

Real time measurement of dichloromethane containing mixtures

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Dichloromethane (DCM), also known as methylene chloride, is typically used as a component of proprietary paint strippers. Occasional workplace fatalities result from its use in GB. The aim of this project was to determine the suitability of commercial, real-time (direct-reading), portable gas detectors to monitor DCM in the presence of other volatile organic compounds typically found in paint strippers. Various types of gas detector (based on photoionisation, infrared and catalytic sensors) were exposed to air mixtures of DCM, methanol and isopropanol.

It was found that high sensitivity photoionisation detectors (PIDs) with high energy UV lamps are approximately 30 times more sensitive than PIDs with low energy UV lamps. Both PIDs can measure DCM at levels below the Workplace Exposure Level (WEL) of 300 ppm (15 minute short-term). They are both cross-sensitive to the other VOCs investigated. However, this may still allow reasonably accurate measurement of DCM, as the concentration of DCM in the vapour phase is typically much greater than the other VOCs. The other types of detector were not suitable for measurement of DCM around and below the WEL.

The high sensitivity PIDs were found to lose sensitivity quite rapidly and do not have a long shelf life when compared to the low sensitivity PIDs. Nevertheless, with care, they can be used to measure low (ppm) levels of DCM. Further work is required to evaluate the effect of hydrogen fluoride, another component of paint strippers, on the performance of PIDs.

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EXECUTIVE SUMMARY

Dichloromethane (DCM), also known as methylene chloride, is typically used as a component of proprietary paint strippers. Breathing in DCM vapour can produce narcotic effects and exposure to skin and eyes may cause irritation. DCM evaporates easily (boiling point: 39.8°C) producing high concentrations of vapour, particularly in confined spaces or where ventilation is inadequate. DCM has a GB work place exposure limit (WEL) for an 8 hr time weighted average of 100 ppm and has been classified as a Category 3 carcinogen in the European Community. Under the Chemicals (Hazard Information and Packaging) (CHIP) Regulations, it has the risk phrase R40 'Possible risk of irreversible effects'. Under the REACH regulations, industrial use of paint strippers in industrial installations is allowed to continue as long as certain safe working practices are followed. Other uses are banned (customer use) or restricted (professional use).

Approximately one workplace fatality occurs every 3½ years in GB involving the use of DCM due to the acute toxic and asphyxiation effects of the vapour. DCM is the major component (typically 70-90% in the liquid) of paint strippers, other materials present may include methanol (10-30%) and hydrogen fluoride (1-10%).

The aim of this project, therefore, was to determine the suitability of commercially available real-time monitors to accurately monitor DCM in the presence of other constituent volatile organic compounds (VOCs) such as methanol and isopropanol in paint strippers. This could help prevent exposures to harmful concentrations of DCM during, and aid in the investigations of incidents arising from, the use of such paint strippers

DCM can be monitored at toxic levels (~ 300 ppm) using MiniRAE 3000 monitors incorporating 11.7 eV lamps (effective measurement resolution of 0.2 ppm). DCM can be monitored at toxic levels using MiniRAE 2000 monitors incorporating 10.6 eV lamps if required, but with a much lower effective measurement resolution (5 ppm).

DCM can be monitored at flammable levels ($\geq 13\%$ v/v) using MultiRAE monitors incorporating electrochemical O₂ sensors (effective measurement resolution: 0.5% v/v). MultiRAE monitors incorporating catalytic bead LEL sensors are poisoned by exposure to DCM preventing them being used in the atmosphere of paint stripper vapour, and Impact monitors incorporating IR LEL sensors show inconsistent sensitivity when exposed to various flammable levels of DCM.

Methanol can only be monitored at toxic levels (~ 250 ppm) using MiniRAE 3000 monitors incorporating 11.7 eV lamps (effective measurement resolution: 0.5 ppm).

Methanol can be monitored at flammable levels ($\geq 6\%$ v/v) using Impact monitors incorporating IR LEL sensors (effective measurement resolution: 300 ppm v/v), MultiRAE monitors incorporating catalytic bead LEL sensors (effective measurement resolution: 654 ppm v/v), and MultiRAE monitors incorporating electrochemical O₂ sensors (effective measurement resolution: 0.5% v/v).

Isopropanol (IPA) can be monitored at toxic levels (~ 500 ppm) using MiniRAE 3000 monitors incorporating 11.7 eV lamps (effective measurement resolution: 0.3 ppm), and MiniRAE 2000 monitors incorporating 10.6 eV lamps (effective measurement resolution: 0.6 ppm).

IPA can theoretically be monitored at flammable levels ($\geq 2\%$ v/v) using MultiRAE monitors incorporating electrochemical O₂ sensors (effective measurement resolution: 0.5% v/v), and MultiRAE monitors incorporating catalytic bead LEL sensors (effective measurement

resolution: 520 ppm). The theoretical characterisation of the Impact monitors incorporating IR LEL sensors to flammable levels of IPA was not possible due to limited availability of technical information on the monitor

The cross-sensitivity of MiniRAE 2000 monitors and MiniRAE 3000 monitors to methanol and IPA prevent selective monitoring of dichloromethane in paint strippers in which appreciable amounts of these chemicals are present.

The reduction in the detected concentration of MiniRAE 3000 monitors at a rate of 1.4 ppm per minute must be taken into account for extended exposure times but for normal exposure times this should not have a significant effect on the operation of the instruments.

Investigations into the effect of HF on the sensing mechanisms of MiniRAE 3000 monitors incorporating 11.7eV lamps may allow them to be used to monitor the levels of DCM in paint stripper as the levels of VOCs other than DCM in the paint stripper investigated here have been found to be negligible. Different makes and specifications of paint stripper should be analysed and the constituents compared to investigate the ranges of the VOC and acidic components. It may then be possible to compile a procedure to allow the monitoring of DCM in some paint strippers without the interference of other chemical vapours contaminating the results to any significant degree. Further investigation into the reliability of MiniRAE 3000 monitors incorporating the 11.7eV lamps over time may also be required.

It is not feasible to use the Gaset FTIR spectrometer to monitor DCM in paint stripper containing HF as this could cause significant and expensive damage to the internal optics. It must also be noted that the Gaset FTIR spectrometer is not certified for use in flammable atmospheres and as such cannot be used if such atmospheres are suspected.

As the response factors of the monitors determined in this investigation were significantly different from those documented by the manufacturers for both DCM and methanol, it would be good practice to check these factors by laboratory exposure to these gases/vapours before use.

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1. INTRODUCTION

Dichloromethane (DCM), also known as methylene chloride, is typically used as a component of proprietary paint strippers. It can be used as a gel (for brush application) or in a dip tank. In all cases, the solvent is allowed to soften the paint film, which is then removed by hand brushing/scraping. With a dip tank process, articles are often dipped in tanks (these may be heated) containing weak acid or alkali solutions, which follow the solvent dip. Finally articles are washed to remove solvent and paint debris.

A ban on some supply and use of paint strippers containing DCM is in force under REACH (European Union regulation concerning the Registration, Evaluation, Authorisation and restriction of Chemicals which came into force on 1st June 2007). For the purposes of this ban, the term 'paint stripper' is taken to mean DCM (or mixtures containing it) intended for stripping paint, varnish or lacquer. Pure DCM (or mixtures containing it) sold and used for other purposes (e.g. degreasing) are not banned and can continue to be sold and used (although not for stripping paint). There are three types of use:

- 'Industrial' use of paint strippers in 'industrial installations' (i.e. facilities where paint stripping takes place) – this is allowed to continue as long as certain safe working practices are followed.
- 'Professional' use by workers where this takes place away from an industrial installation. This is banned, but GB can choose to allow continued safe use by specifically trained professionals.
- 'Consumer' use by the general public, such as DIY. Supply to consumers is banned.

For industrial use, DCM-based paint strippers can continue in industrial installations so long as certain safe working practices are followed. Supply for these uses is also permitted. The required conditions for continued industrial use are:

- (a) effective ventilation in all processing areas, in particular for the wet processing and the drying of stripped articles: local exhaust ventilation at strip tanks supplemented by forced ventilation in those areas, so as to minimise exposure and to ensure compliance, where technically feasible, with relevant occupational exposure limits;
- (b) measures to minimise evaporation from strip tanks comprising: lids for covering strip tanks except during loading and unloading; suitable loading and unloading arrangements for strip tanks; and wash tanks with water or brine to remove excess solvent after unloading;
- (c) measures for the safe handling of dichloromethane in strip tanks comprising: pumps and pipework for transferring paint stripper to and from strip tanks; and suitable arrangements for safe cleaning of tanks and removal of sludge;
- (d) personal protective equipment that complies with Directive 89/686/EEC comprising: suitable protective gloves, safety goggles and protective clothing; and appropriate respiratory protective equipment where compliance with relevant occupational exposure limits cannot be otherwise achieved;
- (e) adequate information, instruction and training for operators in the use of such equipment.

Breathing in DCM vapour can produce narcotic effects. These include drowsiness, headache, giddiness and, at high concentrations, unconsciousness and death. DCM is also a defatting agent and exposure to skin and eyes may cause irritation. DCM evaporates easily (boiling point: 39.8°C) producing high concentrations of vapour, particularly in confined spaces or where

ventilation is inadequate. DCM has been classified as a Category 3 carcinogen in the European Community. Under the Chemicals (Hazard Information and Packaging) (CHIP) Regulations, it has the risk phrase R40 ‘Possible risk of irreversible effects’. The risks posed to human health by DCM in paint strippers have been documented and assessed in several studies^[1-2]. Approximately one workplace fatality occurs every 3½ years in GB involving the use of DCM. A recent fatality was investigated by HSE involving paint-stripping using a DCM based mixture.

DCM is the major component (typically 70-90% in the liquid) of some paint strippers, other materials present can include methanol (MeOH) (10-30%) and hydrogen fluoride (HF) (1-10%)^[3]. The constituent chemicals of a typical stripper and the relevant details are shown in Table 1.1^[4-5]. Isopropanol (IPA) and formic acid are not present in the paint stripper analysed in this investigation but as they may be present in some paint stripping media^[6,7] it is also included in Table 1.1.

Table 1.1: Significant constituents of paint strippers

Constituent	Fraction (%)	LEL (%)	WEL (ppm)	STEL (ppm)	Saturated vapour pressure at 20° C (%)	Molecular mass (Da)
Dichloromethane	70 – 90	13*	100	300	47	84.9
Methanol	10 – 30	6	200	250	13	32.0
Hydrogen Fluoride	1 – 10	Non-flammable	1.8	3	NA (gas)	20.0
Isopropanol	3 – 7	2	400	500	4	60.1
Formic Acid	< 25%	18	5	Not Stated	4.4	46.0

Note:

The molecular weight of air is 29, thus, in the pure vapour phase, DCM, methanol, IPA and formic acid are denser than air whilst HF is lighter than air.

See Appendix 1 for calculation of saturated vapour pressures.

* DCM has no flash point in a conventional closed tester, but it forms flammable vapour-air mixtures at approximately 100 ° C or higher. It has a lower explosion limit of 13%, and an upper explosion limit of 19% in air.

DCM primarily presents a toxic hazard and is usually non-flammable in most but not all conditions. However, the mixture, containing methanol or isopropanol, may become flammable under certain circumstances. This presents a two-fold hazard for inspectors (and emergency services) when gas testing for entry into an area where an incident has occurred. The measurement of DCM as a toxic hazard, and methanol as a flammable hazard, in these situations is not a simple task. There is no guidance on the selection and use of gas monitors under these potentially dangerous and typically difficult circumstances. It is therefore necessary to characterise existing technologies for measurement of these gases/vapours in order to assess their suitability as reliable monitors for testing the atmosphere and personal monitoring.

The aim of this project, therefore, was to determine the suitability of commercially available real-time monitors to accurately monitor DCM in the presence of other constituent volatile organic compounds (VOCs) in paint strippers such as methanol and isopropanol.

The following gas sensing technologies were investigated and compared:

- Photo-ionisation detection (PID) technology for toxic levels of concentration, i.e. around the WELs (8 hr time weighted averages) and STELs (15 minute short term limits) ranging from 100 and 500 ppm
- Catalytic bead (pellistor) sensor technology for flammable concentration levels around the lower explosive limit (LEL), i.e. below/around 2-15% v/v
- Infrared sensor technology for flammable concentration levels around the lower explosive limit (LEL), i.e. below/around 2-15% v/v
- Electrochemical sensor technology to detect levels of oxygen (O₂) deficiency
- Fourier transform infra-red (FTIR) spectrometry for toxic levels of concentration

Details of their operating principles can be found in BS EN 60079-29-2^[8] and BS EN 4554-4^[9]

It must be noted that, with the exception of FTIR, none of the technologies listed are specific for toxic and flammable gases. They are sensitive in various degrees to a range of VOCs or flammable gases and cannot differentiate between any of the gases in those ranges.

2. METHODOLOGY

2.1 MONITORS

The monitors tested for suitability to monitor DCM, methanol and IPA vapour in this investigation are shown in Table 2.1, along with the respective manufacturer, sensing technologies, and the concentration of vapour to which they are sensitive. One Fourier Transform Infrared (FTIR) spectrometer and two of each of the other monitors were used in the tests.

Table 2.1: Monitors investigated

Monitor	Manufacturer	Sensor technology	Detection Range
MiniRAE 2000	RAE Systems	10.6 eV PID	0-10,000 ppm
MiniRAE 3000	RAE Systems	11.7 eV PID	0-10,000 ppm
MultiRAE Plus	RAE Systems	Catalytic Bead LEL	0-100% LEL
Impact	Honeywell	Infra-red absorption LEL	0-100% LEL
*MultiRAE Plus	RAE Systems	Electrochemical O ₂	0-30% O ₂ (0-100% gas)
FTIR spectrometer	Gasmet	FTIR spectrometry	Adjustable

*The characteristics of oxygen deficiency monitors were evaluated only from a theoretical viewpoint.

All the above monitors except for the Gasmet FTIR spectrometer are explosion proof, ie. ATEX certified for use in flammable atmospheres.

The MiniRAEs can be operated with ultra-violet (UV) lamps which emit ionising radiation of two different energies: 10.6 eV and 11.7 eV, and are able to detect gases which have ionisation energies below these values. Both of these lamps were considered in this investigation. The ionisation energies of the significant constituent chemicals of the stripper shown in Table 2.2^[10].

Table 2.2: Ionisation energies of various paint stripper components

Constituent	Ionisation energy (eV)
Dichloromethane	11.32
Methanol	10.85
Hydrofluoric acid	NA
Isopropanol	10.12

Because the lifetime of the 11.7 eV lamp when used in the MiniRAE 2000 has been shown in this and previous investigations to be short lived, the MiniRAE 2000s were used with 10.6 eV lamps installed, while the more suitable MiniRAE 3000s were used with 11.7 eV lamps installed.

Oxygen sensors can be used to deduce the concentration of a gas which displaces air, provided that there is only one displacement gas and that the concentration of oxygen in normal air is 20.9%. The concentration of oxygen (%O₂) in the air/gas mixture is then given by:

$$\%O_2 = 0.209 (100 - \%x)$$

where %x is the percentage of the displacement gas in the gas/air mixture.

Hence

$$\%x = (20.9 - \%O_2) / 0.209$$

If the resolution of the oxygen sensor is 0.1%v/v, then the resolution of the sensor for the displacement gas is approximately 0.5%, as oxygen comprises approximately one fifth of normal air.

2.2 CHARACTERISATION OF MONITORS

The PID monitors were calibrated with 100 ppm isobutylene, the LEL monitors were calibrated with 1% methane (22.7% of the LEL of methane), and the O₂ monitors would theoretically have been calibrated to 20.9% O₂ in air immediately before each set of tests at each concentration of vapour. Each set of tests comprised three exposures of each of the two monitors at each concentration of vapour.

Cylinders containing nominal concentrations of each of the three gases investigated were purchased from BOC, and diluted with clean air as required using mass flow controllers and/or a gas mixing pump (Wosthoff[®] Digamix Gas Dilution System). The details are shown in Table 2.3.

Table 2.3: Test gases

Gas	Nominal concentration	Certified concentration	Mixture accuracy
DCM	500 ppm	483 ppm	± 2% (v/v)
	1%	0.965%	± 2% (v/v)
Methanol	500 ppm	501 ppm	± 2% (v/v)
	1%	0.966%	± 2% (v/v)
IPA	500 ppm	481 ppm	± 2% (v/v)

Between each exposure, the monitors were checked at comparable concentrations of the calibration gas to detect any possible change in the sensitivity of the monitors which may have occurred due to contamination or other effects during the tests. The monitors were again checked at the calibration concentration at the end of each set of tests. Averages of the three exposures at each concentration were used in the analysis. The documented manufacturers' response factors of the PIDs and the LEL sensors to the vapours when compared to those of their calibration gases are shown in Table 2.4^[10,11].

Table 2.4: Manufacturers' response factors of the monitors

Monitor	Response factors compared to calibration gas (%)		
	DCM	Methanol	IPA
MiniRAE 2000 10.6 eV	No response	No response	17
MiniRAE 3000 11.7 eV	112	40	37
MultiRAE Plus LEL	100	67	38
Impact LEL	No data	No data	No data
MultiRAE Plus O ₂	No data	No data	No data
FTIR spectrometer	No data	No data	No data

Note: Response factors are the inverse of correction factors listed in the manufacturer's data sheets

The MiniRAEs were characterised with respect to DCM, methanol and IPA at toxic levels, and the MultiRAEs and Impacts were characterised with respect to DCM and methanol at flammable levels over the range of the concentrations shown in Table 2.5.

The MultiRAE and Impact LEL monitors display the concentrations in percent of the LEL of the gas under investigation. For clarity these display concentrations were converted to the actual gas concentrations using the LELs in Table 1.1 when analysing the results.

The MultiRAE O₂ monitors display the percent concentration of O₂. The change in display concentrations from those in clean air were converted to actual gas concentrations when analysing the results.

Table 2.5: Gases and concentrations used to characterise the monitors

Monitor Lamp (PID Energy)	Display resolution and ideal detection limit	Vapour range	Vapour concentrations		
			DCM	Methanol	IPA
MiniRAE 2000 (10.6 eV)	*1 ppm	Toxic	100 ppm 300 ppm 483 ppm	100 ppm 300 ppm 501 ppm	101 ppm 300 ppm 481 ppm
MiniRAE 3000 (11.7 eV)	0.1 ppm				
FTIR spectrometer	0.1 ppm				
MultiRAE Plus LEL (catalytic bead)	**1% LEL	Flammable	0.5% (4% LEL) 0.75% (6% LEL) 1% (8% LEL)	0.5% (8% LEL) 0.75% (13% LEL) 1% (17% LEL)	0.5% (25% LEL) 0.75% (38% LEL) 1% (50% LEL)
Impact LEL (IR)	1% LEL				
MultiRAE Plus O ₂ (electrochemical)	0.1% O ₂				

*Resolution is 0.1 ppm for readings up to 99.9 ppm and 1 ppm up to 10,000 ppm

**Resolution is 1 ppm on display but 0.1 ppm in datalog, as monitor will normally be used as a personal monitor/warning device, the screen resolution will be the one considered in these investigations

IPA was not investigated experimentally at flammable levels, but was characterised theoretically at those levels along with the MultiRAE O₂ sensor.

The characteristic, extreme acidity of HF and the resulting possible damage to the monitors precluded characterisation of this component of the stripper.

2.3 ANALYSIS OF PAINT STRIPPER

The paint stripper used in this investigation is called 'EFX Strip' and was supplied for analysis by Confederate Chemicals Ltd^[3].

The gases/vapours in the headspace of the container in which the paint stripper was stored were analysed using water leach and ion chromatography to measure the concentration of HF; gas chromatography using a flame ionisation detector to measure the concentration of DCM and/or other volatile organic compounds; and a thermal conductivity detector to determine air components. Gas chromatography using a mass spectrometer detector was used to analyse other minor components in the headspace. The results from this analysis of the constituent gases in the headspace, and the possible effect of the various constituents on the sensing mechanisms of the monitors under investigation, would determine whether the monitors could be used to measure the levels of DCM and methanol in the headspace.

3. RESULTS

3.1 MONITOR RESPONSES - TOXIC CONCENTRATION LEVELS

Calibration checks undertaken throughout the investigation showed the monitors to be operating consistently and satisfactorily.

The responses of the PID based monitors (calibrated to 100 ppm isobutylene) when exposed to toxic levels of DCM, methanol, and IPA are shown in Figures 3.1 to 3.4 and summarised in Table 3.1.

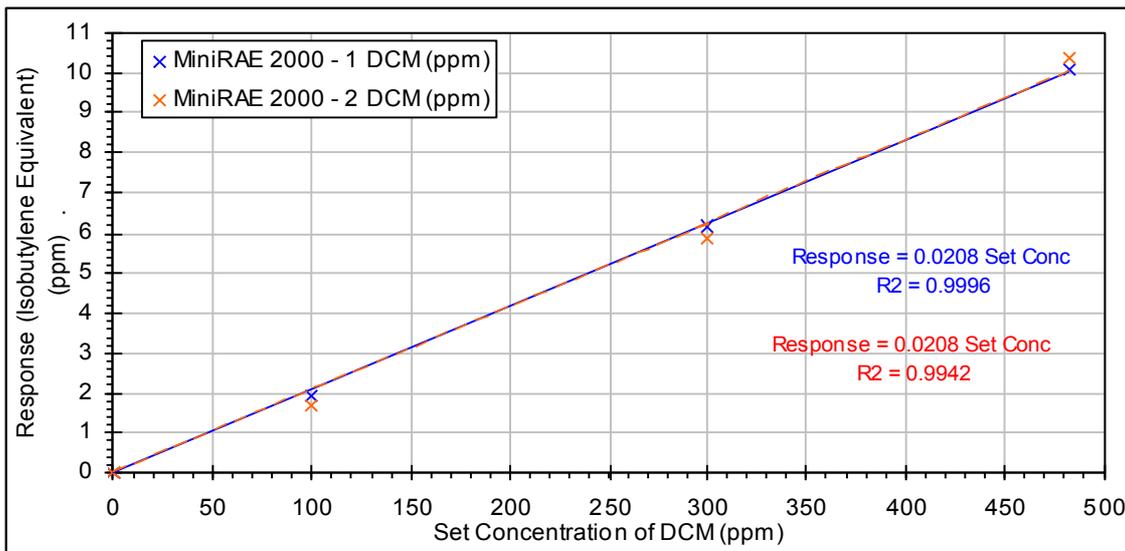


Figure 3.1: Responses of Mini RAE 2000 monitors (10.6 eV lamps) to toxic levels of DCM

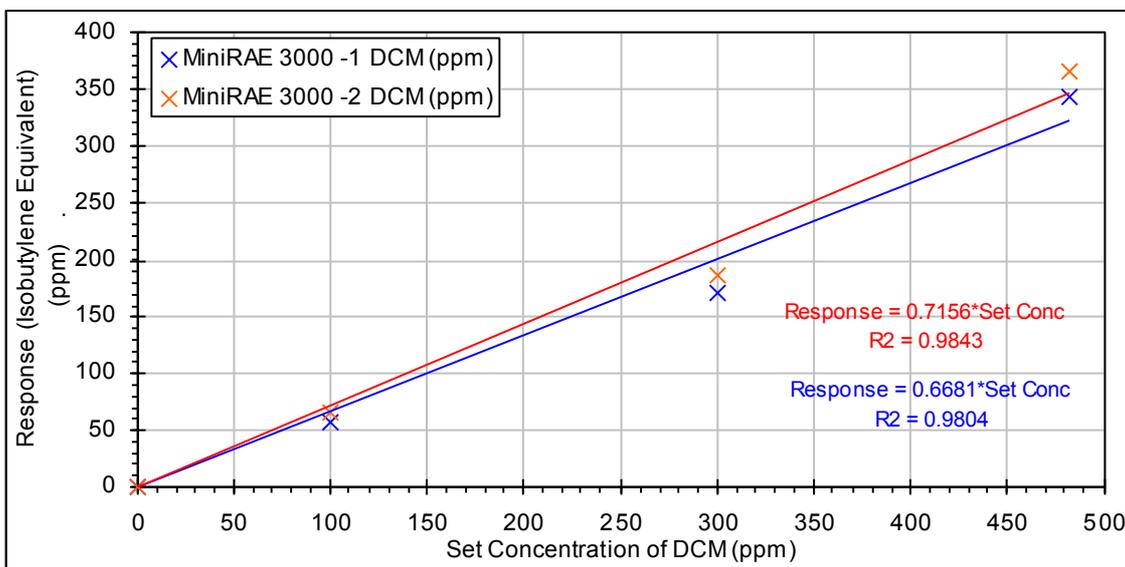


Figure 3.2: Response of Mini RAE 3000 monitors (11.7 eV lamps) to toxic levels of DCM

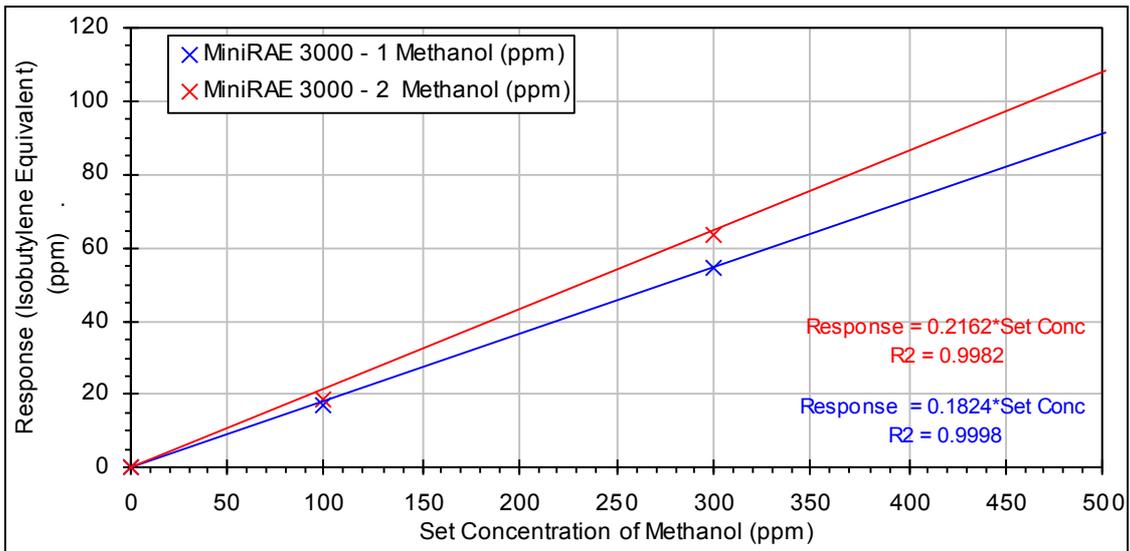


Figure 3.3: Response of Mini RAE 3000 monitors (11.7 eV lamps) to toxic levels of methanol

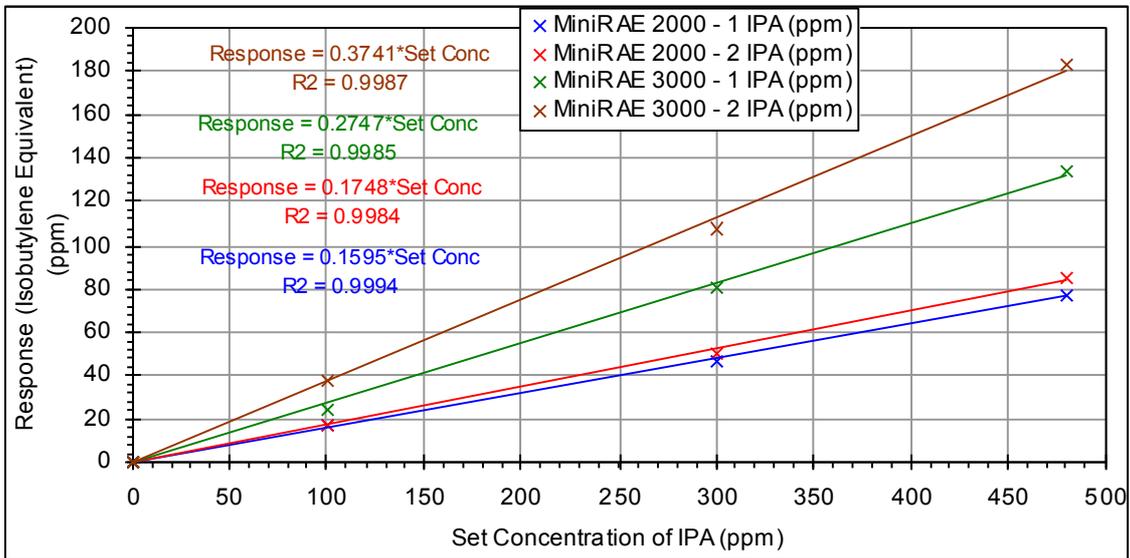


Figure 3.4: Response of Mini RAE 2000 monitors (10.6 eV lamps) and 3000 monitors (11.7 eV lamps) to toxic levels of IPA

Table 3.1: Responses of PID based monitors exposed to toxic levels of DCM, methanol and IPA

Set Concentration of Gas (ppm)	Monitor Reading (isobutylene equivalent) (ppm)			
	MiniRAE 2000 1	MiniRAE 2000 2	MiniRAE 3000 1	MiniRAE 3000 2
DCM				
100	2.0	1.7	57	65
300	6.2	5.9	171	186
483	10.1	10.4	343	365
Methanol				
100	0	0	17	18
300	0	0	55	64
501	0	0	92	110
IPA				
101	17	17	25	37
300	47	51	81	108
481	77	86	134	183

3.2 MONITOR RESPONSES - FLAMMABLE CONCENTRATION LEVELS

Calibration checks undertaken throughout the investigation showed the monitors to be operating consistently and satisfactorily.

The responses of the LEL based monitors (calibrated to 1% methane) when exposed to flammable levels of DCM and methanol are shown in Figures 3.5 and 3.6., and are summarised in Table 3.2. Table 3.2 also shows theoretical responses of LEL based monitors to flammable concentrations of IPA.

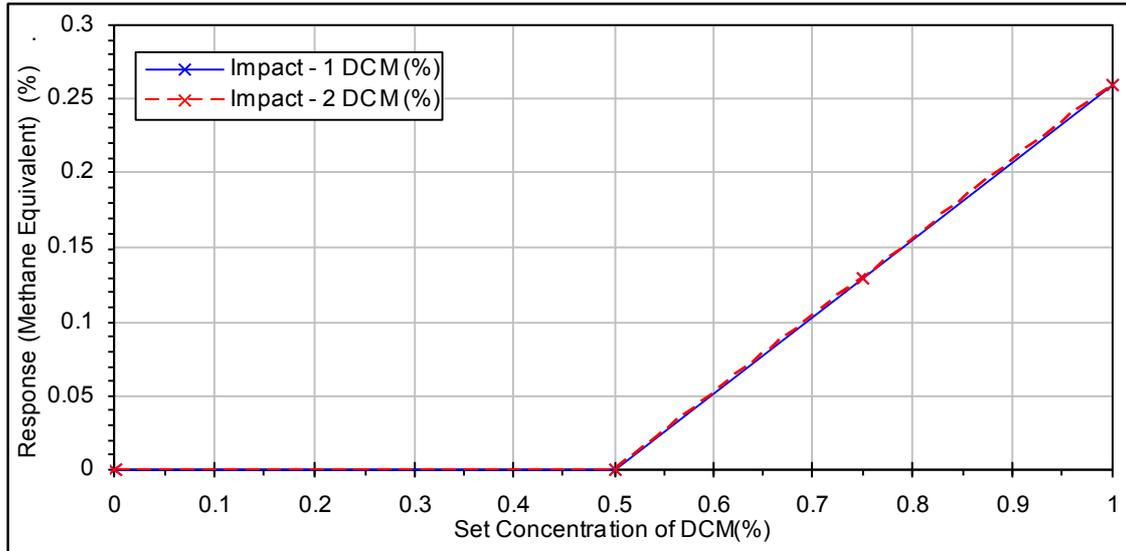


Figure 3.5: Response of Impact IR LEL monitors to flammable levels of DCM

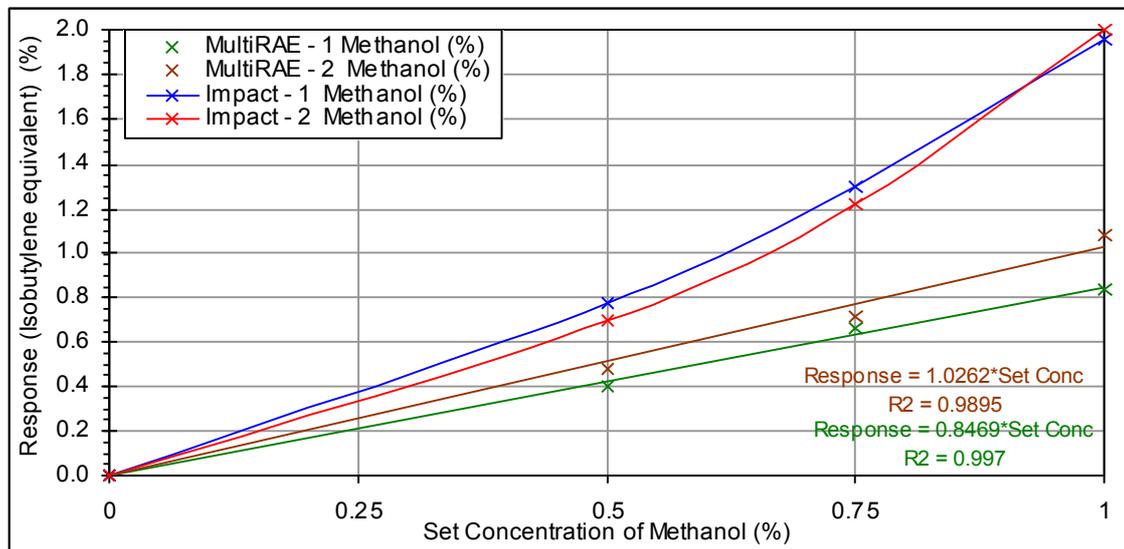


Figure 3.6: Response of MultiRAE catalytic and Impact IR LEL monitors to flammable levels of methanol

Table 3.2: Responses of LEL based monitors exposed to flammable levels of DCM, methanol and IPA

Set Concentration of Gas (%)	Monitor Reading († or converted monitor reading) (% v/v)			
	MultiRAE LEL (cat bead) 1	MultiRAE LEL (cat bead) 2	Impact LEL (IR) 1	Impact LEL (IR) 2
DCM				
0.5	*Detector poisoned	*Detector poisoned	0.0	0.0
0.75			0.13	0.13
1			0.26	0.26
Methanol				
0.5	0.40	0.48	0.78	0.70
0.75	0.66	0.72	1.30	1.22
1	0.84	1.08	1.96	2.00
**IPA				
0.5	0.19	0.19	NA	NA
0.75	0.29	0.29	NA	NA
1	0.38	0.38	NA	NA

*When sensors exposed to DCM, readings were inconsistent, unrepeatable, slow reacting and were seen to degrade over the exposure duration

**Theoretical: See Appendix 2 for explanation of theoretical assumptions

3.3 SUMMARY OF EXPERIMENTAL RESULTS

Table 3.3 shows the average and documented response factor, and the resolution of each type of monitor to each type of gas (see Appendix 2 for explanation of theoretical assumptions).

The concentrations detected by the MiniRAE 3000 monitors incorporating 11.7 eV lamps were seen to reduce as the tests progressed and further tests undertaken on these monitors showed the detected concentration when exposed to 1,000 ppm isobutylene to reduce by 1.4 ppm per minute.

Table 3.3: Average response factor of each type of monitor exposed to each gas

Detector	Ave determined response factor to DCM (%)	Documented response factor to DCM (%)	Determined resolution & ideal detection limit of DCM	Ave determined response factor to methanol (%)	Documented response factor to methanol (%)	Determined resolution & ideal detection limit of methanol	Ave determined response factor to IPA (%)	Documented response factor to IPA (%)	Determined resolution & ideal detection limit of IPA
MiniRAE 2000	2 (±0)	No response	5 ppm	No response	No response	No response	17 (±1)	17	0.6 ppm
MiniRAE 3000	65 (±8)	112	0.2 ppm	19 (±1)	40	0.5 ppm	32 (±1)	37	0.3 ppm
MultiRAE LEL	NA (poisoned)	100	NA	92 (±4)	67	654 ppm	*38	38	*520 ppm%
Impact LEL	Inconsistent	No data	NA	171 (± 27)	No data	300 ppm	No data	No data	NA
MultiRAE O ₂	Not tested	No data	*0.5%	Not tested	No data	*0.5%	Not tested	No data	*0.5%

*Theoretical: See Appendix 2 for explanation of theoretical assumptions

3.4 CHEMICAL ANALYSIS OF PAINT STRIPPER CONSTITUENTS

The results of analysis of the headspace of the container in which the paint stripper was stored are shown in Table 3.4 (see Appendix 3 for details of tests).

Table 3.4: Constituents in the headspace of the container in which the paint stripper was stored

Gas	Concentration
DCM	35.3% (353000 ppm)
Nitrogen	47.7% (477000 ppm)
Oxygen/Argon	13.5% (135000 ppm)
Hydrogen Fluoride	(0.0539%) 539 ppm
Total	96.6%

The chromatogram produced from gas chromatography using a mass spectrometer detector showed the presence of a very large DCM peak (> 99.7% of the total peak area) and a much smaller methanol peak (< 0.3% of the total peak area). No other components were observed in the sample chromatogram. The presence of VOCs other than DCM can therefore be accepted as negligible.

As HF could damage the sensing mechanisms in the monitors, especially the glass based optics in the PID monitors, the presence and concentration of HF found in the headspace prevented the use of the monitors under investigation to determine the levels of DCM and methanol, until further investigations into the effect of HF on the monitors can be undertaken.

4. CONCLUSIONS AND RECOMMENDATIONS

DCM can be monitored at toxic levels (~ 300 ppm) using MiniRAE 3000 monitors incorporating 11.7 eV lamps (effective measurement resolution of 0.2 ppm). DCM can also be monitored at toxic levels using MiniRAE 2000 monitors incorporating 10.6 eV lamps if required, but with a much lower effective measurement resolution (5 ppm).

DCM can be monitored at flammable levels ($\geq 13\%$) using MultiRAE monitors incorporating electrochemical O₂ sensors (effective measurement resolution: 0.5%). MultiRAE monitors incorporating catalytic bead LEL sensors are poisoned by exposure to DCM preventing them being used in the atmosphere of paint stripper vapour, and Impact monitors incorporating IR LEL sensors show inconsistent sensitivity when exposed to various flammable levels of DCM.

Methanol can only be monitored at toxic levels (~ 250 ppm) using MiniRAE 3000 monitors incorporating 11.7 eV lamps (effective measurement resolution: 0.5 ppm).

Methanol can be monitored at flammable levels ($\geq 6\%$ v/v) using Impact monitors incorporating IR LEL sensors (effective measurement resolution: 300 ppm v/v), MultiRAE monitors incorporating catalytic bead LEL sensors (effective measurement resolution: 654 ppm v/v), and MultiRAE monitors incorporating electrochemical O₂ sensors (effective measurement resolution: 0.5% v/v).

IPA can be monitored at toxic levels (~ 500 ppm) using MiniRAE 3000 monitors incorporating 11.7 eV lamps (effective measurement resolution: 0.3 ppm), and MiniRAE 2000 monitors incorporating 10.6 eV lamps (effective measurement resolution: 0.6 ppm)

IPA can theoretically be monitored at flammable levels ($\geq 2\%$ v/v) using MultiRAE monitors incorporating electrochemical O₂ sensors (effective measurement resolution: 0.5% v/v), and MultiRAE monitors incorporating catalytic bead LEL sensors (effective measurement resolution: 520 ppm v/v). The theoretical characterisation of the Impact monitors incorporating IR LEL sensors to flammable levels of IPA was not possible due to limited availability of technical information on the monitor.

The cross-sensitivity of MiniRAE 2000 monitors and MiniRAE 3000 monitors to methanol and IPA prevent selective monitoring of dichloromethane in paint strippers in which appreciable amounts of these chemicals are present.

The reduction in the detected concentration of MiniRAE 3000 monitors at a rate of 1.4 ppm per minute must be taken into account for extended exposure times, but for normal exposure times this should not have a significant effect on the operation of the instruments.

Further investigations into the effect of HF on the sensing mechanisms of MiniRAE 3000 monitors incorporating 11.7 eV lamps may allow them to be used to monitor the levels of DCM in paint stripper, as the levels of VOCs other than DCM in the paint stripper investigated here have been found to be negligible. Different makes and specifications of paint stripper should be analysed and the constituents compared to investigate the ranges of the VOC and acidic components. It may then be possible to compile a procedure to allow the monitoring of DCM in some paint strippers without the interference of other chemical vapours contaminating the results to any significant degree. Further investigation into the reliability of MiniRAE 3000 monitors incorporating the 11.7 eV lamps over time may also be required.

It is not feasible to use the Gaset FTIR spectrometer to monitor DCM in paint stripper containing HF as this could cause significant and expensive damage to the internal optics. It must also be noted that the Gaset FTIR spectrometer is not certified for use in flammable atmospheres and, as such, cannot be used if such atmospheres are suspected.

As the response factors of the monitors determined in this investigation were significantly different from those documented by the manufacturers for both DCM and methanol, it would be good practice to check these factors by laboratory exposure to these gases/vapours before use.

5. REFERENCES

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6. APPENDICES

6.1 APPENDIX 1: CALCULATION OF SATURATED VAPOUR PRESSURE USING THE ANTOINE EQUATION

The Antoine equation is shown in Equation 6.1.

$$\log_{10} P = \frac{A - B}{T + C} \quad \text{Equation 6.1.}$$

Where A, B and C are Antoine coefficients specific to the VOC, T is the temperature in Kelvin and P is the saturated vapour pressure in bar.

Antone Coefficients at temperature of 20°C [6]:

	DCM	Methanol	HF	IPA
Constant A =	4.53691	5.20409	4.9148	4.861
Constant B =	1327.016	1581.341	1556.559	1357.427
Constant C =	-20.474	-33.5	24.199	-75.814

The maximum concentration of the VOC under the stated conditions is the ratio of the saturated vapour pressure and the ambient air pressure, ie

$$MaxConc = \frac{P}{P_{Ambient}}$$

6.2 APPENDIX 2: ASSUMPTION FOR THEORETICAL ANALYSIS

6.2.1 LEL sensor detection of IPA

As the response factor of the MultiRAE LEL sensor to IPA after calibration to methane is documented as 0.38 (correction factor is 2.6, ie. the inverse), then the expected detected concentration when exposed to IPA is 0.38 of the actual concentration ie 1% v/v of IPA will be detected as 0.38% v/v

As the response factor of the Impact LEL sensor to IPA after calibration to methane is not documented, then the expected detected concentration when exposed to IPA cannot be estimated

6.2.2 LEL resolution

Resolution of LEL sensors is 1% of the LEL of the gas under investigation. If this gas is not the gas to which the sensor is calibrated, then a correction factor must be applied to this value to obtain the resolution of the LEL sensor to that gas, ie for a CF of 2, when the display shows 1% LEL the actual value is 2% LEL, and this value is the resolution of the sensor for this gas in terms of % LEL. The LEL resolution must then be multiplied by the actual LEL to give the resolution of the LEL sensor to that gas.

6.3 APPENDIX 3: ANALYSIS OF HEADSPACE GENERATED BY EFX LIQUID

6.3.1 Analysis of headspace generated by EFX liquid for HF

The headspace of the container was sampled for 30 sec at 1.522 l/min on to a glycerol/sodium carbonate treated paper pad. This was then analysed for fluoride by a water leach and ion chromatography.

The result was 447 mg/m³ for the 0.75 litre sample. No fluoride was detected on the back up filter confirming that there was no breakthrough. Analysis of blanks including a blank with laboratory air drawn through it showed no fluoride contamination.

This converts to 539 ppm (ppm = mg/m³ × 24.1/ molecular weight).

6.3.2 Further analysis of headspace generated by EFX liquid

A 2 ml aliquot of the EFX sample liquid was transferred into a 10 ml screw-top bottle fitted with a teflon-rubber septum seal and left overnight. Samples of the headspace were then taken through the septum seal using a 0.5 ml gas tight syringe fitted with a hypodermic needle and analysed by gas chromatography (GC) using a flame ionisation detector (FID), to determine dichloromethane (DCM) and/or other volatile organic compounds (VOC), and a thermal conductivity detector (TCD), to determine air components. Five samples were analysed, producing the results in Table 7.1.

Table 7.1: Results from GC analysis of EFX headspace samples

Test	DCM (%v/v)	N ₂ (%v/v)	O ₂ / Ar (%v/v)	Total (%v/v)
1	31.6	51.9	14.6	98.1
2	39.6	43.0	12.1	94.7
3	33.4	49.8	14.1	97.2
4	35.0	47.3	13.4	95.7
5	36.8	46.6	13.1	96.5
Mean	35.3	47.7	13.5	96.4
SD	3.1	3.4	0.95	1.3
CV	8.7%	7.0%	7.0%	1.3%

Note: This analysis will not detect the presence of hydrogen fluoride (HF)

To check for other minor components in the EFX headspace, a further 0.5 ml sample was taken using the gas-tight syringe, loaded onto a Chromosorb-106 thermal desorption (TD) tube and analysed by GC using a mass spectrometer detector (MSD). The resulting chromatogram showed the presence of a very large DCM peak (> 99.7% of the total peak area) and a much smaller methanol peak (< 0.3% of the total peak area). No other components were observed in the sample chromatogram.

Real time measurement of dichloromethane containing mixtures

Dichloromethane (DCM), also known as methylene chloride, is typically used as a component of proprietary paint strippers. Occasional workplace fatalities result from its use in GB. The aim of this project was to determine the suitability of commercial, real-time (direct-reading), portable gas detectors to monitor DCM in the presence of other volatile organic compounds typically found in paint strippers. Various types of gas detector (based on photoionisation, infrared and catalytic sensors) were exposed to air mixtures of DCM, methanol and isopropanol.

It was found that high sensitivity photoionisation detectors (PIDs) with high energy UV lamps are approximately 30 times more sensitive than PIDs with low energy UV lamps. Both PIDs can measure DCM at levels below the Workplace Exposure Level (WEL) of 300 ppm (15 minute short-term). They are both cross-sensitive to the other VOCs investigated. However, this may still allow reasonably accurate measurement of DCM, as the concentration of DCM in the vapour phase is typically much greater than the other VOCs. The other types of detector were not suitable for measurement of DCM around and below the WEL.

The high sensitivity PIDs were found to lose sensitivity quite rapidly and do not have a long shelf life when compared to the low sensitivity PIDs. Nevertheless, with care, they can be used to measure low (ppm) levels of DCM. Further work is required to evaluate the effect of hydrogen fluoride, another component of paint strippers, on the performance of PIDs.

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