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Worker Personal Protective Equipment (PPE) Tips for Peracetic Acid Use in Pharmaceutical Manufacturing Industry

Executive Summary

Peracetic Acid (PAA) (CAS-No. 79-21-0) is a hazardous chemical found in some products often sold with anti-microbial claims (e.g. sanitizer, disinfectant, sporicide, sterilant). PAA can become airborne and has relatively low exposure limits, however, exposure assessment can be difficult due to its chemical nature and lack of simple, inexpensive, and validated sampling methods. In addition to accurately characterizing potential worker exposure, the regulatory framework for anti-microbial products is useful to understand when performing risk assessments for PAA-containing products to determine appropriate exposure controls. This technical bulletin is intended to help provide health and safety professionals with background information and best practices for the selection of personal protective equipment (PPE), such as respiratory protection, to help control worker exposure to PAA.

Potential Hazards of Peracetic Acid

PAA, also known as peroxyacetic acid, is a strong oxidizer often used as a biocide in disinfectant products. It is present in an equilibrium mixture with hydrogen peroxide and acetic acid (aka vinegar) due to its chemical nature, which rapidly breaks down in the environment to oxygen, water and acetic acid. PAA is corrosive to eyes and skin with direct contact and has some volatility, so worker exposure can occur from inhalation of airborne aerosols and vapours. The hazard classification under the Globally Harmonized System (GHS) will vary depending on the chemical concentration and product formulation, but typical disinfectant products as sold may be classified as flammable, oxidizer, toxic, corrosive and hazardous to the environment.

Figure 1. Example of pictograms that may be found on hazardous chemicals Source: https://echa.europa.eu/regulations/clp/clp-pictograms)

Toxicity data for Peracetic Acid indicates sensory irritation as the suggested endpoint that might be used to derive occupational inhalation exposure limits. In an evaluation of the available data, a combination approach of both an 8-hour Time Weighted Average (TWA) and a Short-Term Exposure Limit (STEL) was recommended for PAA. A range of 0.1-0.2 ppm for the TWA and 0.4-0.5 ppm for the STEL was proposed as a basis for PAA occupational risk management decisions in a 2015 toxicity data review by Pechacek, et al.[1]

Many regulatory bodies have proposed or published Occupational Exposure Limits (OELs) for Peracetic Acid (PAA), Hydrogen Peroxide (HP), and Acetic Acid (AA). An example of published OEL are summarized in the following table:

Country	OEL Type	Peracetic Acid	Hydrogen Peroxide	Acetic Acid	Reference
UK	HSE	None	1 ppm (TWA) 1.4 mg/m3	10 ppm (TWA) 25 mg/m3	www.HSE.gov.uk
Ge	AGW/DFG	0,1 ppm (MAK)	0,5 ppm (MAK)	10 ppm (TWA)	AGW values are workplace limits; MAK (maximum workplace concentration) values are published by DFG but are not legally binding. AGW values can be found in TRGS900 BAuA - Technischer Arbeitsschutz (inkl. Technische Regeln) - TRGS 900 Arbeitsplatzgrenzwerte - Bundesanstalt für Arbeitsschutz und Arbeitsmedizin. DGF values can be found in MAK-Collection | Publisso.
PL	ISAP	0.8 mg/m3	0.4 mg/m3	25 mg/m3	Rozporządzenie Ministra Rodziny, Pracy i Polityki Społecznej z dnia 12 czerwca 2018 r. w sprawie najwyższych dopuszczalnych stężeń i natężeń czynników szkodliwych dla zdrowia w środowisku pracy (sejm.gov.pl)
BE	Werk Belgie	0.4 ppm (STEL)	1 ppm	10 ppm (TWA)	www.werk.belgie.be
NL	SER	None	1.4 mg/m3	10 mg/m3	www.SER.nl

Note the ACGIH Mixture Formula for interpretation of exposure monitoring data, where the sum of the weighted values of all three components of PAA products are used when interpreting monitoring results, is used by NIOSH in a recent publication.[2] The upper end (0.2 ppm TWA) of the proposed OEL range for PAA in the toxicity data review was used in this formula:

$$\frac{[HP]}{1\ ppm} + \frac{[PAA]}{0.2\ ppm} + \frac{[AA]}{10\ ppm} = X, \qquad \text{where X} < 1 \text{ or X} > 1 \text{ for exposure risk judgements}$$

The increasing use of PAA, its ability to become airborne, and relatively low OELs have led to an increased need to review risk assessments and controls, such as PPE, for those applications.

Regulatory Considerations That Influence PPE

Employers' health and safety responsibilities

Peracetic Acid is a hazardous chemical, so workers are expected to have access to hazard information, such as safety data sheets (SDS) and appropriate chemical labelling, in addition to training on how to protect themselves during its handling and use. While the precautionary information provided in the SDS can be used as general recommendations, the employer is expected to conduct a workplace-specific assessment to manage the risk of PAA handling. In addition, an exposure control strategy should be deployed and where PPE is part of that strategy, regulations applicable to PPE selection and use should be followed (see the 3M Respiratory Safety Centre).

Classification, Labelling and Packaging (CLP) Regulation ((EC) No 1272/2008)

CLP is legally binding across the European Member States and directly applicable to all industrial sectors. It requires manufacturers, importers or downstream users of substances or mixtures to classify, label and package their hazardous chemicals appropriately before placing them on the market.[3]

One of the main aims of CLP is to determine whether a substance or mixture displays properties that lead to a hazardous classification. In this context, classification is the starting point for hazard communication.

Once a substance or mixture is classified, the identified hazards (including physical, health, environmental and additional hazards) must be communicated to users. Hazard labelling allows the hazard classification, with labels and safety data sheets, to be communicated to the user of a substance or mixture, to alert them about the presence of a hazard and the need to manage the associated risks.

European Biocidal Products Regulation (BPR, Regulation (EU) 528/2012)

When antimicrobial claims are desired for a PAA-containing product, such as for marketing as a surface disinfectant or sanitizer, the product is regulated as a biocide under the European Regulation 528/2012 covering biocidal products.[4]

Regulation (BPR, Regulation (EU) 528/2012 concerns the placing on the market and use of biocidal products, which are used to protect humans, animals, materials or articles against harmful organisms like pests or bacteria, by the action of the active substances contained in the biocidal product.

The Regulation sets out rules for:

- Approving active substances in biocidal products;
- Authorising the supply and use of biocidal products; and
- The supply of articles treated with biocidal products.

The regulation aims to ensure that biocidal product placed on the market and used, only contain approved active substances that have been authorised.

Individual EU countries are responsible for authorising biocidal products that are made available in their own territory with mutual recognition processes possible between them. Some products can be authorised at the request of companies by the Commission at EU level enabling these companies to make these products available to the entire EU market.

The type of product claims desired will dictate the test methods and subsequent use instructions for the PAA-containing product. Test methods can vary for different claims and product application types such as sprays and wipes.

PAA is approved (under regulation (EU) 528/2012) for use as a biocide in the EU for: human hygiene, disinfection, disinfection, veterinary hygiene, veterinary hygiene, food and animal feeds, drinking water and product preservation.

Additionally, where a chemical is registered under the REACH Regulations, the supplier of substances and mixtures must provide to the recipient information on the product including such content as its health and environmental hazards, physical and chemical characteristics, first aid measures, safe handling and storage and recommendations for exposure control and the appropriate personal protective equipment.

Employers are encouraged to carefully review both the SDS and labels for these products and intended applications when conducting their workplace-specific risk assessments to determine worker handling practices and PPE.

Note since PAA is a strong oxidizer and can degrade quickly, it is important to carefully review the shelf life information on the label. Even when not used for its disinfectant claims, the oxidizing potential relied upon for effective decontamination may be affected by a short shelf life.

Hazardous Drugs and Pharmaceutical Manufacturing Applications

PAA-containing products can have many applications where pharmaceuticals are manufactured, processed or administered. These activities often are accompanied by cleaning, sanitizing, disinfecting, sterilizing or neutralizing and PAA-containing products may be chosen by facilities for all these tasks.

The nature of these cleaning and disinfecting tasks often means repeatedly using higher PAA concentrations spread over large surface areas, which may result in significant worker exposures. Keep in mind that regulated products must be used according to label directions, which can limit opportunities for reducing exposure by changing the way a product is used (such as not spraying when the product label indicates to apply using a sprayer or not maintaining a wet surface for the appropriate contact time).

Worker Exposure Assessment Methods

Exposure assessment is a key component of managing the risk when workers are handling PAA-containing products and a required step in the process of determining the need for respiratory protection. Understanding potential inhalation exposure can be broadly grouped into two types: qualitative and quantitative exposure assessment. Air monitoring accomplishes the latter, as the objective is to quantitate the amount of airborne PAA in the worker's breathing zone during relevant tasks. Air monitoring methods can be divided into two main types: direct-reading where a device can provide results right away, often in real-time as the work tasks are being conducted; and methods that require laboratory analysis, so results are not available until later and typically only represent an average concentration over the time period sampled (Time-Weighted Average (TWA)). Qualitative exposure assessments are those which do not involve actual measurements, but instead may rely on data from studies or judgements about exposure potential based on mathematical modelling, professional experience, or other inputs.

Air monitoring for PAA can be challenging and should only be conducted by trained health and safety professionals. Since airborne PAA is accompanied by hydrogen peroxide and acetic acid, one challenge is to separate those components. Some methods are not able to accomplish this and cross-reactivity may be problematic. Because the chemistry is highly reactive, another challenge can be in measuring the PAA concentration before it degrades. If airborne aerosol as well as vapor is being generated, then vaporization from the aerosol as well as reactivity during this process can further complicate exposure characterization. This same reactive and mixed nature of the airborne chemistry makes qualitative exposure assessment using modelling equations very difficult.

Understanding potential exposure variables has historically meant considering all aspects of the worker interface with the contaminant source, such as the task being performed, available ventilation or other engineering controls, and aspects such as the length of time spent in the various exposure scenarios. Concentration of the chemical(s) being used is another important variable and can be particularly relevant for disinfectant products such as PAA. These products can be used at a variety of concentrations depending on the application, such as sanitizer vs. disinfectant vs. sterilant. Sometimes the products are sold at one concentration considered "ready-to-use" but many are sold in concentrated form which may be diluted to a variety of strengths depending on the intended use. It is important to consider possible dilution error with concentrated products, even with automated proportioner systems, as exposure potential might change significantly if correct dilution is not followed. Contact time is another potential exposure variable relevant for disinfectants because it can influence the amount of chemical available for volatilizing from surfaces being cleaned. This is the amount of time, usually in minutes, that the entire surface must remain visibly wet with product for the corresponding microbial kill claim desired. For example, the same product might have a sanitizing (lower) kill claim at a lower concentration and/or contact time but might be capable of a sporicidal (higher) kill claim when used at a higher concentration or longer contact time.

With air monitoring being the primary method for understanding PAA exposure, and therefore risk, it is important to understand the limitations of current air sampling methods, so exposure is not underestimated when performing a risk assessment.

Direct-reading air monitoring methods are available for PAA but both require equipment that can be expensive and require some level of training to use. Electrochemical sensors and Fourier-Transform Infrared Spectroscopy (FTIR) are the technologies currently in use to monitor PAA directly in the workplace and both can provide real-time results. Methods that require laboratory analysis will first collect air samples on some type of media, which might vary depending on the type of analysis and if the intent is to capture airborne aerosol, vapor, or both. The sample media is then sent to the laboratory where the general analytical technique is often High-Performance Liquid Chromatography (HPLC). The use of accredited laboratories familiar with this type of industrial hygiene chemistry work is recommended if this type of air sampling is pursued.

Few published studies exist that might be used for understanding potential exposure, below is a brief summary of their data:

- Field evaluation of five workplace settings where PAA products were used for non-critical surface disinfection tasks tested the feasibility of a new PAA air sampling and analysis method. Results ranged from the detection limit of 0.013 ppm to 0.4 ppm.[5]

- Data from a graduate student study on non-critical surface disinfectant exposure assessment was given as part of a presentation at APIC 2018 - The Industrial Hygienist's Role in Improving Safety for Patients and Workers. This study compared exposure from several different disinfectant chemistries, including peracetic acid monitored using FTIR. STEL exposure scenario results indicated only PAA exposure exceeded the OEL of 0.4 ppm.[6]
- Field evaluation of semi-critical disinfection tasks (endoscope re-processing) using PAA product to evaluate a new PAA air sampling and analysis method indicated short term exposure to PAA could be elevated under some circumstances but the 8-hour TWA exposure was low.[7]
- A NIOSH Health Hazard Evaluation (HHE) where over 40 air samples were collected during use of a PAA product in healthcare non-critical surface disinfection, all below OELs.[2]

PPE for Worker Protection

PPE use requires an assessment be conducted and documented to determine appropriate PPE for worker tasks. Risk assessments should consider both the hazard and the potential exposure. Qualitative and/or quantitative exposure assessment, such as through air sampling, are often done to help evaluate inhalation exposure. In some industries such as pharmaceutical manufacturing, the practice of occupational exposure banding may be used to help establish risk management measures (see 3M OEB Bulletin for more information). While typically used for potent compound exposure, this approach might be useful for other applications where there are relatively low exposure limits and difficulty in accurately characterizing exposure.

Exposure controls that reduce inhalation exposure should be considered when an employer's risk assessment indicates that the respiratory hazard may result in adverse health effects. All applicable regulations on the selection and use of respiratory protection must be followed. Part of respiratory protection selection is consideration of the Assigned Protection Factor (APF) needed, based on the level of exposure. Also, consideration needs to be given to any Immediately Dangerous to Life or Health (IDLH) level that might have been established. Note in 2015, US National Institute for Occupational Safety and Health (NIOSH) published a draft IDLH for PAA of 0.64 ppm; however, numerous comments resulted in a NIOSH re-evaluation of the proposed IDLH with no additional proposals to date. Another thing to keep in mind are the points at the beginning of this paper on the additional chemicals present with PAA and application of the ACGIH mixture formula when determining exposure.

Respirator manufacturers may also have publications which can help with respirator selection for PAA. Information on the type of respirator (including cartridge and filter if applicable) recommended, along with cartridge service life data should be requested of the manufacturer to help satisfy requirements of the local regulations on the use of respiratory protection. See the 3M Technical Bulletin "Respiratory Protection for Hydrogen Peroxide, Peracetic Acid, and Acetic Acid" for more information on 3M respirator products for PAA. Respiratory protection that includes suitable eye protection, such as a full facepiece respirator or PAPR with appropriate headgear, may be considered due to the eye irritation potential of PAA-containing products. Selection of appropriate PPE should also consider the need for eye and skin protection due to the potentially irritating or corrosive nature of PAA. Tasks that may result in eye or skin contact with liquid may require eye and face protection, gloves and body coverings such as coveralls. Vapour or aerosol presence may require goggles or respiratory protection that includes suitable eye protection. Manufacturer-provided selection guides may be helpful in choosing appropriate eye and skin protection. Keep in mind the nature of the task, including chemical concentration and extent of potential eye and skin contact, when selecting PPE. More information on 3M products can be found at www.3M.com/workersafety.

References

[1] Pechacek, N. et. al. Evaluation of the toxicity data for peracetic acid in deriving occupational exposure limits: A minireview. Toxicology Letters 233 (2015) 45-47.
[2] Hawley, B. et. al. Evaluation of exposure to a new cleaning and disinfection product and symptoms in hospital employees, NIOSH HHE Report No. 2015-0053-3269.
[3] Classification, Labelling and Packaging (CLP) Regulation ((EC) No 1272/2008) https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32008R1272
[4] Biocidal Products Regulation (BPR, Regulation (EU) 528/2012) EUR-Lex - 32012R0528 - EN - EUR-Lex (europa.eu)
[5] Nordling, J. et. al. Description and evaluation of a peracetic acid air sampling and analysis method. Toxicology and Industrial Health 33 (2017) 922-929.

[6] Thompson, K. et. al. APIC 2018 Education Session 3009 - The Industrial Hygienist's Role in Improving Safety for Patients and Workers, Industrial Hygiene Exposure Assessment: Non-Critical Surface Disinfectants. Minneapolis, MN.
[7] Pacenti, M. et. al. Air Monitoring and Assessment of Occupational Exposure to Peracetic Acid in a Hospital Environment. Industrial Health 48 (2010) 217-221.

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