MEASUREMENT OF PGMEA USING PHOTOIONIZATION DETECTORS

WHAT IS PGMEA?
Propylene Glycol Mono-Methyl Ether Acetate (PGMEA), CAS 108-65-6, is an organic compound with the formula C₆H₁₂O₃. This combustible compound has an odor similar to ether, and it is a clear, colorless liquid primarily used as a solvent. In 1999 global production estimates were 100,000 to 500,000 tons/year (IUCLID 1999). Further data on the properties of PGMEA are available from any Material Safety Data Sheet (for example: MSDS) posted in the workplace, a supervisor, an Industrial Hygienist, or Chemist. Select data are presented below:

Typical Properties:
- Molecular Weight: 132.16 g/mol
- Density @ 20°C (68° F): 0.967 g/cm³
- Flash Point Closed Cup, 42° C (108° F)
- Vapor Pressure @ 20°C (68° F): 2.8 mmHg
- Lower Flammability in Air: 1.3% v/v
- Upper Flammability in Air: 13.1% v/v

Where is PGMEA Used?
PGMEA is used in a number of industrial, commercial, and consumer sectors and products that include:
- Silkscreen printing and other ink-based uses
- Household cleaning agents
- Solvent-based coating (paint, auto, industrial)
- Oils, fats, resins, and lacquers
- Semiconductor manufacturing

Why Should We Monitor PGMEA?
PGMEA is a known eye irritant. While it is not listed as a carcinogen, it does target a number of critical organs (liver, kidneys, etc.) and the central nervous system (CNS). In addition, studies on rats and mice (Miller et al., Toxicol. Appl. Pharm. 75 521-530 (1984)) reveal that inhalation exposure causes degeneration of nasal tissue related to the sense of smell. Spills and leaks of this chemical can also lead to explosions if the concentration were to reach a value between the LEL and UEL in Air in the presence of an ignition source. Therefore, the chemical presents a threat to the health and safety of personnel and property.
In 2011 the American Industrial Hygienist Association (AIHA) established an 8-hour Time Weighted Average (TWA) of 50 parts per million (ppm). A National Occupational Health Study published in 1983 by the Centers for Disease Control (CDC) estimates PGMEA was ranked 251 out of over 12,000 chemicals that employees were exposed to in the workplace.

This chemical has migrated from manufacturing applications into the consumer market, and it is produced on a large scale. Given the movement by an organization that serves the needs of occupational, environmental health, and safety professionals to establish an exposure limit for the workplace, it is important for businesses to be well-informed and to monitor appropriately in their workspace.

MEASUREMENT TECHNIQUES FOR PGMEA: PID VS. GC/FID/MS VS. COLORIMETRIC TUBES

Photoionization detectors (PIDs) measure VOCs and other toxic gases in low concentrations, from ppb (parts per billion) up to 15,000 ppm (parts per million, or 1.5% by volume). A PID is a very sensitive broad-spectrum monitor which can be configured to scale readings for a particular compound.

Many industrial processes include VOCs such as PGMEA. The sensitivity of PIDs to VOCs and their fast response time make them an invaluable tool for employee exposure monitoring and for quickly executing HazMat response tasks, including:

- Initial personal protective equipment (PPE) assessment
- Leak detection
- Perimeter establishment and maintenance
- Spill delineation
- Decontamination
- Remediation
- Confined space entry


PID Pros
- Immediate result, “point and shoot”—responds in seconds
- Accurate and Precise to within ±10%
- Low cost to operate and maintain
- Does not require a chemist to operate
- Little to no sample handling, storage, or preparation
- Continuous real-time monitoring with alarm capabilities
- Datalogging

PID Cons
- Broad-spectrum monitor

A PID is ideal for continuous monitoring of personnel working with PGMEA and making personal protective equipment (PPE) decisions based upon AIHA’s TWA limit of 50 ppm, as well as a powerful HazMat response tool for PGMEA incidents and other toxic industrial chemicals. For examples of PID use in response to spill delineation, leak detection, perimeter monitoring, and remediation, refer to RAE Systems Application Note AP-203: PIDs as HazMat Response Tools, pages 4 through 6.

WHY NOT USE GC-FID OR GC-MS FOR TWA MEASUREMENTS OF PGMEA?

There are two laboratory-based techniques for analyzing PGMEA. The first is the Environmental Protection Agency TO-15 (EPA) and the second is the National Institute for Occupational Safety and Health (NIOSH) Glycol Ethers Method 2554. These methods rely upon either Gas Chromatography Flame Ionization or Mass Selective Detectors (GC-FID/MS). The pros and cons of GC-FID/MS are summarized below:

GC-FID/MS Pros
- Accurate and precise
- Selective method

GC-FID/MS Cons
- High cost to outsource testing or maintain a GC lab
- Turnaround time is hours or days so cannot use for TWA monitoring
- Results are based on a snapshot, not a continuous sampling
- Incapable of providing alerts or alarms
- Reactive form of protection (not proactive)
To summarize, Gas Chromatography techniques have three major drawbacks related to monitoring PGMEA. First, the GC-FID/MS techniques have a long turnaround time due to its need for sample collection, shipment, sample and standard preparation, subsequent analysis, and data interpretation. Second, if this is the only technique available to you, then you must use it without the benefit of a point-and-shoot reading to acquire information about an incident. Third, the cost to maintain a GC lab, pay a chemist, or outsource the analysis is quite high. The GC-FID/MS techniques are ill suited for making immediate and TWA decisions.

**WHAT ABOUT COLORIMETRIC TUBES AND METAL OXIDE SENSORS FOR PGMEA?**

Colorimetric tubes have been the foundation of HazMat response gas detection for years. They are an accepted and proven means of measuring many toxic gases and vapors at ppm levels. Colorimetric tubes are inexpensive, but have limitations:

- Tubes only provide one-time snapshots. They do not provide continuous monitoring with alarms.
- The “spot check” nature of tubes also makes them more prone to sample error.
- Tubes are slow to respond. They give readings in minutes rather than seconds.
- Tube readings are subject to interpretation.
- Tubes expire

Metal Oxide, Sensors (MOS) are among the oldest and least expensive measurement technologies used in portable instruments. While MOS sensors can detect a very wide range of contaminants, they have a number of shortcomings that limit their effective use in PGMEA detection.

- These have limited sensitivity, with detection limits usually in the tens of ppm making them inappropriate for TWA monitoring.
- They can be poisoned and dirtied and not easily cleaned.
- The response time of a MOS is slow, relative to a PID.

**RAE SYSTEMS PRODUCTS FOR MONITORING PGMEA**

Regulatory agencies such as the EPA use RAE Systems PIDs for PGMEA and other VOC detection. Having the same technology as the regulatory agencies instills confidence these data are reliable and will stand up to scrutiny during compliance visits and audits. The creation of a TWA value by AIHA for PGMEA is a new standard. RAE products are ready with pre-programmed correction factors, documentation, and technical staff to support your monitoring needs.

**MiniRAE 3000, MultiRAE, and ToxiRAE Pro PID:** Three RAE Systems instruments with PIDs.