

MEASUREMENT OF SELECTED ORGANIC VAPORS IN INDUSTRIAL AREA

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ABSTRACT

The organic vapors of methyl methacrylate and butyl acrylate are adsorbed from air on high activity charcoal, desorbed with carbon disulfide and quantified using a gas chromatograph (GC) equipped with a suitable detector and capillary capability. 3M Organic Vapor Monitor (OVM) contains a single charcoal adsorbent pad that is designed to adsorb organics vapor of butyl acrylate, methyl methacrylate in industrial environments that are analyzed and measured by laboratory for environmental impact assessment (EIA).

Key words: Vapor organic, Industrial environment, Gas Chromatography, GC-MS

1. INTRODUCTION

Threshold Limit Values (TLV) and Permissible Exposure Limit (PEL) standards are the most cited organic contaminant airborne standards [1]. There are three categories for TLVs that are: (1) Threshold Limit Value-Time Weighted Average (TLV-TWA) is the concentration for a normal 8-hour workday and a 40 hour workweek without adverse effects, (2) Threshold Limit Value-Short Term Exposure Limit (TLV-STEL) is the concentration for a short period of time (15 minute) without suffering from irritation, chronic or irreversible tissue damage, and (3) Threshold Limit Value-Ceiling (TLV-C) is the concentration that should not be exceeded during any part of the working exposure.

Acrylic acid is the simplest unsaturated carboxylic acid which has double bond and carboxyl group with the formula $\text{CH}_2=\text{CHCOOH}$. Acrylic acid undergoes the typical reactions of a carboxylic acid and forms acrylic esters - basic alkyl esters are methyl and butyl acrylate. Acrylic acid and its esters undergo the reactions of the double bond which readily combine with themselves or other monomers such as methacrylates to form homopolymers or co-polymers which are used in the production of coatings, super absorbent polymers, flocculants, as well as fibres and plastics. Methyl methacrylate is released to ambient air from production facilities, end-product manufacturers and storage [2].

Methyl methacrylate (MMA, Molecular Weight:100.12, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$) is one ester of the unsaturated C4 carboxylic acid and contains small amount of hydroquinone or hydroquinone mono-methyl ether to inhibit spontaneous polymerization. The term of metha indicates an additional methyl group attached to the alpha carbon of acrylic acid. Butyl acrylate (BA: $\text{CH}_2=\text{CHO}(\text{O})\text{O}-(\text{CH}_2)_3\text{CH}_3$, Molecular Weight:128.17) contains hydroquinone (1000ppm) or hydroquinone methyl ester (15 or 200 ppm) to prevent polymerization in organic synthesis [3]. Butyl acrylate (BA) and methyl methacrylate (MMA) are organic compounds that can be adsorbed by certain adsorbent and have higher recoveries when desorbed with carbon sulfide. The aim of their production is to manufacture in acrylic plastics, resins for sheeting and industrial applications such as

polymerization homo polymers, emulsion polymers for latex paints and textile, cast poly methyl methacrylate sheets, surface coating resins and molding powders for plastic industries.

Methyl methacrylate and butyl acrylate are extremely volatile and can easily form high vapor concentration at room temperatures. They are regulated as a toxic chemical under Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 and 40 CFR part 372 (TLV-TWA=100 ppm; 410 mg/m³ for MMA and 10 ppm, 41mg/m³ for BA) [4]. Methyl methacrylate monomers are used in a wide variety of industrial applications including some areas of personal hygiene.

The toxic effects of butyl acrylate and methyl methacrylate are due to the monomer, the polymer appears inert, and the severity of effects is believed to be inversely proportional to the degree of polymerization [3]. Therefore, they must not be flushed to surface water or sanitary sewer system or allow material to contaminate ground water systems but it is incinerated in closed containers. Treatment of wastewater must be in accordance with applicable Federal, State/Provincial, and Local Regulations.

Water and soil experiments conducted under biological treatment conditions suggest that the biodegradation of methyl methacrylate may be significant in the ambient aquatic environment [2]. Methacrylate and butyl acrylate are chemically (1) biodegradable with acclimatized sewage sludge; (2) exhibited a 47% theoretical oxidation to CO₂ in 10 days, using 19-day acclimatized sewage as microbial inoculum; and (3) underwent 100% degradation in 20 hours with activated sludge as the source of microorganisms [2].

The 3M organic vapor monitors (OVM) is used to sample 8 hour TLV-TWAs to collect a sufficient quantity of organic vapor contaminant for analysis. 3M monitor contains a single charcoal adsorbent pad and is designed to be analyzed by an environmental laboratory to control a variety of organic vapor such as methyl acrylate and butyl acrylate [1]. It is not used for some chemical compounds such as formaldehyde, methanol, methyl chloride and organic solids because of adverse interactions with the sorbent material [1].

This paper aims to develop an analytical method to measure vapor organics concentrations of butyl acrylate, methyl methacrylate that used in manufacture of polymers synthesis, desorbed with carbon disulfide and analyzed by gas chromatography - mass spectrometer detector (GC-MS) in Central Laboratory for Environment Quality Monitoring (CLEQM). More specifically, this analytical method is documented and approved to increase Central Laboratory for Environment Quality Monitoring (CLEQM)' field activities such as air contamination monitoring. Furthermore, this is study assesses these organic chemicals in industrial area according to the American Industrial Hygiene Association (AIHA) manual [5-6] and evaluates contamination level in air at workplace.

2. EXPERIMENTAL

The environmental methodology measurement is carried out according to international standard environmental methods [1] that include 3M 3500/3520 Organic Vapor Monitors. The organic vapors are adsorbed on high activity charcoal, desorbed with carbon disulfide and quantified using gas chromatograph (GC) equipped with a mass spectrometer detector (MS) and the recovery is calculated. This analytical procedure is applied to measure methacrylate and butyl acrylate in environmental samples in an industrial area (summer 2006 and winter 2007).

2.1 Sampling

Methyl methacrylate and butyl acrylate are monitored in the environment by sampling with an adsorption tube (monitor and analyzed [7]). Two groups of environmental samples are collected from five locations in an industrial environment using Organic Vapor Monitors (OVM) - 3M Brand No. 3500 with 180 milligrams of activated carbon for each collection layer in a Teflon matrix at summer and winter with the same time for the same locations. A blank control sample are prepared at the monitoring site and collected with the samples. The environmental samples have the following records: Monitor number to indicate the location of sample, Time of exposure (minutes = 240 min.) and Temperature

(summer 2006 and winter 2007 seasons). After sampling with (OVM) the retaining ring and white barrier film are removed and discarded. The clear elution cap is snapped into place and the ports should be securely sealed with the plugs

2.2 Materials

Solvents: Carbon Disulfide - Aldrich (HPLC grade - handled in a hood)

Standards: Stock standards solutions of monomers (MMA, BA) are stored in the laboratory refrigerator for 1-5 days (only).

2.3 EQUIPMENT

Gas Chromatograph: Hewlett Packard (HP, Model 5890A equipped with a mass spectrometer detector (GC-MS) and auto-sampler HP model G/S/3A, G/S12AX and analytical Columns: HP-SMS

Autosampler Vials: 2 ml with Teflon lined caps.

Microliter Syringes: Hamilton (or equivalent) 1 μ L - 5 mL. These syringes are guaranteed accurate to +/-1% full scale and are used without further calibration.

Typical Parameters for Gas Chromatographs conditions:

Oven Temp: 40°C	Final value: 180-225°C
Detection Temp: 250°C	Injection Temp: 225 °C
Initial Time: 3 min	Final Time: 3min
Equilibrium Time: 0.5 to 2 min	Program Rate: 10 C/min
Chart speed: 0.50 cm/min	%Offset: 10
Threshold: 0.04	Peak width: 0.04, Attn: 2 ³
Split Ratio: 30:1 (15:1 at low levels, 60:1 at high levels of compound is expected)	

2.4 Analytical Procedure

Add 1.5 mL of the de-sorption reagent (CS₂) to the monitor through the central port. After standing for 30 minutes with occasional gentle agitation, the eluent is decanted into a marked 2 mL vial, sealed and a 1 to 5 uL sized sample is automatically introduced into the gas chromatograph. The area of the peak of interest is recorded and the amount in mg is determined from the standard curve.

Calibration Standards

Concentrations of standards are chosen to bracket the expected concentrations in samples. Standards are prepared methyl methacrylate (MM) to butyl acrylate (BA), with 1:1 ratio of stock dilution. A calibration curve is prepared using seven standards concentrations of methacrylate to butyl acrylate concentrations that are (1) 2.5:2.6, (2) 5:5.2, (3) 10:10.4, (4) 20:20.8, (5) 50:52, (6) 75:78 and (7) 100:104 µg/L respectively.

Internal quality control samples are run with each set of standards and samples.

3.5 Calculation

The weight of contaminant(s) is determined in each sample by use the calibration data (regression equation) generated from the prepared standards. The sample weight is corrected by subtracting any interfering contributions from a control blank. The time-weighted-average concentration of the environmental samples can be calculated by knowing the length of the sampling period, the contaminant weight determined by gas chromatography (GC-MS), the recovery coefficient and the molecular weight.

Regression Equation:

$$\text{ppm} = \frac{\left(\frac{\text{mg}}{\text{mL}}\right)(\text{mL})(24.45)}{(\text{SR})(r)(\text{MW})(10^{-3})}$$

Where:

- mg/mL = amount found from calibration curve by GC-MS
mL = elution volume (usually 1.5 mL)
SR = Sampling rate (31.8 Cm³/min)
t = sampling time (240 min)
MW = molecular weight (128.17, 100.12) for MMA and BA respectively
r = recovery \simeq 1

Recovery Coefficient

The recovery coefficient is determined by vapor-state spiking of 3M organic vapor monitors and is calculated as follows:

$$W = (K_o) \times (C) \times (t) \times (10^{-6} \text{ m}^3/\text{cm}^3)$$

Where:

W = Amount of liquid injection in milligrams, K_o = Sampling rate of monitor cm³/min.

C = Average concentration in mg/m³, t = Sampling time in minutes

Recovery Coefficient (r) is \simeq 1 and 0.97

3. RESULTS AND DISCUSSION

This procedure covers the method of analyzing samples to determine the amount of organic vapor present in the air. More specifically, this procedure is to be used for those organic vapors which can be collected by 3M Organic Vapor Monitors and desorbed with carbon disulfide or other suitable solvents.

The data of methacrylate and butyl acrylate measurements were performed to determine the organic pollution in industrial environment. Furthermore, Threshold Limit Values (TLV) limits are applied to evaluate the concentration for a normal 8-hour workday without adverse effects (TLV-TWA). Moreover, the organic pollution level is determined.

3.1 Calibration Line

The seven standards of methacrylate : butyl acrylate concentrations (2.5:2.6, 5:5.2, 10:10.4, 20:20.8, 50:52, 75:78 and 100:104 $\mu\text{g/L}$) are presented as straight line as shown in Fig. (1-A) and the retention time for MMA peak is illustrated as shown in Fig. (1-B).

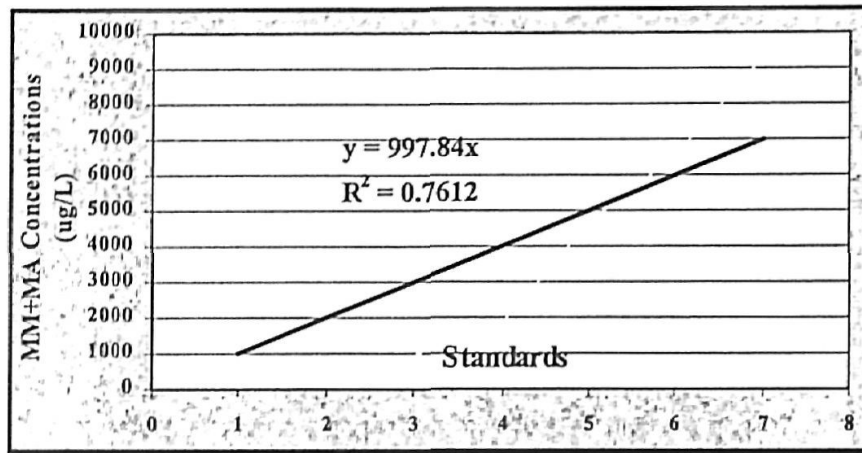


Fig (1-A)

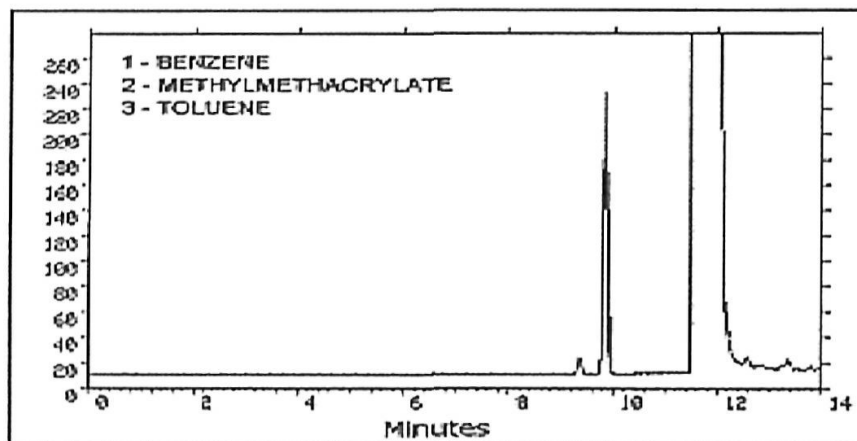


Fig.(1-B)

Fig. 1 Standard Concentrations of Methyl methacrylate: Butyl acrylate and GC-MS Chart

3.2 Environmental Trend of Organic Vapors

The study focused on measurement of the organic compounds from environmental samples in industrial area that are: butyl acrylate and methyl methacrylate. These compounds are selected to develop an analytical method using a gas chromatograph (GC-

MS) and measure in airborne to estimate the organic contamination in industrial environment.

From the data obtained in Table (1), methyl methacrylate vapors showed higher concentrations at 240 minutes in winter season (January 2007) than summer season (June 2006). These values increased spatially distance from source pollution that showed the maximum concentrations of organic vapors releasing with polymerization process in airborne.

Table (1) Methyl methacrylate and Butyl acrylate Concentrations of Organic Vapors Measured in an Industrial Area

Sample Locations		Organic Vapors			
		methyl methacrylate (MM)		butyl acrylate (BA)	
		GC-MS ug/L	Conc. In Air (PPM)	GC-MS ug/L	Conc. In Air (PPM)
1	June 2006	621	29.8	0.00	0.00
2		918.5	44.08	56.0	2.07
3		2107	101.13	54.5	2.01
4		2710.5	130.1	38.73	1.61
5		5709	279.6	40.9	1.7
6	Jan.2007	583.6	28.58	36.9	1.38
7		1770.4	86.7	42.3	1.52
8		2197.6	107.62	41.5	1.74
9		2765.6	135.45	61.7	1.68
10		6368.2	305.67	68.7	2.54

Figure (2) demonstrates the comparative analysis for organic vapors in seasons: butyl acrylate and methyl methacrylate in industrial environment. This comparison showed that methyl methacrylate vapors have higher concentrations (summer: 57.6-611.34 ppm) and (winter: 59.6-558.4 ppm) at 8 hours temporally and increased spatially with source pollution of polymerization process in airborne reached to about six times of airborne standards (TLV-TWA: 100ppm). Marked increase of methyl methacrylate in January month (2007) although temperature in winter lower than that in summer, results from the

high organic vapors that represented increasing of polymerization process with low ventilation capacity. In addition, the butyl acrylate concentration (TLV-TWA:10ppm) that release in low concentration in comparative with methyl methacrylate due to material ratio of polymerization synthesis requirements and due to its lower vapor pressure.

Threshold Limit Values ((TLV-TWA: normal 8-hour workday without adverse effects) limits are applied for environmental impact assessment (EIA) at different locations. The application showed that methacrylate concentrations in air violate the TLV-TWA limits (100ppm) at sample locations near source pollution while butyl acrylate concentration in air is within TLV-TWA limits (10ppm) at all sample locations. This difference in measurements is due to higher vapor pressures of methacrylate than those of butyl acrylate which lead to the organic pollution in the industrial environment.

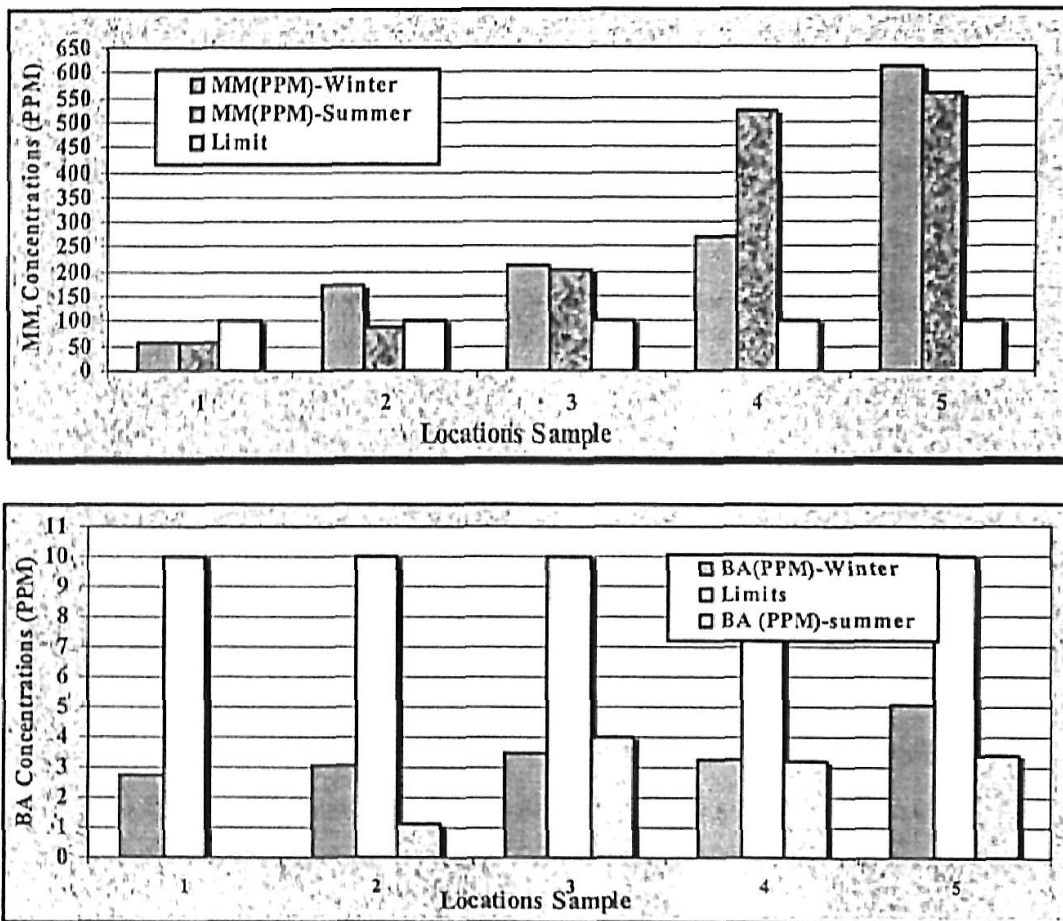


Fig.(2) Methyl methacrylate and Butyl acrylate Concentrations in Industrial Environment

4. CONCLUSION

Butyl acrylate (Acrylic ester) and Methyl methacrylate (Methyl acrylate) are used in polymerization organic synthesis that methyl methacrylate contains small amount of hydroquinone or hydroquinone mono-methyl ether to inhibit spontaneous polymerization and butyl acrylate contains hydroquinone (1000ppm) or hydroquinone methyl ester (15 or 200 ppm) to prevent polymerization. The 3M organic vapor monitors (OVM) is designed to collect organic vapors and analyzed by an environmental laboratory. It contains a single charcoal adsorbent pad that is used as 4 hour sample TLV-TWAs to collect the previous organic vapor and analyse using GC-MS. 3M monitor

This study aims to develop an analytical method to measure vapors of Butyl acrylate; Methyl methacrylate adsorbed using GC-MS. This procedure covers the method of analyzing samples to determine the amount of organic vapor present in the air. More specifically, this procedure is to be used for those organic vapors which can be collected by 3M Organic Vapor Monitors and desorbed with carbon disulfide or other suitable solvents.

Threshold Limit Values ((TLV-TWA: normal 8-hour workday without adverse effects) limits are applied for environmental impact assessment (EIA) at sample locations. The application showed that methacrylate concentrations in air violate the TLV-TWA limits (100ppm) at sample locations near source pollution while butyl acrylate concentration in air within TLV-TWA limits (10ppm) at all sample locations. This difference in measurements is related to high vapor pressure of methacrylate than vapor pressure of butyl acrylate which leads to the organic pollution in the industrial environment.

5. RECOMMENDATION

Water experiments conducted under biological treatment conditions suggest that the biodegradation of methyl methacrylate may be significant in the ambient aquatic environment. These organic: methacrylate and butyl acrylate are (1) biodegradable with acclimatized sewage sludge; (2) exhibited a 47% theoretical oxidation to CO₂ in 10 days, using 19-day acclimatized sewage as microbial inoculums; and (3) underwent 100%

degradation in 20 hours with activated sludge as the source of microorganisms. It is recommended: Monitoring of technical ventilation system and following the international recommendation (ACGIH, 1974).

6. REFERENCES

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