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# Investigations into the distribution of hydrocarbon concentrations in underground tanks of petrol stations

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**Abstract**

Underground tanks in petrol stations for the storage of petrol need not be equipped with flame-arresting devices provided some conditions stipulated in the relevant technical rules are met. These conditions are to ensure that the gas atmosphere in storage tanks is always overrich. Investigations carried out in an arrangement of tanks corresponding to the practice showed that the air entering the tank during the delivery of petrol leads to a dilution of the gas atmosphere in the tank and that the upper explosion limit is not reached in partial volumes. These partial volumes are thus explosive. The extent of the explosive partial volumes essentially depends on the impulse associated with the inflowing air. The greater this impulse, the stronger the evaporation of petrol and the smaller the explosive partial volume to be expected. The limitation of the delivery rate to 200 l/min as required in the *Technische Regeln für brennbare Flüssigkeiten* (TRbF, Technical rules for flammable liquids) [4] is therefore an unsuitable criterion to ensure an overrich tank atmosphere.

## 1. Legal bases

The construction and operation of petrol stations and their storage tanks is regulated by the Verordnung für brennbare Flüssigkeiten (VbF, Ordinance on flammable liquids) [1] and the Technische Regeln für brennbare Flüssigkeiten (TRbF, Technical rules for flammable liquids) [2–4]. In accordance with these, all openings of storage tanks through which flames may be transmitted into the storage tank must be equipped with flame-arresting devices. In a number of cases, such devices may, however, be dispensed with, for example, for the underground storage of petrol, providing [4], (1) the soil overlying the tank is at least 0.8 m in height, (2) petrol is delivered discontinuously, (3) the delivery rate per tank cannot exceed 200 l/min, and (4) the upper explosion point of the stored petrol is below −4 °C.

Requirements (1), (2) and (4) are usually complied with at every petrol station in Germany. The requirement under (3) is more problematic. So far, petrol stations have

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been equipped with only a few dispensers for each product, and compliance with this requirement has normally been possible, because – with a maximum pump rate of approx. 40 l/min per dispenser pump – the connection of five delivery pumps per tank compartment has been permissible. Due to the fact that more and more petrol stations are now equipped with multi-product dispensers – i.e. dispensing devices designed for the delivery of all products offered – the number of dispensers per product and consequently the maximum possible delivery rate per tank compartment are considerably increased so that the requirement under point (3) can no longer be met.

## 2. Experimental plant

To conduct the investigations, an experimental plant on petrol station scale was set up on the premises of the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig. The main item of this plant (Fig. 1) is an underground storage tank constructed in compliance with DIN 6608 part 2 [5] and provided with two compartments with a capacity of $10\,m^3$ and $20\,m^3$, respectively. The petrol can be pumped over from one compartment to the other at a rate of up to $30\,m^3/h$. Venting of the tank compartments is ensured by vent pipes (DN 50) 4 m in height, in compliance with TRbF 112 [3] , which are connected with the cover of the respective dome via elbow pipes. The elbow pipes can be exchanged so that the diameter of the air inlet openings can be varied (DN 25, DN 40 and DN 50).

The composition of the gas atmosphere of the storage tank was determined by a complementary measurement using an Oxymat 5M-type oximeter made by Siemens. Sampling was made through tubes, which were introduced into the tank through an orifice flange arranged on the dome cover and which were connected with the measuring instrument by flexible PTFE tubes. The tubes could be vertically moved in the orifice flange thus allowing the vertical distribution of the concentration in the tank to be determined. The horizontal distribution of hydrocarbon was measured with the aid of angled steel pipes whose horizontal sections differed in length. The hydrocarbon concentrations stated in this paper indicate the volume content of hydrocarbons mixed with air, in percent.

## 3. Petrol used in the experiments

Petrol of the grade “Eurosuper” [6] was used for the investigations. As petrol is a mixture of different hydrocarbons, samples of the petrol and of the gas phase above the liquid were examined by gas chromatography (Table 1). There is a difference between the composition of the gas phase and the liquid phase. Almost no aromatic compounds are involved in the liquid/gas phase transition and thus only traces can be detected in the vapour phase.

It was found experimentally that the lower explosion limit of the test petrol was at a hydrocarbon content of the mixture of approx. 1.3%, and the upper explosion limit

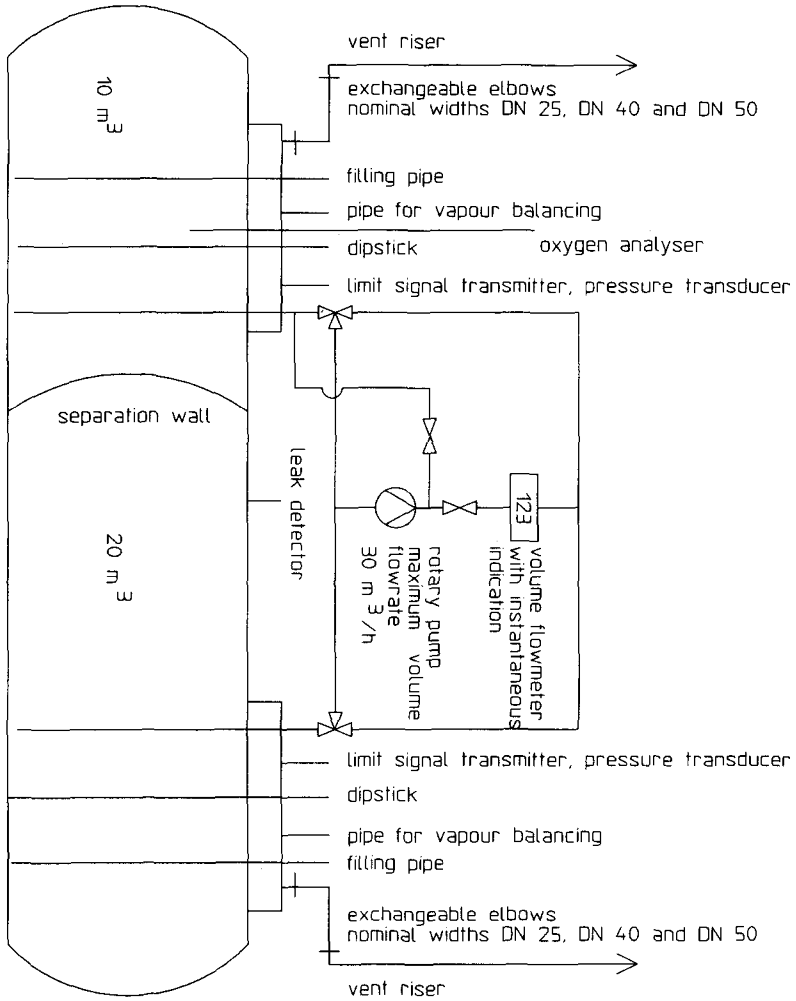


Fig. 1. Schematic diagram of the experimental plant.

at a content of approx. 7.7%. A comparison of these explosion limits with the values stated in the literature [7], i.e. a hydrocarbon content of 0.6–1% for the lower explosion limit and of 6–8% for the upper explosion limit, shows that the literature value and the experimental value agree for the upper explosion limit. In contrast to this, the lower explosion limit determined experimentally deviates from the value given in the literature. It should, however, be noted that, for the ignition tests, a vapour mixture was taken from the tank whose composition is not representative of the composition of the liquid phase of petrol.

Table 1
Composition of the liquid phase and the vapour phase of the petrol used in the experiments (expressed as percentage by mass)

| | Liquid | Vapour |
|---|---|---|
| Pentane (butane) | 1.87 | 27.76 |
| Hexane | 15.84 | 46.87 |
| C6 aromatic compounds | 3.62 | 0.88 |
| Heptane | 26.36 | 22.73 |
| C7 aromatic compounds | 16.57 | 1.76 |
| Octane | 4.65 | |
| C8 aromatic compounds | 20.80 | |
| C9 aromatic compounds | 8.44 | |
| C10 aromatic compounds | 1.85 | |

## 4. Development of the concentration in the apex line of the tank

In a series of experiments, Schön's statement [8] was verified according to which the gaseous atmosphere in tanks is found to form in horizontal layers. To check this, the hydrocarbon concentrations were determined for several horizontal planes, for each horizontal plane at three measurement points. The concentration values at all measurement points of each measuring plane were equal within the scope of the measurement uncertainty, meaning that there are in fact completely horizontal layers in the vapour space. Differences in the concentration were only found in the vertical direction.

Further investigations covered the influence which the two most important parameters, i.e. delivery rate of the liquid and diameter of the air inlet opening, exert on the distribution of the concentration in the vapour space. The concentration in the apex line of the tank was determined as a function of the volume delivered from the tank. Fig. 2 compares the concentration curves of four measurement series carried out at different delivery rates (50, 100, 200 and 400 l/min). For a delivery rate of 400 l/min, after a rapid decrease in concentration at the beginning of the test, the concentration remains relatively constant until it gradually decreases from a delivered volume of 4500 l and reaches a concentration of approx. 11% at the end of the experiment. The jump at the beginning of the experiment is due to the fact that the originally small gas volume (500 l) is strongly diluted by the inflowing air and the dilution effect cannot be compensated by the evaporation of petrol. As the experiment continues, evaporation (caused by the liquid boundary layer being disturbed by the inflowing air jet) ensures that the hydrocarbon concentration stays approximately constant. Only in the lower half of the tank the inflowing air jet does no longer reach the liquid surface, because the liquid level recedes, and therefore the disturbance of the liquid surface and thus the evaporation are reduced.

At a delivery rate of 200 l/min, the concentration of the hydrocarbons in the gas phase also decreases very rapidly to values of about 20%, and it then continues decreasing to reach 5% at the end of the experiment. The influence of the inflowing air

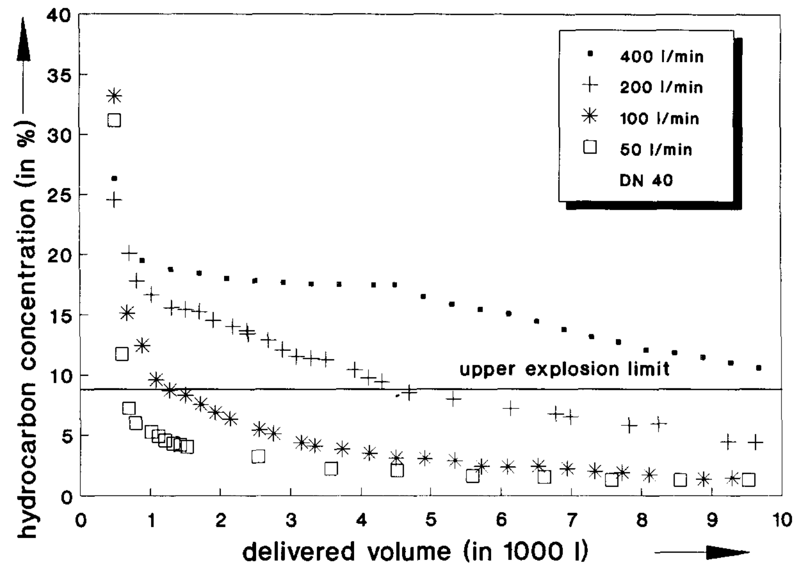


Fig. 2. Hydrocarbon concentration in the apex line of the tank as function of the amount of delicered volume, variation of the delivery rate, initial filling ratio: 95%, final filling ratio: 5%, DN 40 inlet opening, measurement height: 2 m.

jet is not as great as at a delivery rate of 400 l/min, i.e. the boundary layer between the phases is disturbed only at the beginning so that evaporation clearly decreases later on. When the experiment continues over a prolonged period of time, basically only a mixing of the inflowing air with the vapour phase in the tank takes place, and this is the case for the two lower delivery rates. At a delivery rate of 100 l/min, the concentration falls below the upper explosion limit of approx. 8% after about 500 l of petrol have been delivered, and until the end of the experiment the concentration decreases down to a hydrocarbon content of 1%, i.e. it reaches the lower explosion limit. The concentration decreases even more rapidly at a delivery rate of 50 l/min. In this experiment the hydrocarbon concentration already dropped to values of less than 1% after 3500 l of petrol had been delivered. In both cases, the inflowing lighter air settles upon the heavier vapour/air mixture, which sinks with the liquid level.

The size of the air inlet opening strongly influences the time-dependent concentration in the apex line of the tank (Fig. 3). With a DN 25 inlet opening, the concentration decreases in the beginning from 31% to 24% to remain almost constant when the experiment is continued. A similar development is observed for a DN 40 inlet opening. The concentration jump is much greater here: in the first half of the experiment, the hydrocarbon concentration remains constant at 19%, and it gradually decreases to 11% in the second half. The initial jump in the concentration is also observed with a DN 50 inlet opening. However, as the experiment is continued a constant decrease in the concentration down to a final value of 4% is observed, the tank atmosphere reaching the explosive range (upper explosion limit: approx. 8%) already after a volume of about 3500 l has been delivered.

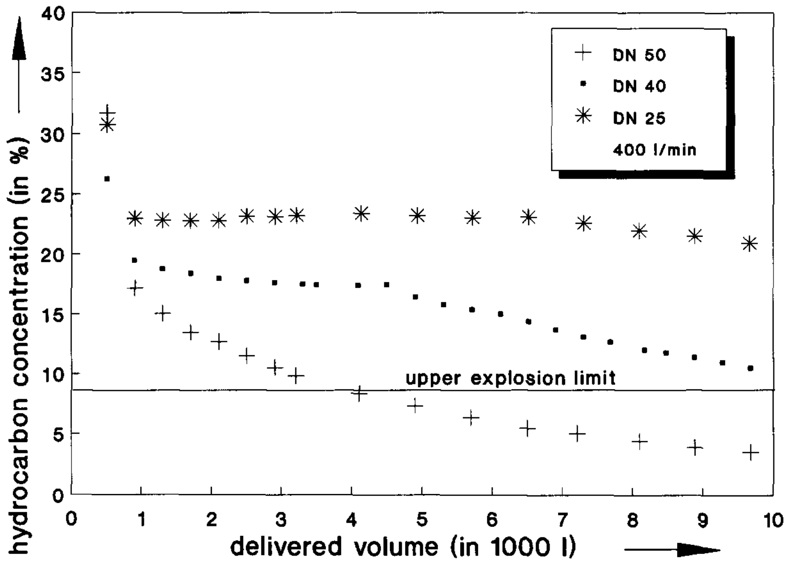


Fig. 3. Hydrocarbon concentration in the apex line of the tank as function of the amount of delivered volume; variation of the inlet opening diameter; 400 l/min delivery rate; initial filling ratio: 95%; final filling ratio: 5%; measurement height: 2 m.

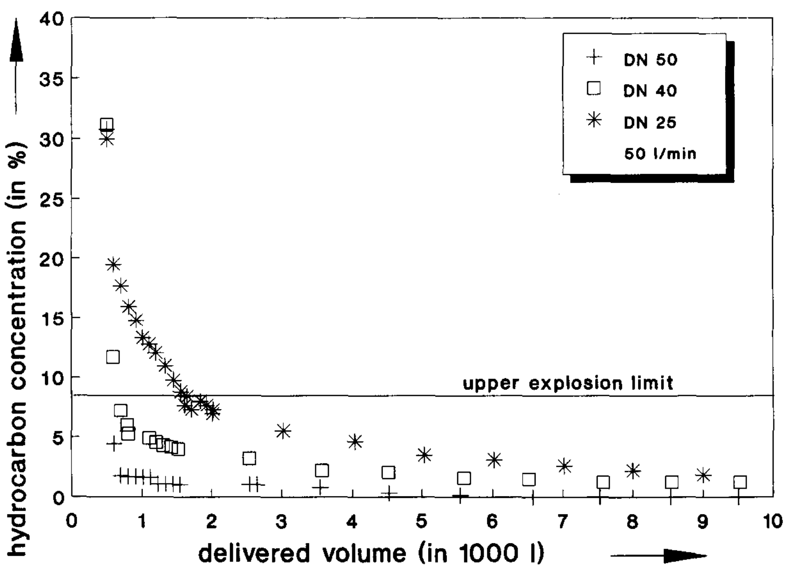


Fig. 4. Hydrocarbon concentration in the apex line of the tank as function of the amount of delivered volume; variation of the inlet diameter; 50 l/min delivery rate; initial filling ratio: 95%; final filling ratio: 5%; measurement height: 2 m.

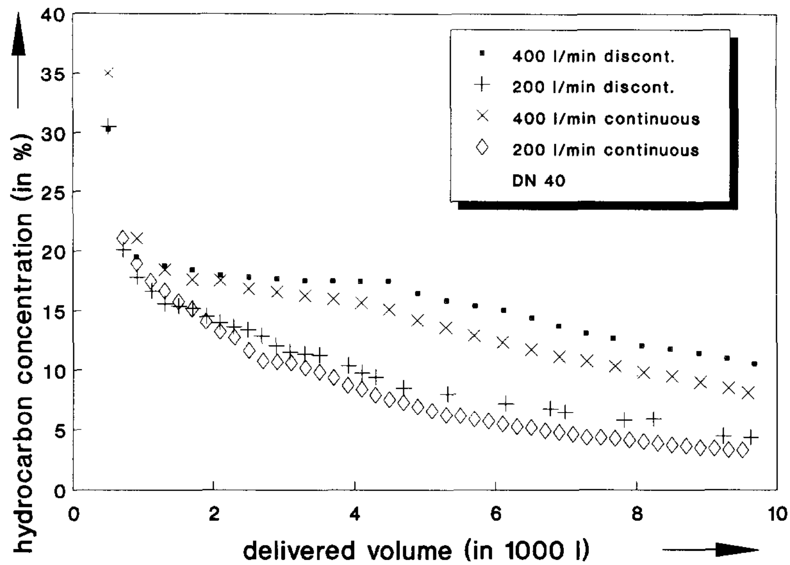


Fig. 5. Hydrocarbon concentration in the apex line of the tank as function of the amount of delivered volume; comparison of continuous/discontinuous delivery; initial filling ratio: 95%; final filling ratio: 5%; DN 40 air inlet opening; measurement height: 2 m.

When the pump rate is reduced to 50 l/min, a strong decrease in the concentration is found for each of the air inlet diameters investigated (Fig. 4). Even with a DN 25 air inlet opening the concentration remains below the upper explosion limit after a volume of only 1600 l has been delivered. At a delivery rate of 50 l/min, the velocity of the inflowing air is so small for all air inlet openings tested that the inflowing air jet no longer reaches the liquid surface; this leads to clearly lower evaporation.

All the experimental results stated so far were obtained during discontinuous delivery of the liquid. This means that a certain volume was delivered, pumping interrupted and the vertical concentration profile recorded. It is to be assumed that further evaporation and saturation of the vapour atmosphere took place in the intervals between pumping processes. Fig. 5 shows for two different delivery rates at the one hand the concentrations recorded during discontinuous delivery and, for comparison, on the other hand the concentrations recorded during continuous delivery. As had been expected, the concentration values in the apex line measured during continuous delivery were slightly lower than those measured during discontinuous delivery.

## 5. Vertical distribution of the concentration after the tank has been emptied to a large extent

The influence of the velocity of the inflowing air becomes even more evident in the vertical profile obtained at the end of the experiment (Fig. 6). For reasons of clarity,

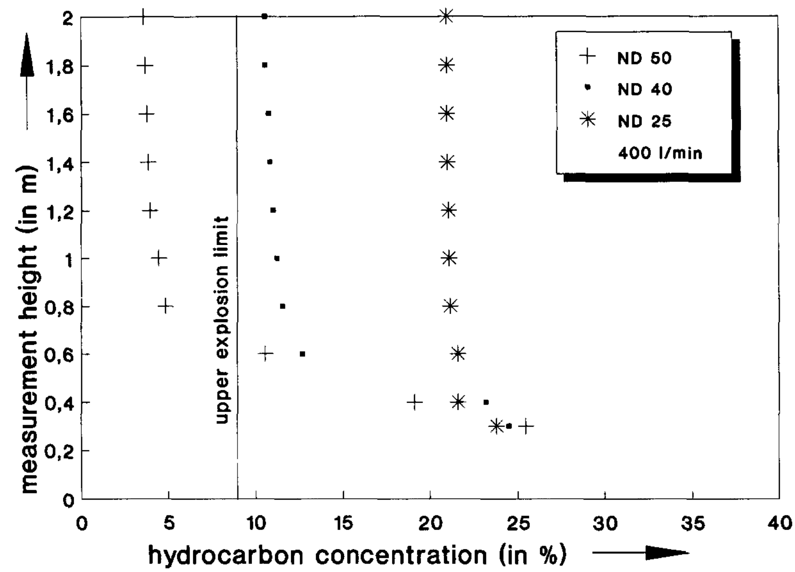


Fig. 6. Vertical concentration profile after the tank has been emptied to a large extent; variation of the inlet opening; delivery rate: 400 l/min; initial filling ratio: 95%; final filling ratio: 5%.

the measurement height – given by the position of the measurement point on the vertical tank diameter – has been plotted on the ordinate and not on the abscissa as is common practice with an influencing parameter. As can be seen, larger volumes of increasingly lower hydrocarbon concentration develop when the inlet opening is enlarged. This is due to the fact that evaporation decreases when the impulse of the inflowing air is reduced.

When the inlet opening is relatively large (DN 50), the inlet velocity of the air amounts to only 1.69 m/s. The inflowing air settles upon the heavier mixture, which sinks as the liquid level recedes. Mixing and equilibrating processes take place only to a limited degree so that the hydrocarbon concentration in the apex line of the tank becomes lower. The difference in the concentration down to the interface is correspondingly great (30%). The higher inlet velocity of 2.69 m/s with a DN 40 opening causes a stronger mixing of the vapour space in the upper half of the tank. This in turn increases the mass transport from the lower layers to the apex line of the tank so that the concentration is in this case clearly higher than with a DN 50 inlet opening. With a DN 25 opening, the penetration depth of the air jet (at an inlet velocity of 6.79 m/s) is so great that the total contents of the tank is mixed, the hydrocarbon concentration being relatively high (a volume fraction of 21%). The transition area is clearly smaller and limited to the immediate vicinity to the liquid surface. Compared with the experiments with DN 40 and DN 50 inlet openings, the high impulse of the inflowing air jet clearly enhances the mass transport mechanisms. It is remarkable that, with a DN 50 inlet opening, the explosive mixture fills 70% of the tank, whereas the

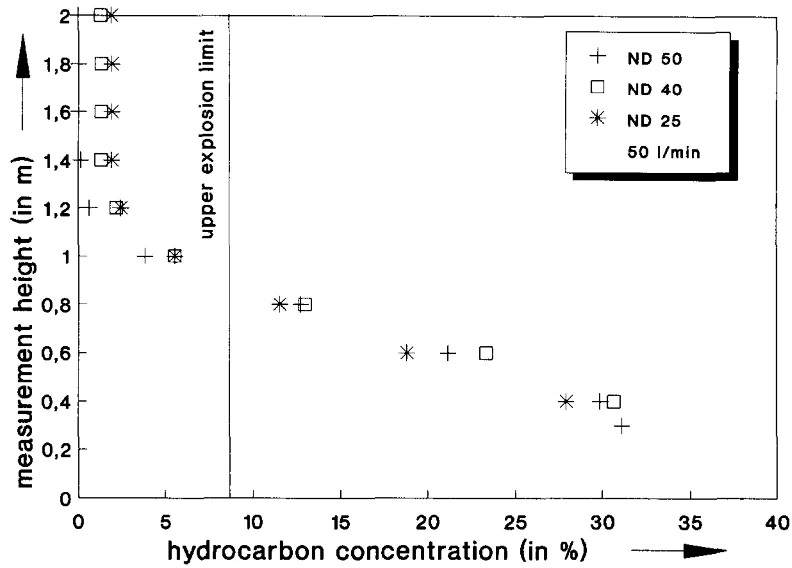


Fig. 7. Vertical profile of the concentration after the tank has been emptied to a large extent; variation of the inlet opening; delivery rate: 50 l/min; initial filling ratio: 95%; final filling ratio: 5%.

concentration remains always above the upper explosion limit when the small DN 25 inlet opening is used.

The formation of explosive volumes in the tank is even more pronounced if the delivery rate is further reduced (Fig. 7). Under these conditions, more than half of the tank volume may be in the range of explosive concentrations.

Part of the investigations into the concentration distribution in the vapour space were repeated in a second tank compartment of equal diameter, however with twice the capacity (Fig. 8). Starting at a filling ratio of 75%, both compartments were emptied down to a filling ratio of 25%. The vertical concentration profiles for both tank compartments recorded at the end of the experiments do not differ significantly at equal pump rates. The slightly higher concentration values measured in the 20 $m^3$ compartment are to be attributed to the clearly larger liquid surface in the tank prone to evaporation and to the fact that twice the time was required for pumping because twice the volume had to be delivered.

## 6. Investigations by means of the schlieren technique

To gain a better insight into the dynamics of the inflow and mixing processes, an experimental arrangement was set up to carry out investigations on a model tank made of transparent material using the schlieren technique. The main item of this arrangement is a model tank in the form of a horizontal cylinder, 0.3 m in diameter and 0.15 m in length. The bottom of the tank is provided with a throttleable outlet to

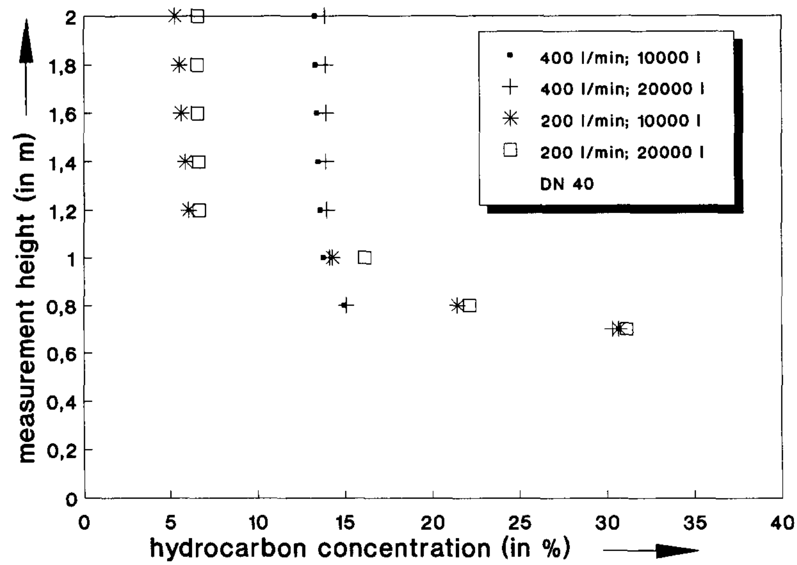


Fig. 8. Vertical profile of the concentration; comparison of two tank compartments of different capacities of 10,000 l and 20,000 l; diameter of the inlet opening: DN 40; initial filling ratio: 75%; final filling ratio: 25%.

adjust the delivery rate. The apex is equipped with a ventilation aperture, which allows pipe sections with inside diameters of 1 mm, 3 mm and 5 mm to be screwed in to realize different jet impulses. The schlieren photographs were taken with a video camera.

Fig. 9 shows as an example a schlieren photograph in which the incoming air jet only just fails to reach the liquid surface. The air jet penetrates into the vapour space like a needle and causes only a mixing and a counter flow in the concentric trumpet-like area. The largest part of the vapour space is only insignificantly disturbed by the air jet so that the hydrocarbon concentration remains unchanged in this area. The vapour thoroughly mixed by the air jet rises in the vapour space and – as the lighter layer – settles upon the heavier vapour layer saturated with hydrocarbon. The interface at the liquid is not disturbed by the air jet so that evaporation is low.

If the velocity of the inflowing air is increased, the air jet reaches the liquid surface (Fig. 10). The interface is disturbed and evaporation clearly increases. The heat of vaporization required for evaporation results in the liquid cooling down – indicated by the Schlieren-striae in the liquid phase. The air jet impulse leads to a more thorough mixing of the vapour space and to the vapour becoming more homogeneous, with the hydrocarbon concentration being at the same time essentially higher.

## 7. Petrol with lowered vapour pressure

The losses incurred during the handling of petrol due to emission are essentially influenced by the vapour pressure of the petrol. One possibility of reducing these

Fig. 9. Schlieren photograph. Air jet does not reach the liquid surface.

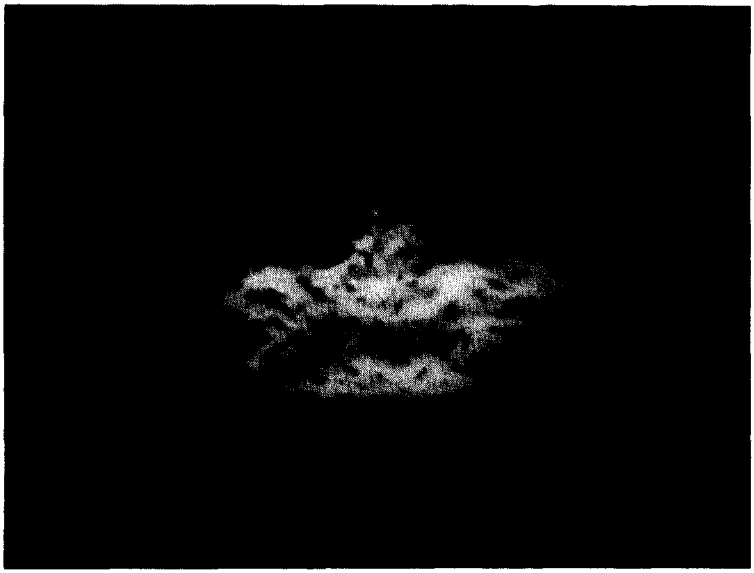

Fig. 10. Schlieren photograph. Air jet reaches the liquid surface.

losses is to reduce the petrol's vapour pressure by decreasing the amount of low-boiling components usually admixed to the petrol during production. To determine the influence of petrol with lowered vapour pressure on the distribution of the

Table 2
Composition of the liquid phase of "Eurosuper" and of a petrol with lowered vapour pressure (expressed in percentage by mass)

| | Eurosuper | Petrol (reduced) |
|---|---|---|
| Pentane (butane) | 1.87 | 2.14 |
| Hexane | 15.84 | 5.30 |
| C6 aromatic compounds | 3.62 | 0.55 |
| Heptane | 26.36 | 11.89 |
| C7 aromatic compounds | 16.57 | 12.94 |
| Octane | 4.60 | 11.38 |
| C8 aromatic compounds | 20.80 | 16.98 |
| C9 aromatic compounds | 8.44 | 18.06 |
| C10 aromatic compounds | 1.85 | 5.71 |
| C11 aromatic compounds | | 3.78 |

hydrocarbon concentration in the vapour space, some of the experiments were repeated using special petrol (Reid vapour pressure: 450 mbar [9]). Table 2 compares the composition of the petrol with lowered vapour pressure with the commercial "Eurosuper" petrol. The composition of the former is clearly shifted towards higher hydrocarbons (C8–C11). The experiments with petrol with lowered vapour pressure have shown that the saturation concentration of 26% in the vapour phase resulting from the modified composition of the petrol is by 5% lower than that of commercial petrol. This reduces evaporation during the pump-over process and shifts the vertical distribution of the concentration towards lower concentrations. This favours the formation of explosive volumes in the vapour space of the tank (Fig. 11).

## 8. Summary and conclusions

The vertical concentration profiles in the vapour space were determined for four delivery rates (400, 200, 100 and 50 l/min) and three different diameters of the air inlet opening. Preliminary experiments confirmed Schön's statement [8] of horizontal layers in the tank. Contrary to previous expectations, hydrocarbon concentrations in the explosive range were found in partial ranges of the tank's vapour space, at the delivery rates up to 200 l/min so far permissible and with the customary air inlet openings (DN 40 and DN 50). At a delivery rate of 400 l/min, the hydrocarbon concentration was clearly higher and, with one exception, always above the upper explosion limit, i.e. in the non-explosive range. It turned out that the velocity of the inflowing air and thus the penetration depth of the air jet decisively influenced the distribution of hydrocarbon concentration in the tank. The longer the period during which the inflowing air jet reaches the liquid surface (interface), the higher the hydrocarbon concentration and the total hydrocarbon content in the vapour space at the end of the experiment. These observations were confirmed in investigations using the schlieren technique. Lowering of the Reid vapour pressure of the petrol used in the

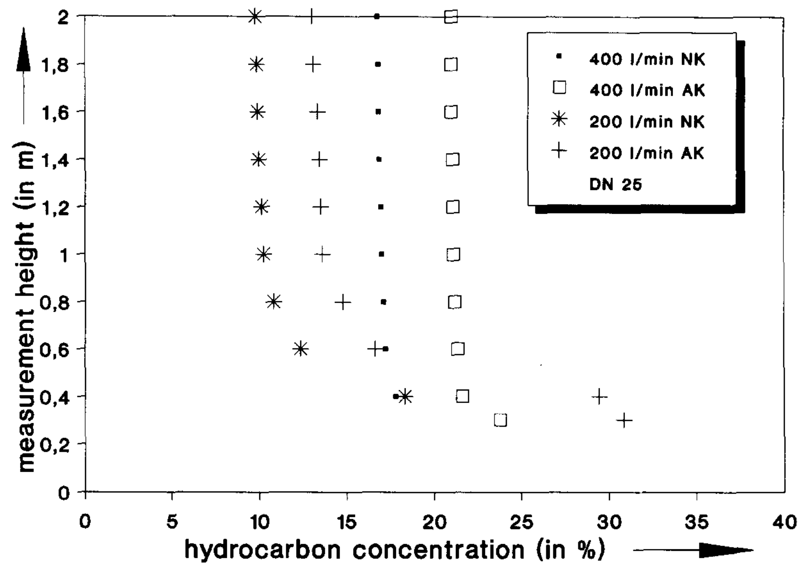


Fig. 11. Vertical profile of the concentration after the tank has been emptied to a large extent. Comparison of "Eurosuper" (AK) with petrol with lowered vapour pressure (NK); initial filling ratio: 95%; final filling ratio: 5%.

tests led to vertical concentration profiles, all of which were at lower values and thus in the explosive region rather than in the non-explosive.

The experiments have shown that it is just at the delivery rates of up to 200 l/min so far permissible that volumes with explosive atmosphere are formed in underground storage tanks. A delivery rate of more than 200 l/min results in a higher impulse of the inflowing air and thus in a higher hydrocarbon concentration in the vapour phase as a result of evaporation. With a view to the development of explosive vapour/air mixtures, the exceeding of the maximum delivery rate of 200 l/min stated in TRbF 120 [4] therefore does not mean a deterioration of the conditions in the tank. From this it follows that the present assumption, i.e. that higher delivery rates would lead to an inadmissibly strong dilution of the tank atmosphere, is false. According to TRbF 120, flame-arresting devices must be provided only if the specified maximum delivery rate can be exceeded; considering the result of the above investigations, this limitation appears no longer justified, as explosive atmosphere may develop at any delivery rate chosen.

Comprehensive retrofitting and converting of tanks in petrol stations are not necessary provided the tanks are sufficiently explosion pressure impact proof. More extensive investigations have shown [10] that a pressure increase up to a maximum of 5 bar is to be expected in the tank in the case of an ignition. The tanks in compliance with DIN 6608 normally used meet this requirement of pressure impact resistance.

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