

Evaluation of techniques for *in situ* determination of explosion hazards in asphalt tanks

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It is clear from recent work in our laboratory and elsewhere that the traditional method of assessing the explosion hazards in asphalt tanks, by comparing storage temperature to material flash point, is not reliable in many circumstances. In response to the need for better evaluation methods, several techniques for monitoring the composition of the vapour space of asphalt tanks have been evaluated. Methods were investigated which determine the combustibility of the vapour space and which analyse for more specific compounds which are indicators of smouldering coke deposits - a major ignition hazard in asphalt tanks. Simple methods, easily applied routinely by manufacturing personnel, are shown to be of adequate accuracy by comparison to more complex methods yielding more complete information but also requiring more extensive equipment and expertise. Applicability of each method to five different classes of asphalt is discussed. Strengths and weaknesses of conventional flash point tests are also discussed; they are shown to be of limited use in assessing explosion hazards with air blown asphalt and solvent deasphalting residuum.

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In spite of the extensive use of hot asphalt for over a century, little has been published on the nature of explosion hazards in tanks containing this material. Published work has emphasized that the flash point of the material stored is the most important factor in determining whether enough fuel is present in the vapour space for combustion¹⁻³.

Dimpfl⁴, in a pioneering paper, emphasized that factors unrelated to simple evaporation of asphalt are common causes of the build-up of combustibles in asphalt tanks. He cited smouldering coke deposits on the inner roof and shell of the tank, incidental thermal cracking, light hydrocarbons from solvent deasphalting processes, contamination from crude feed/vacuum residuum heat exchanger leaks, and unstripped light hydrocarbons generated during air blowing as being potential sources of vapour space fuel not detected by flash point tests. He emphasized the role of smouldering coke in depleting oxygen and elevating carbon monoxide and carbon dioxide in the tank vapour space and pointed out its potential as an ignition source, with or without the catalysing effect of iron sulphide. Dimpfl proposed a thermal gravimetric protocol to test for the

pyroforic nature of these deposits. This method was later refined by Rajeshwar⁵. Dimpfl's conclusions concerning the explosive nature of the vapour spaces were based on his use of gas chromatography (g.c.) analyses of nine tank vapour spaces for C₁ to C₆ hydrocarbons. Details of this technique were not published. In spite of his valuable contribution, Dimpfl was not able to predict what material and storage conditions tended to give explosive vapour spaces. His final conclusion was that the safe storage of asphalt is an unpredictable art.

In a paper related to the present work, Trumbore and Wilkinson⁶ analysed results of an extensive vapour space testing programme utilizing a variety of techniques including combustion meters, detector tubes, analysis of charcoal tube samples and gas bulb samples by g.c. and infrared spectroscopy (i.r.). The tests were run on asphalt tanks of laboratory, pilot plant and full plant size storing a variety of different asphalt products. Basic differences were seen in the generation of combustible gas vapours in tanks storing four classes of asphalt materials: flux (basically soft vacuum tower residuum), paving asphalts, solvent deasphalting residuum, and air-blown asphalts. Classical methods of thinking about and troubleshooting these hazards were clearly shown to work only for flux and paving asphalts

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(and can break down even for these materials) and were not applicable to solvent deasphalting residuum and air-blown asphalts. The latter were shown, for the first time, to pose a special problem due to their continued reactivity after undergoing the air blowing process. Time and temperature were critical parameters in determining and controlling the degree of this problem. Simple measurement techniques were developed to monitor all these hazards. These techniques, along with the more sophisticated methods which were used to confirm the simpler techniques (and are still used to troubleshoot special problems), are discussed in detail in this paper.

Methods

Combustion meter measurements

Measurements of total combustible gas and oxygen were made in pilot (1000 gallon) and plant scale tanks using Mine Safety Appliances combustion meters 261, 260, and 360⁷. These meters are commonly used for measurement of empty tank atmospheres to determine the safety of tank entry. They measure oxygen as a percentage of the tank atmosphere and combustible gas as a percentage of the lower explosion limit (LEL). Calibration is done using both room air (21% oxygen, 0% LEL) and a gas standard with composition of 15% oxygen and 0.75% pentane (50% LEL).

The oxygen measurement is made by an electrochemical cell which allows oxygen to diffuse to an electrode slowly enough that the electrode reaction keeps the concentration of oxygen around it at zero. The current generated by the electrode reaction is therefore proportional to the rate of diffusion which in turn is proportional to the concentration of oxygen in the atmosphere. In order to analyse the tanks for smouldering coke deposit hazards these meters should be capable of detecting oxygen over a range from 0 to 21%. Many reactions occur in asphalt vapour spaces which lower the oxygen level. In certain instances steady state concentrations of below 10% have been seen and in those cases measurement capabilities to 0% are desirable to detect a decrease caused by smouldering deposits. In other tanks the normal oxygen level is over 19%.

The combustible gas measurement is made by catalytically burning the vapour on a treated filament and sensing the total combustibles by the change in resistance of the treated wire as it heats up. Other methods of detection are available, but were judged to be less applicable to hot asphalt vapour spaces. One example is the measurement of combustibles by detection of the change in semiconductor resistance caused by surface adsorption of the combustible gases. This method, by design, is most sensitive to carbon monoxide and then to methane. It is used in meters assessing the efficiency of fired heaters⁸. Other methods measure the ability of the vapour to cool a heated filament. Since asphalt tank atmospheres are tremendously varied in composition we feel strongly that the combus-

tion technique is superior.

In using these meters on hot asphalt tank vapour spaces several precautions are taken to protect the meter and to prevent flashback from the meter to the tank. A metal probe, typically a length of 3/16 in. (- 4.8 mm) copper tubing (chosen for its flexibility), is inserted into the tank. The sample is drawn through the tube, through a length of rubber tubing, to a 2 in. (50.8 mm) long cotton filter, then to a liquid trap before entering the meter. The meter itself has a mesh filter at the entrance which the gas must pass through prior to entering the oxygen sensor chamber and then the combustible gas sensing chamber. The sample is then drawn through the built-in pump and out of the meter.

A simple modification of this sampling technique is to insert a charcoal tube in the line between the tank and the meter. The charcoal tube adsorbs higher hydrocarbons and can therefore be used to measure very light combustible fractions. We have found the cut-off for charcoal adsorption in this system to be at propane; in the asphalt tank application, propane and larger are adsorbed, ethane and smaller are not. This method is important to distinguish between combustible gas build-up caused by thermal degradation, where the combustible vapours (primarily methane and carbon monoxide) will pass through the charcoal tube and are measured, and build-up caused by solvent contamination, which even in the case of propane is trapped by the charcoal and not measured⁶.

A second modification of the combustion meter sampling technique is needed to measure combustible levels above the meter limit of 100% LEL or where oxygen levels are too low to adequately support combustion on the meter filament (below 10%)⁷. A rotameter is used to bleed various amounts of fresh air into the meter along with the tank vapour. The LEL values are then plotted on graph paper versus the fresh air flow and a straight line is extrapolated through the data to zero fresh air flow. Naturally, the closer to zero flow that measurements are made the more accurate the extrapolation.

Detector tube measurements

As mentioned above, a lower than normal oxygen reading can be used to provide a first indication of a potential smouldering coke hazard. Measurements of the products of incomplete combustion, namely carbon monoxide, carbon dioxide, and water vapour can be used to verify the possibility of this problem. The simplest measurements of these specific compounds involve using detector tubes and a small (100 ml) hand pump to draw the sample through the tube at a specified rate and total volume. These tubes have indicator material in them which reacts with the species in question and changes colour. At the end of the sampling period the vapour concentration of that constituent can be read off the calibrated tube at the transition line where the colour change stopped. Many reactions are used to detect different compounds and

several have known interactions with other species which may limit their use in different circumstances. The manufacturers (MSA, Draeger, Sensidyne/Gas-Tech, etc.) provide this information with the detector tubes.

Detector tubes were also investigated to measure hydrocarbon combustibles as an alternative or adjunct to a combustion meter reading. These tubes are used by first drawing enough vapour through them to change the colour of the indicator in the entire tube. The volume of vapour, as measured by the number of pump strokes necessary to accomplish this, is used to calculate concentration from data provided with the tubes.

Detector tube measurements were made in laboratory scale vessels as well as in the pilot and plant scale tanks.

Gas chromatography measurements

A more complete profile of the organic species in the tank and pilot scale vapour spaces was obtained by drawing known volumes of vapour through a charcoal tube, sealing and freezing the tube to limit loss of the sample, and then desorbing the organics on the charcoal with carbon disulphide and analysing by g.c.. Analyses were performed by two different laboratories (Chemir and the OCF Organic Analytical Laboratory) using packed columns with flame ionization detectors. Sampling was done with the charcoal tube both inside and outside the sampled vapour space. With readily condensable vapours the tube must be inside the tank for accurate readings. For very light fractions which could not be collected with charcoal tubes the samples were drawn into a 150 ml stainless steel cylinder and similarly analysed.

In addition to their use as a check on combustion meter readings, these techniques are useful to analyse for specific hydrocarbon contamination, for example residual solvent in solvent deasphalting residuum.

Infrared analyser measurements

A number of asphalt tank vapour samples were analysed at the production facility using a Miran 1A infrared analyser. The Miran 1A is a single-beam infrared spectrometer equipped with a gas cell and path length adjustable in steps from 0.75 to 21.75 m. The Miran 1A was calibrated prior to this application using pure methane and the closed-loop calibration system (CLCS) technique recommended by the manufacturer. Literature values from the Miran 1A manufacturer were used to obtain estimates of the other compounds analysed by the Miran 1A.

The asphalt vapour samples were obtained using the 150 ml stainless steel sampling bulbs. A combustible gas meter was used to draw the asphalt tank vapour space sample through the bulbs; both Drierite and charcoal tubes were used between the tank and the bulb to remove moisture and higher hydrocarbons, respectively. The vapours contained in the bulbs were then analysed by incorporating them into a modified CLCS. After flushing the Miran 1A gas cell with

zero-grade nitrogen the gas cell valves were closed and the CLCS assembled. Instrument readings for zero positions at the various wavelengths were recorded for the zero nitrogen background, and the Miran 1A gas cell and bulb valves were then opened. The CLCS pump was activated to transfer, mix, and dilute the bulb contents into the total CLCS volume. Instrument readings in the absorbance mode were then obtained for methane and the other compounds using wavelengths appropriate for each compound.

After quantitative information was obtained, the Miran 1A was set to appropriate scan parameters and a scan of the vapour sample was acquired (2.5-14.5 μm). The maximum path length (21.75 m) was used for all of the above measurements. The Miran 1A experimental technique has been described in more detail by Wolfersberger⁹.

In addition to the samples from production tanks, a number of vapour samples from laboratory trials were also analysed. The Miran 1A procedure used was analogous, except that a tube containing Drierite was incorporated into the CLCS to remove moisture from the samples.

Results

Combustion meter evaluations

A major objective of this work was to determine the usefulness of the simple combustion meter and detector tube approaches to quantify, at least approximately, the composition of the vapour spaces in a variety of asphalt tanks. *Table 1* summarizes measurement of total and light end (carbon monoxide, methane, and ethane) combustible gas using both a combustion meter and the more complex approaches of g.c. and i.r. analysis of gas samples and charcoal tube samples. All of these data were taken on actual production scale equipment storing five different classes of asphalt. In order to facilitate comparison to combustion meter readings all concentrations are expressed as a percentage of the lower explosion limit for that particular gas mix. Calculations of %LEL from composition data were made using Le Chatelier's rule¹⁰. Results indicate that the methods agreed well enough for practical loss prevention purposes, i.e. to indicate hazards as the concentration of combustible gas approaches and exceeds the LEL. Good agreement was obtained without making any correction for specific species measured, although corrections are suggested by the manufacturer⁷. The only exception to the generally good agreement was the case of cutback asphalts where the combustion meter results were much lower than those obtained using g.c. analysis of a charcoal tube sample. The disagreement in cutback asphalt results is due to solvent vapours condensing in the tubing leading to the combustion meter.

The hot (i.e. minus cutbacks) asphalt data is also presented in *Figure 1* to further emphasize the agreement and the range investigated. The results are scattered around the line of equality closely enough to

Table 1. Comparison of combustion meter readings with other measurements of Combustible gas

Asphalt in tank	Combustion meter (%LEL)	Other method (%LEL)	Combustion meter with charcoal tube (%LEL)	Other method for CO, CH ₄ , C ₂ H ₅ (%LEL)	Other method
Air-blown asphalts			80	80	Miran i.r.
			71	78	Miran i.r.
			20	33	Miran i.r.
			46	35	Miran i.r.
	122	117	64	40	Miran and charcoal tube
Solvent deasphalted residuum	15	7			Miran i.r.
	12	7			Miran i.r.
	280	219	10	4	Charcoal tube
Roofers flux	11	10			Charcoal tube
	4	7			Charcoal tube
Paving asphalt	4	5			Charcoal tube
	21	23			Charcoal tube
Cutback asphalt	168	738	0	0	Charcoal tube
	66	495	1	0	Charcoal tube

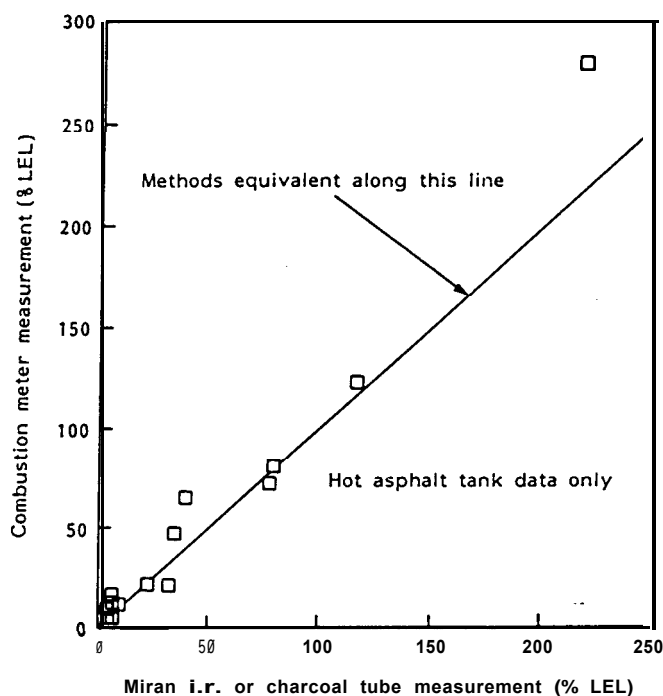


Figure 1 Comparison of LEL values determined by different methods

allow accurate identification of a potentially hazardous tank condition. At Trumbull plants the indicated error was used to set levels of measurement which trigger appropriate action. The one point which is relatively far from the line is the reading at 280% LEL. This is not of practical concern since the reading is so high that the error cannot mask the hazard. In fact the error is undoubtedly caused by the extrapolation technique, which is usually only necessary in tanks already above the lower explosive limit and thus already identified as hazardous.

To compare the above methods of asphalt vapour space evaluation with the traditional methods consider what conclusions would be drawn from flash point testing on the above samples. In the case of the cutback

asphalt, using the Tag method, and in the case of the Roofers' flux and the paving asphalt, using the Pensky-Martens closed cup or the Cleveland open cup method, the actual material flash point would have indicated the hazard in the material relative to storage temperature quite well. In fact, the Tag flash point test is superior to the combustion meter evaluation of cutback combustibility because of the systematic error in the latter caused by condensation of vapours. Note, however, that isolated problems have been encountered with flux and paving tanks where combustible gas build-up caused by thermal cracking and contamination were not detected by flash point testing.

In the case of the air-blown asphalts a large portion of the combustible gas is found to be of such small molecular weight that it is not trapped by a charcoal tube and therefore is detected by the combustion meter/charcoal tube combination. This fraction will be lost in the process of taking the sample and preparing it for the flash point test and in these cases the flash point test only determines part of the tank explosion hazard. With the solvent deasphalting residuum the labile solvent contamination is a large enough molecule that it is trapped by the charcoal tube thus allowing the combustion meter/charcoal tube test to distinguish this problem from one of thermal cracking. The contaminant (typically propane or a pentane) is still readily lost even in a carefully run closed cup flash point test and therefore once again traditional means of assessing asphalt tank explosion hazard is inadequate. In the actual air blown asphalt and SDA tanks referred to in Table 1 both materials were stored under 227°C with flash points of 288°C or greater, and yet combustible gas compositions well into the explosive range were encountered.

Detector tube evaluations

Table 2 presents results of measurements of carbon dioxide and carbon monoxide concentration in vapour spaces of plant tanks and laboratory reactors, all containing hot asphalt. Both detector tube and infrared

Table 2 Comparison of results of detector tube measurements with other measurements of vapour components

Asphalt in vessel	Scale	Component measured	Detector tube result (%) ^a	Miran i.r. result (%) ^a
Air-blown asphalt	Plant	CO	1.2	1.0
			2	< 1
			5	> 1
			> 0.4	0.4
			> 0.4	0.4
		CO ₂	3	> 1.3
			2.3	> 1.3
Solvent deasphalted residuum	Plant	CO ₂	4.4	> 1.3
			2.5	> 1.3
			3.5	> 1.3
			0.2	< 0.5
			> 0.4	> 0.4
Air-blown asphalt	Lab.	CO	160 ppm	230 ppm
			250 ppm	250 ppm
			400 ppm	340 ppm
			400 ppm	330 ppm
			0.22	0.32
			0.30	0.31
			> 1.2	2.1
			0.6	0.67
			0.4	0.49
			Air-blown asphalt	Lab.
> 280 ppm	800 ppm			
0.50	0.46			
0.60	> 0.3			
1.0	> 0.4			
		0.9	> 0.4	

^a Except where otherwise indicated

analyser results are listed. Exact comparisons are difficult in many cases because limits of the measuring method were reached and only a minimum or maximum possible value was indicated. In all but one of these cases, however, the values are consistent between methods. In cases where a direct comparison of measured values is possible, the agreement is generally good over a very wide range of values. This is also seen in Figure 2, and is remarkable considering the semi-quantitative use that is made of the methods, namely the indication of probable smouldering coke deposits if these readings are much larger than normal in the asphalt tank in question.

Tests were done in the laboratory to evaluate the use of water vapour detector tubes, which were of interest because they could be used to determine a third product of smouldering coke combustion. To determine whether hydrocarbon interactions are important in application of the tubes to asphalt tanks, mixtures of hydrocarbons and water vapour in air were prepared and tested in the laboratory. Water vapour was generated by bubbling air through water at 25°C; a water vapour-heptane mix was generated by first bubbling air through 0°C heptane generating a 1.5 vol% stream of heptane in air, then through the same water bath. A mixture of natural gas and water vapour was generated by simultaneously metering air and natural gas to obtain a 6% gas in air concentration and then bubbling through a water bath. Assuming the

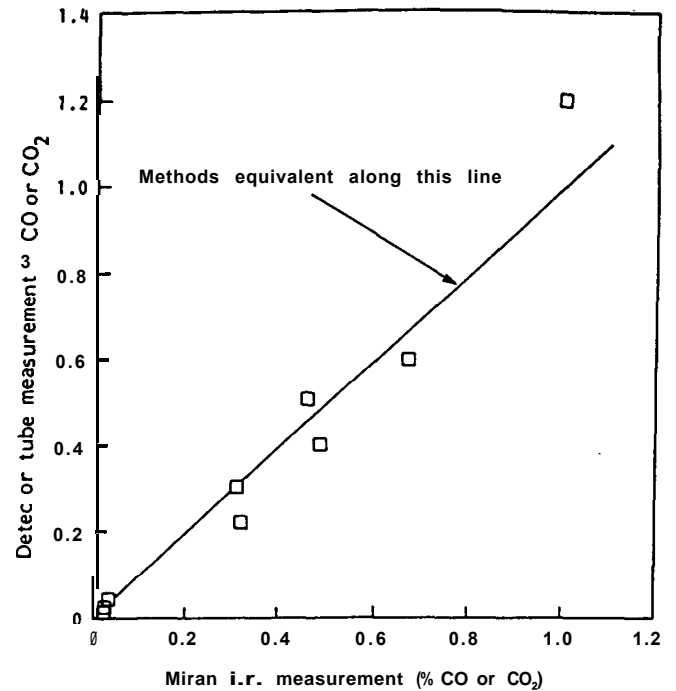


Figure 2 Comparison of CO, CO₂ levels determined by different methods

air was saturated with water vapour the reading taken with the detector tube should have been 23 mg l⁻¹. With only water vapour in the air stream the tubes indicated 19 mg l⁻¹ with the heptane-water vapour mix in the air the reading was 21 mg l⁻¹, and with the natural gas-water vapour mix in the air stream the reading was 21 mg l⁻¹. From these measurements hydrocarbon interference with the measurement of water vapour should not be a problem.

Finally, detector tubes sold to measure hydrocarbons were evaluated in the laboratory to determine their sensitivity to specific compounds. These tubes would be useful if they could give a total weight per volume indication of the hydrocarbons present, because the LEL for hydrocarbons expressed in these units is relatively constant¹⁰. Known weights of hydrocarbons were placed in a flask and evaporated, or in the case of natural gas, gas and air were simultaneously metered into a flask for a known concentration. The number of pump strokes were then determined to saturate the detector tube and calculations were made on the weight and volume of hydrocarbon needed to achieve saturation. To be effective as a tank monitoring device with vapours from hot asphalt, the saturation values would have to be concentration- and species-independent. Results are given in Table 3. The amount of material needed to saturate the tubes is seen to be relatively independent of concentration, but it is highly dependent on species. Only 3 mg of heptane need be drawn through the tube to get saturation while 35 mg of natural gas is required to get the same reaction. Without knowing the composition of hot asphalt tank vapours these detector tubes are of virtually no use. It remains to be seen whether these tubes have a use in

Table 3 Measurements with hydrocarbon detector tubes

Hydrocarbon measured	Hydrocarbon concentration (vol %)	Weight to saturate detector tube (mg)	Volume to saturate detector tube (ml)
Natural gas	6.0	35.3	54.0
	3.0	33.4	51.0
Propane	1.30	16.4	9.1
	0.60	15.1	8.4
Butane	0.50	4.7	2.0
	0.20	3.8	1.6
Pentane	0.47	5.5	1.9
Hexane	0.17	2.4	0.7
Heptane	0.29	3.0	0.7
	0.15	3.1	0.8

certain special cases where the vapour is dominated by a few, definable species, as is the case in cutback tanks.

Conclusions

Combustion meters of the type tested are sufficiently accurate for detection of fuel build-up in hot asphalt tank vapour spaces.

Combining charcoal tubes with the combustion-meter gives an easy way to distinguish between different asphalt tank explosion hazards.

Flash point tests do not give accurate indications of explosion hazards in tanks containing air-blown asphalt or solvent deasphalting residuum.

Combustion meter determinations are not useful in evaluating cutback asphalt tank vapour spaces and will lead to severe underestimation of explosion hazard in these tanks.

Detector tubes are applicable to the evaluation of levels of carbon monoxide, carbon dioxide, and water vapour in hot asphalt tanks.

Detector tubes designed to give overall readings of hydrocarbons are too species-dependent to be of use in hot asphalt tanks.

Note. The data given in this paper should not be construed as recommending changes in practices that have been successful in avoiding asphalt tank explosions in the past. All manufacturing operations are different and the safety procedures that work in one are not necessarily directly transferable to another. It is hoped, however, that the clearer view of asphalt tank safety presented in this paper will lead to better engineering practice with these tanks and fewer explosions in asphalt plants.

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