ANALYSIS AND TOXICOLOGY
OF LE MAITRE SMOKE FLUIDS

by

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1. INTRODUCTION

Le Maitre smoke fluids are materials supplied by Le Maitre for use in their smoke generators. A reservoir is charged with the water-based fluids, which are forced by pneumatic pressure into a heated chamber. Here the fluid is immediately vaporized and expands. On passing into the atmosphere a mist or smoke is formed as a result of condensation of the vaporized material.

A series of tests have been carried out on the two Le Maitre smoke fluids and the smoke generated from them. The objectives of the tests were:

i) To confirm that the composition of the fluids were as stated by the manufactures.

ii) To establish whether the water soluble organic components were involved in any chemical reaction during smoke generation.

iii) To determine the nature of the products of any such reactions.

iv) To review the available evidence for the safety of the atmospheres generated particularly in respect of individuals who would be exposed to the atmospheres.

The experimental work primarily involved the technique of gas-liquid chromatography. This is a sophisticated instrumental technique for the precise analysis of mixtures of volatile organic compounds. Mixtures are passed through a column in a stream of carrier gas. Various components of the mixture move through the column at different rates and thus the individual components arrive at the end of the column at different times, that is, the mixture is separated. Column effluent is monitored by a highly sensitive detector. The time of passage through the column is characteristic of a particular substance and the size of the signal from the detector is an accurate measure of the amount of substance.

2. EXPERIMENTAL AND RESULTS

2.1 Le Maitre Fluid A
2.1.1. Analysis of the fluid

The composition of the fluid was supplied and there tests were to confirm the composition.

Standard samples of the components propylene glycol and water were obtained and an analytical procedure for their analysis was developed. Details of the analysis are given in table 1. Although the system should not produce a response to water there was in fact an early peak attributable to the compound. This artifact is not unusual and created no problem. Propylene glycol eluted as a symmetrical peak within 10 minutes.

When samples of Le Maitre Smoke Fluid were examined a single large peak was produced in the chromatogram the retention time coincided with that

of propylene glycol. When the sensitivity of the detector was increased a second peak, which did not coincide with water, became visible. This was, however, a minor component probably representing less than 2% of the total. It was concluded that the propylene glycol and water were the major components and further tests were carried out on this basis.

2.1.2. Analysis of the Smoke Generated

The primary objective of the analysis was to confirm that the smoke also contained propylene glycol and that no products other than stated, resulted. Two series of tests were carried out. One series examined the smoke as a vapour injected directly into the gas chromatograph and the other tests involved condensing the smoke in a liquid and the subsequent analysis of the resulting solution.

Direct injection of the vapour was done with a 2ml. gas tight syringe. Samples of the smoke were taken into the syringe from the exhaust tube of the gas generator and introduced directly into the gas chromatograph. The analytical conditions were as given in Table 1. The resulting chromatogram showed two peaks, one of which coincided with water and a second later peak. However, the retention time was different from that of injections of liquid propylene Glycol and the peak was broader. When a reference injection of standard propylene glycol vapour was made the peak coincided with that of the smoke sample. Peak broadening is an effect often associated with the injection of relatively large volumes of gas and the phenomenon may result in the combination of two peaks into an apparently single peak. Thus although vapour injection was an attractively simple method of determining the concentration of propylene glycol in the smoke it was first necessary to establish that its use did not mask the presence of other compounds. Hence the need to examine condensed samples of smoke.

Smoke was condensed by trapping in water. The water was contained in a Dreschel bottle connected to a Factory Inspectorate Mark 1 portable pump. Smoke was drawn from the generator and bubbled through the water at a rate of 500ml. min. $^{-1}$. Sampling was carried on for 15 minutes after which time the resulting solution was analyzed. The analytical conditions were the same as previously. 10ml injection of the solution were made into the gas chromatogtaph. The only peaks apparent were those resulting from water and propylene glycol. This result suggested that propylene glycol was the only organic compound present and that no decomposition had occurred. Further confirmation was achieved by using a temperature programming technique. The gas chromatograph oven temperature was slowly increased in a controlled way instead of the normal isothermal operation. Temperature programming allows the separation of peaks which are combined together under isothermal conditions. A program from 60 to 200^{0}C at 4^{0}C min $^{-1}$. was used but once again the only peaks produced were the water peak and the major peak coinciding with propylene glycol. At this stage it was assumed that propylene glycol was the only compound of significance, and so the vapour injection

technique could be used for the quantitative analysis of smoke atmospheres. The peak broadening would not be masking other substances.

2. Quantitative Analysis of the Atmospheres Produced

The primary objective of the tests was to measure the concentration of propylene glycol present in the smoke and to express this as a function of reduced visibility and light intensity.

The tests were carried out using a glass chamber 40cm x 30cm x 30cm. Light from a source was passed through the chamber and detected by a photocell positioned on the opposite wall of the chamber. The light path used was thus 30cm. The reduction in photocell signal was used as a measure of the degree of obscuration produced when smoke from the generator was passed into the chamber.

Simultaneously a sample of the atmosphere was withdrawn from the chamber using a 2ml. gas--tight syringe and introduced into the gas chromatograph for analysis. The standard analytical conditions were used.

Initially a single atmosphere was generated and repeated samples taken and analyzed in order to obtain information on homogeneity of the atmosphere. Subsequently further atmospheres were generated and vapour samples taken for analysis. The results obtained are presented in Table 2.

2.2. Le Maitre Fluid B

2.2.1. Analysis of the fluid

The objective was once again to confirm the supposed composition of the fluid. This was carried out in similar fashion to Le Maitre Fluid A. Samples of glycerin were injected into a gas chromatograph operating under the conditions listed in Table 3. Subsequent injection of the fluid showed glycerin to be the only organic component. It should be noted that the peaks produced were of poor shape since glycerin is a substance not readily amenable to chromatographic analysis.

2.2.2. Analysis of the Smoke Generated

As for Le Maitre fluid a two series of tests were carried out.

Firstly the smoke generated was condensed in water by pumping through a Dreschel bottle containing the absorbing solution. Samples of the condense were subsequently analyzed and shown to give a similar chromatogram to that of the virgin fluid. There was no indication of decomposition having taken place.

Attempts were then made to inject the vapour directly into the gas chromatograph. This was not successful since the already broad peaks were so distorted by the injection of the large volume of vapour as to make them useless. After various unsuccessful attempts at devising a more suitable system it was decided simply to use the detector with no attempt at saturation. A tube

containing only glass yarn was used to connect the injector to the detector. Even using this system there was a degree of peak broadening for the vapour injected but it was useable.

Testing of the opacity of the generated atmosphere also produced additional problems with condensation of the glycerin on the walls of the test chamber. To overcome this the light source and photo multiplier were positioned inside the chamber. This overcame the condensation problems to a large extent. The result obtained are shown in Table 4.

3. DISCUSSION

3.1. Analysis of Smoke Atmospheres

The results show that there was no measurable decomposition of either propylene glycol or glycerin during the smoke generation process and so only these compounds need to be considered for the toxicology studies. There may have been some slight decomposition but at a level insufficient to be shown by the techniques used here. Such decomposition if it occurs at all, is unlikely to be significant.

Quantitative analysis of the generated atmospheres shows a potentially wide range of concentration. It was found that plots of light transmission against concentration for the two atmospheres were similar and the following discussion applies to both materials. Attempts were made, with some success, to relate light transmission and light absorbance with vapour concentration. In this respect, if absorption of the radiation by the chemical species was the only mechanism operating Beers Law would be expected to apply. This draws a linear relationship between absorbance and concentration given a constant pathlength. Such a linear relationship is also expected for attenuation of light by scattering by dilute aerosols. however, as can be seen in Figure 1, this relationship does not apply well here. There is clearly a curved function indicating that the attenuation of the light in this case is not well described by simple theory. Since we are dealing here with scattering by a concentrated (and probably polydisperse) aerosol, in which multiple scattering events are significant, such a non-linear relationship between vapour concentration and absorbance is not an unexpected result.

A further complication is the heterogeneous nature of the generated atmospheres. Duplicate samples of the atmospheres through the vessel showed a range of vapour concentration indicating the rather variable nature of the atmospheres produced. On occasions this phenomenon was clearly visible as clouds of vapour moved through the chamber. In this respect Le Maitre B seemed to produce a much more consistent and stable smoke. Atmospheres of this character are typical of real circumstances and so are not a disadvantage of the smoke generator. It does, however, tend to make the correlation of vapour concentration with light reduction more difficult. As a result there is inevitably a loose relationship between absorbance and vapour concentration and in the circumstances the results in Figure 1 are satisfactory. They show that there is an empirically determined relationship and serve as a guide to the vapour

concentration which can be generated and used. Highest concentrations measured where 1150 mg.m^{-3} although there is little doubt that concentrations well above this could be generated. in this case the light intensity would have been so reduced that no meaningful measurements could have been made. It is estimated that the highest concentration capable of generation is of the order 1500 mg.m^{-3}. depending of circumstances.

In practical application of the smoke generator, light transmissions over distances greater than our 'test' distance of 30cm are likely to be of interest. Accordingly we have estimated, from our data, approximate light transmissions for concentration of 100, 200, 500 and 1000 mg/m^3. of vapour at distances (in each case) of 1,2, and 5m. There dates are presented in Table 5. The table shows, for example, that a vapour concentration of 200 mg/m^3. Possesses a light transmittance of about 3% for a 2 meter path. These data should be taken as approximate values only, and not necessarily as measures of 'visibility', since the latter concept involves, in practical situations, questions of colour and contrast between an object and its surroundings.

3.2. Safety of the Smoke Generated

A MAJOR CONSIDERATION IN SMOKE GENERATION IS THE SAFETY OF INDIVIDUALS EXPOSED TO THE SMOKE. Many substances have been shown to be harmful to individual health either in the short or the long term. Clearly it would be inadvisable to generate atmospheres containing potentially hazardous substances. The work described above has shown that only a single substance other than water is present in the smoke produced.

The recognized limits of industrial exposure to chemicals in the work place are the threshold limit values (T.L.V.). There are of three types

i) The time weighted average T.L.V. (T.W.A.T.L.V.) which refers to a maximum average concentration to which an individual may be exposed throughout a working lifetime. It assumes an exposure time of up to 40 hrs/week for many years.

ii) A short term exposure limit (S.T.E.L.) which is a concentration greater than the (T.W.A.T.L.V.) to which an individual may be exposed for periods not exceeding 15 minutes.

iii) A ceiling concentration which may never be exceeded.

It must be stressed that the T.L.V. concept relates to industrial exposure and so is selective in those of the population to whom it applies.

There are not T.L.V. data for every conceivable substance, and neither propylene glycol or glycerin are listed. The lack of data cannot be taken to mean that a substance is either completely harmless or highly dangerous, rather that it has not presented a particular industrial problem. In this case it is presumably because under normal conditions they are relatively innovative and so unlikely to accumulate in significant concentrations. In the absence of T.L.V. it is necessary to consider what other information is available.

3.3. Toxicology of Propylene Glycol & Glycerin

Propylene glycol is an allowable constituent of foodstuffs and pharmaceutical products. it is contained, for example, in soft drinks and suntan lotions. Although neither of these are inhaled there is no reason why this route should pose an additional hazard. Experiments on rats and monkeys have shown that exposure to saturated atmospheres for up to eighteen months produces no ill effects. Equally no effects have been noted in man as a result of inhalation.

Glycerin is also allowed in foodstuffs and pharmaceuticals and is very widely used. It is also used as a bacteriostat. No toxicity effects on animals or man have been noted even at concentration well in excess of those relevant here.

THUS NEITHER OF THE SUBSTANCES USED IN THE SMOKE GENERATORS HAS BEEN SHOWN TO HAVE ANY ADVERSE EFFECTS IN MAN.

In general, it is prudent to avoid undue exposure to any substance but there is no reason to suppose that any harmful effect will result even from continued exposure to the smoke generated. In typical use where the exposure is restricted and limited there is every reason to consider the devices safe.

4.0 Conclusions

1) The composition of the fluids were as stated by the manufactures.

2) There was no evidence that during smoke generation either propylene glycol or glycerin degraded to form other compound.

3) The generators are capable of producing concentration in excess of 1500 $mg.m^{-3}$ which would result in visibility being reduced to less than 1 metre. At increasing concentration in excess of the saturation level precipitation may become a problem.

4) No threshold limit values exist for limiting industrial exposure to either propylene glycol or glycerin. Other toxicological data show that these compounds present no known hazard to health.

References

1. Handbook of environmental data on organic chemicals, K. Verschueren, (1983).
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TABLE 1

ANALYTICAL CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSIS
OF PROPYLENE GLYCOL

Gas Chromatograph: PYR G.C.D.

Detector: Flame Ionisation

Column: 2 Metre x 1/4in. outer diameter glass

Stationary Phase: 10% Carbonwax 20M

Oven Temperature: 150 Degrees C

Injector Temperature: 250 Degrees C

Detector Temperature: 250 Degrees C

Carrier Gas: Nitrogen at a flowrate of 30ml/min

TABLE 2

LIGHT PENETRATION OF PROPYLENE GLYCOL

Concentration (mg.M^{-3})	Transimittance*	Absorbance
0	1.00	0
60	0.77	0.12
195	0.57	0.25
310	0.47	0.33
1150	0.27	0.70

* Measured for 30cm path

TABLE 3

ANALYTICAL CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSIS
OF GLYCERINE

Gas Chromatograph: PYR E.C.D.

Detector: Flame Ionisation

Column: 2 Metre x 1/4in. outer diameter glass

Stationary Phase: F.F.A.P.

Oven Temperature: 100 to 200 Degrees C at 4 Degrees min^{-1}

Injector Temperature: 250 Degrees C

Detector Temperature: 250 Degrees C

Carrier Gas: Nitrogen at a flowrate of 30ml/min^{-1}

TABLE 4

LIGHT PENETRATION OF GLYCERINE ATMOSPHERES

Concentration Absorbance (mg.M $^{-3}$)	Transimittance*	
0	1.00	0
88	0.78	0.105
159	0.73	0.14
220	0.66	0.18
630	0.37	0.43

* Measured for 30cm path

TABLE 5

CALCULATED LIGHT TRANSMIITTANCE FOR CONCENTRATIONS OF VAPOR

Concentrations of Vapour, mg/m^3	Light Transmittance, % for Distance Indicated		
	1m	2m	5m
100	35	12	0.5
200	18	3.0	2×10^{-2}
500	4.0	0.16	1×10^{-5}
1000	1.0	0.01	1×10^{-8}