent, suffocating odor, highly irritating

Formaldehyde – Physical and Chemical Properties

- Odor thresholds: 50 ppm (water)0.5-1.0 ppm (air)
- Soluble in water and organic solvents
- Incompatibility: reacts with alkalies, acids and oxidizers
- Conversion factor: 1 ppm = 1.23 mg/m^3

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Formaldehyde – History

- Low cost and high purity have made formaldehyde one the **MOST** important chemicals in the world
- Between 1958 and 1968 the annual production growth rate averaged 11.7% (1988 to 1997 - 2.7% growth rate)
- In 1992 formaldehyde ranked 22nd among the top 50 chemicals produced in the United States

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USF HEALTH

Formaldehyde – History

- In 1998 the total United States annual production capacity was 11.3 billion pounds
- 3 manufacturers are responsible for 50% of US production
  - Georgia-Pacific Resins
  - Hoechst Celanese Corporation
  - Borden, Inc.

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Formaldehyde - Production

- Formaldehyde is manufactured from methanol using a two-step process which involves a metal catalyst
  - Silver is used as a catalyst and the methanol is heated to 600-650°C at atmospheric conditions resulting in exothermic and endothermic reactions and yields of 86-90% formaldehyde

Formaldehyde - Production

The other process uses a metal oxide such as vanadium pentaoxide or iron oxide-molybdenum oxide at atmospheric pressure and 300-400°C resulting in an exothermic reaction

Formaldehyde Import/Export

- In 1994 the US imported 87 million pounds and exported 25 million pounds of formaldehyde respectively
- In 1997 the US imported 140 million pounds of formaldehyde
  - (source: Chemical Marketing Reporter)

Formaldehyde – Uses in Cosmetics and Cleaning Agents

- Formaldehyde has been used in consumer goods to deter spoilage by microbial contamination including the following:
  - Cosmetics, soaps, shampoos, hair preparations, deodorants, lotions, make-up, mouthwashes, nail products, bubble bath oils, cuticle softeners, nail creams, vaginal deodorants, shaving creams
  - Concentrations in these products range from 0.4% to 4.5%
    - Trace amounts found in cosmetics have also been attributed to the use of formaldehyde as a disinfecting agent on the manufacturing equipment

Formaldehyde – Uses in Cosmetics and Cleaning Agents

- It is also used as a preservative in household cleaning agents, dishwashing liquids, fabric softeners, shoe-care agents, car shampoos, waxes and carpet cleaning agents
  - The content of formaldehyde is generally less than 1% in these products

Formaldehyde – Uses in Human Medical Applications

- Medical uses account for approximately 1.5% of total production volume which is relatively small
- Past medical uses have included the following
  - use in vasectomy procedures
  - foot anti-perspirant or preservative for these products
  - treatment for athlete's foot
  - sterilant for cysts prior to their surgical removal

Formaldehyde – Uses in Veterinary Applications

- Formaldehyde has been used therapeutically as an antiseptic, a fumigant, and for treatment of the following:
  - Tympany
  - Diarrhea
  - Mastitis
  - Pneumonia
  - Internal bleeding

Formaldehyde – Uses in Veterinary Applications

- Formaldehyde has also been used to protect dietary protein in animal feed stocks and has been used as a food additive to improve the handling characteristics of animal fat and oilseed in cattle food mixtures

Formaldehyde – Miscellaneous Uses

- Synthesis of chelating agents
- Tissue preservative and disinfectant in embalming fluid
- Disinfectant for dwellings, ships, utensils, clothing
- Fumigant to prevent spoilage of wheat and oat stores
- Soil sterilant for mushroom production
- Germicide and fungicide for plants and vegetables
- Insecticide
- Slow-release fertilizer

Formaldehyde – Miscellaneous Uses

- Manufacture of glass mirrors
- Explosives
- Artificial silk
- Dyes
- Waterproofing fabrics
- Preserving and coagulating latex rubber
- Anti-oxidizer additive for synthetic rubber
- Tanning and preserving animal hides
- Biocide in metal cutting fluids

Formaldehyde – Building Material Uses

- Formaldehyde is used as a chemical intermediate in the manufacture of organic compounds and examples include:
  - Plywood and melamine adhesives/resins
  - Abrasive materials
  - Insulation
  - Laminates
  - Phenolic thermosetting agents
  - Resin curing agents

Formaldehyde – Occupational Concerns

- Workers can inhale formaldehyde as a gas or vapor or it may be absorbed through the skin as a liquid
- Workers may be exposed to formaldehyde during the manufacturing of treated textiles, or the production of resins
- Other potentially “at risk” groups include health care professionals, medical lab technicians, mortuary employees and even teachers and student who handle biological specimens preserved in formaldehyde based solutions
- NIOSH estimates 1,329,332 individuals are at risk for occupational exposure to formaldehyde

Formaldehyde – Exposure Effects

- Formaldehyde is regarded as a sensitizing agent that can cause an immune system response upon initial exposure
  - Repeated exposures may cause severe allergic reactions of the skin, eyes and respiratory tract
- Formaldehyde is also a suspected human carcinogen linked to cancers of the lung and nose

Formaldehyde – Exposure Effects

- Acute exposures are highly irritating to the eyes, nose and throat and often induce coughing and wheezing; ingestion may be fatal
- Chronic low level exposure may result in asthma-like conditions or dermatitis
- Concentrations of 20 ppm are considered by NIOSH to be Immediately Dangerous to Life or Health (IDLH)

Formaldehyde – Occupational Regulations

- The Occupational Safety and Health Administration (OSHA) seeks to protect workers from the effects of formaldehyde by limiting exposure and enforcing employers compliance with it formaldehyde specific standard
- The standard is 29 CFR 1910.1048 – Formaldehyde
- This standard is also applicable to and referenced in the OSHA construction standard 29 CFR 1926.1148 citing identical requirements in accordance with the general industry standard

Formaldehyde – Elements of 1910.1048

- The 1910.1048 standard applies to all occupational exposures including exposure to formaldehyde gas, its solutions, and materials that release formaldehyde
- The standard establishes a permissible exposure limit (PEL) of 0.75 ppm as an 8-hour time weighted average (TWA)
- The standard also establishes an "action-level" of 0.5 ppm as an 8-hour TWA and a short term exposure limit (STEL) of 2 ppm for 15 minutes

Formaldehyde – Elements of 1910.1048 Sampling Requirements

- The standard requires employers to monitor employees covered by the standard in order to determine their exposure to formaldehyde
- Sampling must be representative and repeated when exposures are at or above the PEL or STEL
  - See: 1910.1048(d) Exposure Monitoring

Formaldehyde – Elements of 1910.1048

- The standard also has requirements for the following:
  - Establishment of regulated areas – 1910.1048(e)
  - Methods of compliance – 1910.1048(f)
  - Respiratory protection – 1910.1048(g)
  - Protective equipment and clothing – 1910.1048(h)
  - Hygiene protection – 1910.1048(i)
  - Housekeeping – 1910.1048(j)
  - Emergencies – 1910.1048(k)
  - Medical surveillance – 1910.1048(l)
  - Hazard communication – 1910.1048(m)
  - Employee information and training – 1910.1048(n)
  - Recordkeeping – 1910.1048(o)

Formaldehyde – Elements of 1910.1048

- Employees who suffer significant adverse effects from formaldehyde exposure must be reassigned to a job with little or no exposure and this protection may last up to 6 months!
- All mixture or solutions with greater than 0.1% formaldehyde must be labeled
- All materials capable of releasing formaldehyde to the air at a concentration of 0.1 ppm must be labeled
- Any material capable of releasing formaldehyde at concentrations above 0.5 ppm must be labeled as
  - **"potential cancer hazard"**

Formaldehyde – Elements of 1910.1048

- Recordkeeping requirements
  - Employee exposure records must be maintained for 30 years
  - Employee medical records must be maintained for 30 years after employment ends!
  - The employer must allow access to medical and exposure records by the current and former employees or their designated representative upon request

Formaldehyde – Other Occupational Recommendations

- The American Conference of Governmental Industrial Hygienists (ACGIH) has established a threshold limit value (TLV) for formaldehyde of 0.3 ppm with a ceiling designation indicating that this value should not be exceeded during the work shift
- The ACGIH has not yet developed a biological exposure indices (BEI) value for formaldehyde
- The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 0.016 ppm as an 8-hour TWA
- The Deutsche Forschungsgemeinschaft (DFG) Maximale Arbeitsplatz Konzentration (MAK) for formaldehyde is 0.3 ppm

Formaldehyde – Methods of Occupational Exposure Assessment (Liquid Phase)

- Formaldehyde in air may be trapped by a variety of impinging methods including the following:
  - Impingers filled with water
    - These sample degrade quickly with 50% loss reported for holding times of 50 hours or more
  - Impingers filled with sodium bisulfite
    - These samples appear relatively stable with holding times ranging from 1-4 weeks

*Those samples collected using water or sodium bisulfite must undergo an additional chemical derivatization prior to analysis

Formaldehyde – Methods of Occupational Exposure Assessment (Liquid Phase)

Impingers filled with an acidic aqueous solution of 2,4-dinitrophenylhydrazine (DNPH), which reacts with the DNPH to form the 2,4-dinitrophenylhydrazone derivative

Impingers can also be filled with a buffered Girard-T reagent

Impingers can be messy and are subject to fluid loss!

Formaldehyde – Methods of Occupational Exposure Assessment (Solid Phase)

- The formation of the formaldehyde 2,4-dinitrophenylhydrazone derivative using DNPH has allowed the development of solid phase sampling media with proven success
- Examples include:
  - silica gel coated with DNPH
  - DNPH coated glass fiber filters

Formaldehyde – Methods of Occupational Exposure Assessment (Solid Phase)

- Other derivative methods include the collection of formaldehyde as dansylhydrazone by passing the sample over porous glass particles coated with dansylhydrazine

- Formaldehyde collected as its oxazolidine derivative is accomplished by passing the sample over the polymeric sorbent XAD-2 which is coated with hydroxymethyl piperidine

Example NIOSH Method for Formaldehyde

- NIOSH Manual of Analytical Methods (NMAM), Fourth Edition
- **FORMALDEHYDE 2016**
- $H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000
- **METHOD: 2016, Issue 2 EVALUATION: FULL Issue 1: 15 January 1998**
- **Issue 2: 15 March 2003**
- **OSHA :** 0.75 ppm; 2 ppm STEL
- **NIOSH:** 0.016 ppm; C 0.1 ppm; carcinogen
- **ACGIH:** C 0.3 ppm; suspected human carcinogen
- (1 ppm = 1.23 mg/m3 @ NTP)

Example NIOSH Method for Formaldehyde

- **PROPERTIES:** Gas; BP -19.5°C; specific gravity 1.067
  - (air = 1); explosive range 7 to 73% (v/v) in air
- **NAMES & SYNONYMS:** methanal; formalin (aqueous 30 to 60% w/v formaldehyde); methylene oxide
- **SAMPLER:** CARTRIDGE
  - (Cartridge containing silica gel coated with 2,4-dinitrophenylhydrazine)
- **FLOW RATE:** 0.03 to 1.5 L/min
- **VOL-MIN:** 1 L @ 0.25 mg/m^3
- **-MAX:** 15 L @ 2.5 mg/m^3

Example NIOSH Method for Formaldehyde

- **SHIPMENT:** Place caps onto cartridge. Ship on ice.
- **SAMPLE**
- **STABILITY:** 34 days @ 5 °C [1]
- **BLANKS:** 2 to 10 field blanks per set, 6 to 10 media blanks per set
- **TECHNIQUE:** HPLC, UV DETECTION
- **ANALYTE:** 2,4-dinitrophenylhydrazone of formaldehyde
- **EXTRACTION:** Elution with 10 mL of carbonyl-free acetonitrile
- **INJECTION VOLUME:** 20 µL

Formaldehyde – Methods of Occupational Exposure Assessment

- These liquid and solid phase methods are "active" methods involving the movement of air over the sample media of choice using a calibrated sampling pump

Formaldehyde – Methods of Occupational Exposure Assessment (Passive Device)

- Commercially prepared sample collection devices which rely on passive diffusion are readily available
- These passive badges work by stabilizing the formaldehyde as an adduct with sulfite after the formaldehyde passes through a diffusion membrane

Formaldehyde – Residential Concerns?

- Are formaldehyde concerns in residential settings a modern day issue?
  - The answer is YES and the reasons are complex but understandable
- The need for cheap building products has pushed sourcing from the United States and Canada to other nations and the quality control and quality assurance procedures employed at these "new" production facilities may lack the rigorous measures expected in the United States and Canada.

Formaldehyde – Residential Concerns?

Product litigation is also a major concern of domestic suppliers and in large part accounts for the QA/QC procedures developed in the past

Formaldehyde – Residential Concerns A Case Study - Background

- In August of 2005, Hurricane Katrina; a Category 4 storm, made landfall affecting the majority of US gulf coast states
- In October 2005, the Federal Emergency management Agency (FEMA) began providing temporary housing in the form of portable trailers to displaced families that had been previously displaced
- Spring 2006, US gulf coast physicians begin reporting increases in upper respiratory issues in children living in FEMA supplied temporary housing

Formaldehyde – Residential Concerns A Case Study - Background

- In the spring of 2006 FEMA became aware of elevated formaldehyde levels in FEMA trailers in Louisiana and Mississippi
- These reports prompted the Department of Homeland Security Office of Health Affairs (DHS-OHA) to contact the Centers for Disease Control on behalf of FEMA and initiate an investigation
- The investigation has focused on evaluating levels of formaldehyde in FEMA supplied temporary housing

Formaldehyde – Residential Concerns A Case Study - Background

- Over 100,000 temporary housing units (THUs) were supplied to gulf coast residents by FEMA
- Initially the CDC's Agency for Toxic Substances and Disease Registry (ATSDR) provided guidance to THU occupants suggesting that they increase ventilation and reduce temperature and relative humidity to lower formaldehyde levels
- The ATSDR also recognized that the formaldehyde levels in the THUs constituted a potential health concern

Formaldehyde – Residential Concerns A Case Study – Study Design

- The Division of Environmental Hazards and Health Effects under the National Center for Environmental Health put together a study design to answer the questions posed by CDC

Formaldehyde – Residential Concerns
A Case Study – Study Components

- Goals and Objectives
  - Determination of formaldehyde levels in occupied FEMA owned THUs in gulf coast locations
- Procedures and Methods
  - Study data consisted of the following;
    - A one-hour continuous sample measurement of formaldehyde
    - A concurrent sample measurement of indoor temperature and relative humidity
    - A short questionnaire administered to the adult residents
    - A walkthrough survey to access indoor and outdoor environmental conditions

Formaldehyde – Residential Concerns
A Case Study – The One-Hour Sample

- The primary outcome variable was the one-hour concentration of measured formaldehyde
- 519 THUs were randomly chosen for study inclusion
- Other variables including indoor temperature, indoor relative humidity, physical characteristics of the THU, and recent activities conducted in the THU were recorded for analysis

Formaldehyde – Residential Concerns
A Case Study – Exp. Assessment Quest.

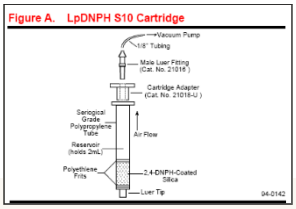
- A short questionnaire was administered to the primary adult resident of the THU by the sample collector during the 1-hour sample collection process
- The questionnaire documented demographic variables of the THU occupants, # of hours spent in the trailer, occupant smoking status, frequency of air conditioning, heating and window use
- Other activities such as cooking, vacuuming, etc., were also recorded

Formaldehyde – Residential Concerns
A Case Study – Walkthrough

- The interior and exterior condition of each THU were observed and documented by study personnel for the following factors;
  - The presence of holes
  - Leaks
  - Mold
  - Type of cooking fuel
  - Presence of smoke detectors

Formaldehyde – Residential Concerns
A Case Study – Sample Collection

- The 1-hour sample of formaldehyde was collected in the center of the THU primary living room; sitting height of adult
- Supelco S10 LpDNPH cartridges were used
- NIOSH Method 2016 was used for analysis



Formaldehyde – Residential Concerns
A Case Study – Sample Collection

- During sample collection the residents were asked to configure the trailer windows and doors as they were when the residents slept; no cooking or smoking allowed
- Samples were collected using personal sampling pumps operated at a flow rate of 500 ml/min (± 50 ml/min)
- Every tenth sample had duplicate collected; media blanks and field blanks were submitted as well
- Temperature and relative humidity values were data logged 5 minutes before and 5 minutes after the 1-hour period of sample collection

Formaldehyde – Residential Concerns
A Case Study – Study Findings

- In February 2008, FEMA and the CDC put out a joint press release
- Headline: *FEMA to Expedite Relocation of Residents From Temporary Housing Units*
- Preliminary results found higher than typical indoor exposure levels of formaldehyde in THUs used as emergency housing in the gulf coast
- 519 THUs were evaluated between December 2007 and January 2008

Formaldehyde – Residential Concerns
A Case Study – Study Findings

- The indoor formaldehyde levels taken as an average of all units was approximately 77 parts per billion (ppb)
- Normal Indoor formaldehyde levels in non-concern settings are commonly in the 10-20 ppb range
- The levels measured in the gulf coast THUs ranged from 3 ppb to 590 ppb

Formaldehyde – Residential Concerns
A Case Study – Study Findings

- Results of the study were hand delivered to participating residents and personnel made available for explanation
- Long term exposure to the average levels measured (77 ppb) is linked to increased cancer risk and increased risk of respiratory illness

Formaldehyde – Residential Concerns
A Case Study – Study Findings

- The current CDC/ATSDR Minimal Risk Levels (MRLS) for formaldehyde are as follows:
  - Inhalation: Chronic – 0.008 ppm = (8 ppb)
  - Inhalation Intermediate – 0.03 ppm = (30 ppb)
  - Inhalation Acute – 0.04 ppm = (40 ppb)

The majority of values measured greatly exceeded the chronic MRL

This would be considered a significant public health risk!

Formaldehyde – Residential Concerns
A Case Study – Study Findings

- Residents remaining in THUs have been advised by CDC and FEMA to spend as much time outdoors in fresh air as possible and ventilate their THUs as much as possible.
- Increased temperatures were positively correlated with increased formaldehyde concentrations
- With summer approaching FEMA began moving an average of 900 households per week out of THUs into more permanent housing solutions

Formaldehyde – Residential Concerns
A Case Study – Moving Forward

- As a result of this study CDC has suggested other initiatives including the following;
  - Identifying health effects associated with long term residence in THUs
  - Assessing formaldehyde levels across different manufacturers and types of THUs to identify factors which reduce or raise levels

Formaldehyde – Residential Concerns A Case Study – Moving Forward

- Study low-cost alternatives at reducing formaldehyde levels in current THUs
- Establish a long-term study of the children which resided in these THUs

Formaldehyde – What Have We Learned?

- Formaldehyde is an extremely important chemical from several different perspectives which include:
  - Financial
  - Volume of production
  - Use in industry
  - Recognition as an occupational health concern
  - Recognition as a public health concern

Take Away Thoughts

- As we move toward a global economy and shift production towards other countries what tradeoffs are we willing to accept for the cheaper goods received?
- Formaldehyde and indoor air quality issues were once thought a thing of the past as we can see this is no longer the case
- What other “things of the past” might become our reemerging hazards of the future?