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Hazardous petrol hydrocarbons from refueling with and without vapour recovery

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The paper is based on two preceding reports in Swedish on vapour recovery and vapour alkenes. The studies provided arguments for general vapour recovery in Sweden as the first European country. A short history in Swedish is available.

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ABSTRACT

Hydrocarbons in air at pioneering European service stations with vapour recovery systems were determined. Vapour recovery was found capable of eliminating 99% of exposure during refueling and more than 95% of emissions to air. Vapour recovery is now being rapidly introduced at Swedish service stations as a result of demands referring to environmental and health hazards.

The analytical technique applied permitted samples corresponding to a single refueling procedure to be analyzed. Sampling on an adsorbent tube was followed in the laboratory by thermal desorption and capillary gas chromatography. All prominent hydrocarbons were well separated on a methyl silicone phase. These include benzene and the alkenes of special interest with respect to health hazards.

The particular importance of alkenes with respect to formation of ozone and other photo-oxidants is discussed. The four isomeric butenes and the six isomeric pentenes were determined and found to constitute about 10% by weight of the petrol vapour. The highly reactive 2-alkenes were more abundant than the 1-alkenes.

INTRODUCTION

Next to vehicle exhaust, petrol vapours constitute one of the most prominent portions of the volatile organic compounds in the air of urban areas (O'Shea and Scheff, 1988). Vapour recovery systems at service stations were introduced several years ago in California and other US regions as part of ozone abatement programs. In Europe, the ozone-related forest decline now leads to a similar pressure for decreased hydrocarbon emissions.

Studies of occupational exposure to petrol vapours have focused on benzene (Nordlinder and Ramnäs, 1987) although many other hydrocarbons have been measured (Rappaport et al., 1987). The widespread public exposure to the carcinogenic benzene from refueling strengthens arguments for vapour recovery, particularly in densely populated areas.

In Europe, vapour recovery was introduced in 1986 at a service station in Göteborg, Sweden. Since then, other Swedish stations have followed at an increasing rate. The present study compares hydrocarbon concentrations at stations with and without vapour recovery. New analytical concepts are applied to achieve the required sensitivity and the separation of hydrocarbons of particular interest. Special emphasis is given to alkenes.

METHODS

Our widely applicable methods for sampling and analysis of ambient hydrocarbons in air were described in some detail in an early report (Mattsson and Petersson, 1982). Therefore, basic concepts are given briefly here and modifications applied in the study of petrol vapours are emphasized.

Sampling

Conventional personal sampling pumps were used coupled by narrow-bore teflon tubing to injector glass liners filled with 60/80 mesh Tenax GC as adsorbent. To avoid breakthrough of the most volatile hydrocarbons, air flows as low as 1 ml/min and total sampling volumes as low as 1 ml were chosen for certain samples. Samples exactly corresponding to the refueling time were obtained by stopping the air flow through the teflon tubing when refueling was finished. Air volumes were determined by relating the total sampling time to the time between two pump strokes. Sampling volumes for ambient air nearby service stations were of approximately 100 ml. The adsorbent tubes were carefully enclosed and protected against contamination before and after sampling.

Laboratory analysis

The adsorbent tube was placed into the injector of the gas chromatograph (Carlo Erba). Thermal desorption onto the cooled analytical column was accomplished at 200°C by passing through the helium carrier gas. The fused silica open tubular column (25 m x 0.33 mm i.d.) was coated with a 0.5 um thick layer of cross-linked methylsilicone (BP-1). Starting from 0°C, oven temperature was increased by 2°C/min during analysis. Detection was by flame ionization and chromatogram, retention times and automatic peak integration were obtained from reporting integrators. Peak identities were confirmed by comparisons with known samples and literature data. A response factor determined for _n_-heptane was used for all non-aromatic hydrocarbons.

Complementary results for several duplicate and other samples were obtained on a different analytical system based on separations on an Al_2O_3 column (Nordlinder et al., 1984). Comparisons between the two systems permitted control of breakthrough losses, response factors and incompletely resolved hydrocarbons. Methylpropene and 1-butene were not resolved on the methylsilicone column but were well separated on the Al_2O_3 column as were all other isomeric butenes and pentenes.

RESULTS

The results given were obtained from about 50 samples. For each sample 20-30 individual hydrocarbons were determined. The concentration of petrol vapour hydrocarbons was found to depend heavily on weather and wind, on service station design, on the sampling point and on the individual's refueling technique. Therefore, results representing unusual conditions are not presented. No samples were taken at low temperatures and high wind-speeds favouring low concentrations. On the other hand no samples were taken at very high ambient temperatures, and samples clearly affected by spill from refueling were excluded.

Chromatographic separation

The chromatogram reproduced in Fig. 1 illustrates the separation of the petrol hydrocarbons which were determined. The sample was taken a few meters from a large service station with vapour recovery and also a few meters from nearby traffic. Therefore, the sample represents not only petrol vapour but also to some extent hydrocarbons from auto exhaust.

The non-polar methylsilicone stationary phase retains hydrocarbons mainly according to molecular weight or rather according to boiling point. Consequently the hydrocarbons studied elute in order of an increasing number of carbon atoms. Cycloalkanes and aromatic hydrocarbons appear later than the corresponding *n*-alkanes. For isomers, methylalkanes appear before *n*-alkanes, 2-methylalkanes before 3-methylalkanes and 1-alkenes before 2-alkenes.

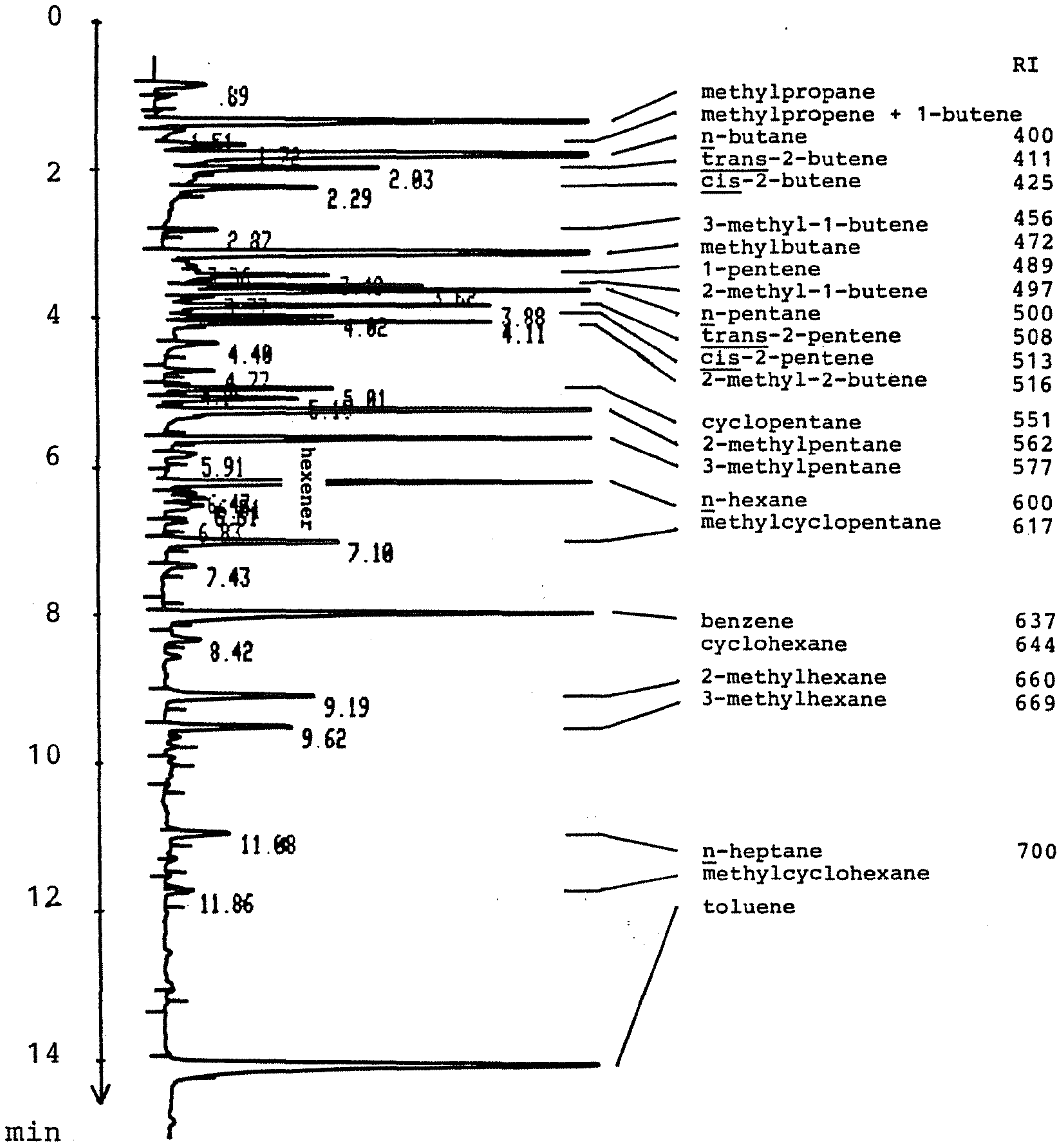

Fig. 1:

Gas chromatographic separation of ambient hydrocarbons at a service station near traffic in Göteborg, Sweden (Retention index given between 400 and 700).

The chromatogram illustrates that resolution is not particularly deteriorated by the thermal desorption technique applied for introduction of the sample. Furthermore the separation characteristics of the column permit determination of virtually all prominent components of petrol vapour. It is interesting to note that all six isomeric pentenes are clearly resolved. The retention index scale may facilitate identification on non-polar columns. Retention data for a considerable number of C_4-C_6 alkenes exist (Cox and Earp, 1982) but reported data for alkenes in petrol vapours are scarce.

Composition of vapours

In Table 1, results demonstrating the composition of hydrocarbons in the air at service stations are given. Priority is given to alkenes. The first column refers to petrol vapours (approximately 100 mg/m^3) in the breathing zone on refueling. The second column refers to polluted air (approximately 1 mg/m^3 of vapour hydrocarbons) a few meters from a service station and near traffic. The chromatogram reproduced in Fig. 1 corresponds to one of the samples taken at the latter position.

The results given for refueling are thought to be fairly typical of the composition of petrol vapours in Sweden and Western Europe. Isobutane (methylpropane), n-butane and isopentane (methylbutane) were found to be the major hydrocarbons in vapours in agreement with reports from the petroleum industry in Europe (Concawe, 1987) as well as the United States (Rappaport et al., 1987). The benzene content found to be about 2% is about twice as high as in the United States (Rappaport et al., 1987). This is explained by the higher content of benzene in European petrol. The ten butenes and pentenes were found to amount to about 10% of the vapour hydrocarbons. The alkenes originate primarily from the petrol fraction produced by catalytic cracking which has increased considerably in Europe during the past few years.

Table 1. Alkenes and selected other hydrocarbons in inhaled petrol vapours at refueling and in ambient air at a service station near to traffic.

Boiling point °C		Vapours % weight[*]	Ambient air % weight[**]
	Butenes		
− 7	Methylpropene	0.6	0.4
− 6	1-Butene	0.5	0.4
+ 1	*trans*-2-Butene	1.3	1.1
+ 4	*cis*-2-Butene	1.3	0.7
	Pentenes		
+ 20	3-Methyl-1-butene	0.4	0.2
+ 30	1-Pentene	1.0	0.5
+ 31	2-Methyl-1-butene	1.3	0.8
+ 36	*trans*-2-Pentene	1.4	1.0
+ 37	*cis*-2-Pentene	0.8	0.5
+ 39	2-Methyl-2-butene	1.6	1.1
	Arenes		
+ 80	Bensene	2.2	3.2
+111	Toluene	1.6	5.7
	Alkanes		
− 10	Methylpropane	21	19
0	Butane	29	25
+ 28	Methylbutane	16	13
+ 36	Pentane	5.3	5.4
+ 69	Hexane	1.4	2.3
+ 98	Heptane	0.2	0.5

[*] Average of four samples taken simultaneously on June 22, 1988.

[**] Average of six samples taken simultaneously on June 15, 1988; excludes C_1-C_3 hydrocarbons.

Volatile hydrocarbons such as butanes and butenes are considerably enriched in petrol vapours compared with liquid petrol. Pentanes and pentenes tend to be somewhat enriched. The percentage of benzene is more than twice as high in liquid petrol as in vapours. The higher the boiling point of a specific hydrocarbon, the smaller its fraction in vapour compared with liquid petrol. Consequently, fully vapourized petrol spillage and unburnt petrol hydrocarbons from automobile tailpipes contribute to a higher percentage of high-boiling hydrocarbons. This is clearly evident in Table 1 for the sample taken adjacent to a service station.

Alkenes

Alkenes are much more reactive than other hydrocarbons of petrol vapour in the formation of photo-oxidants. Alkenes are also of particular interest with respect to health hazards because partial metabolic conversion to genotoxic epoxides may occur. Total alkenes are almost twice enriched in vapours compared to liquid petrol because of their volatility (Braddock, 1987). For these reasons the alkenes in petrol vapours were studied in more detail than the other hydrocarbons. Earlier studies from the petroleum industry have not emphasized alkenes and report only scattered and to some extent obviously unreliable alkene data (Rappaport et al., 1987; CONCAWE, 1987).

In Table 2, alkene concentrations are given for different localities and occasions with each set of data representing the average of several simultaneously taken samples. The results for refueling without vapour recovery demonstrate that the pentene fraction of the vapours is larger than the butene fraction and the 2-alkene fraction larger than the 1-alkene fraction. Inspection of the part of the chromatograms where the 18 isomeric hexenes appear indicates that their fraction of the vapours was about 1% as compared with about 4% for the butenes, 6% for the pentenes and 2% for benzene.

Table 2. Concentrations of alkenes (mg/m^3) in the air at two service stations in the summer of 1988.

	Refuelling No recovery June 7 14.10,22°C 4 Samples 1.0 min	Refuelling No recovery June 22 10.45,15°C 4 Samples 0.7 min	Refuelling Recovery June 10 10.35,21°C 4 Samples 2.8 min	Ambient air Recovery June 15 14.00,22°C 6 Samples 19 min
Methylpropene	1.3	0.7	0.01	0.009
1-Butene	1.3	0.6	0.01	0.009
trans-2-Butene	3.4	1.7	0.02	0.023
cis-2-Butene	3.0	1.7	0.02	0.015
3-Methyl-1-butene	0.7	0.4	0.00	0.005
1-Pentene	1.4	1.1	0.01	0.011
2-Methyl-1-butene	2.1	1.6	0.01	0.018
trans-2-Pentene	2.4	1.7	0.01	0.021
cis-2-Pentene	1.3	0.9	0.01	0.011
2-Methyl-2-butene	3.0	2.1	0.01	0.024
Benzene	3.7	2.1	0.05	0.063

Table 3. Concentrations (mg/m^3) of hydrocarbons of service stations with and without vapour recovery (1987).

	Inhaled air on refueling			Ambient air 3 m downwind		
	Recovery No roof April 28 15°C	Recovery Roof May 14 10°C	No recovery Roof April 28 15°C	Recovery No roof April 28 14°C	Recovery Roof May 18 8°C	No recovery Roof May 14 13°C
Methylbutane	0.45	1.84	53	0.04	0.18	9.6
Pentane	0.15	0.75	21	0.02	0.08	3.0
Benzene	0.06	0.29	5.0	0.02	0.07	0.48

Vapour recovery

The system for petrol vapour recovery introduced in Sweden in 1986 was the Healy assist system. A bellow on the nozzle permits vacuum-assisted returning of vapours to the storage tank during refueling. Our reported measurements refer to samples taken at service stations equipped with this recovery system.

The results shown in Table 2 for two comparable service stations with and without vapour recovery demonstrate the potential of the vapour recovery technique. Proper handling of the vapour recovery nozzle almost completely eliminates emissions from the petroltank of the automobile during refueling.

The results shown in Table 3 illustrate that concentrations in the breathing zone during refueling are typically about ten times higher than in a sector 3 m downwind. A large effect of vapour recovery is evident in both positions. The results also illustrate a marked tendency towards higher concentrations at pumps under a roof than at pumps without a roof. This is explained by the restricted vertical mixing caused by a roof.

The results given in Tables 2 and 3 demonstrate that recovery lowers vapour concentrations during refueling to about 1% of those recorded without recovery. This is provided that the vapour recovery nozzle is handled correctly. People unfamiliar with the technique or nervous because of our sampling procedure often made mistakes and were found to be exposed to higher concentrations. Significantly lower concentrations, most often about 90% lower, were obtained with than without recovery in these cases as well.

In summary, our results and experiences indicate that vapour recovery combined with elementary information on its use can eliminate about 99% of vapour exposure during refuelling. Allowing for some spill of petrol, vapour recovery can also eliminate at least 95% of the emissions to air from refueling.

DISCUSSION

The environmental impact of petrol vapours and photo-oxidant formation from petrol vapours is usually discussed in terms of total emissions. Health hazards from petrol vapours have been studied mainly for occupational exposure to the well-known carcinogenic component benzene. The reported content of petrol vapours, especially with respect to alkenes, makes it possible to conduct a more detailed discussion of environmental and health hazards.

Photo-oxidant formation

With respect to first-day formation of ozone in high concentrations, alkenes are of particular importance. Modelling of the London plume indicates that 3% of butenes and pentenes in the morning hydrocarbon emissions may give rise to about 30% of the ozone formed in the plume 3 hours later (Hough and Derwent, 1987). The reason for the rapid formation of ozone from alkenes is their high reactivity towards the hydroxyl radical (Atkinson, 1985) and towards ozone (Atkinson and Carter, 1984). The reaction of alkenes with ozone produces aldehydes and radicals which speed up net photo-chemical formation of ozone. Most other hydrocarbons of petrol vapour are unreactive towards ozone, and the prominent alkanes react about ten times more slowly than alkenes with the hydroxyl radical.

The reaction rate of 2-alkenes with ozone is more than ten times higher than that of 1-alkenes. During the summertime sunny days of interest with respect to photo-oxidant formation, reaction with the hydroxyl radical may compete for 1-alkenes whereas 2-alkenes should react preferentially with ozone. 2-Methyl-2-butene is the most reactive of the ten butenes and pentenes and also appears to be among the most abundant alkene in petrol vapour. Its atmospheric summer half-life should be typically much shorter than one hour.

It is evident that the contribution of petrol vapours to photo-oxidant formation can be decreased in several ways. A lowered content of alkenes from catalytic cracking in the petrol decreases first-day ozone formation. The individual can contribute by refueling in the afternoon rather than in the morning and on other occasions unfavourable to ozone formation. However, vapour recovery should be a much more efficient method for reducing the overall contribution of service stations to photo-oxidant formation.

Public exposure

It is generally recognized that public exposure levels must be kept much lower than regulated occupational levels. This has led to demands for vapour recovery primarily at service stations near to housing areas. Customers and particularly refueling motorists are exposed to much higher short-time concentrations than people living in the neighbourhood which adds to the arguments for vapour recovery. With respect to the well-known effects of organic solvents on man, it also appears reasonable to minimize exposure to petrol hydrocarbons before driving with respect to traffic safety. In Sweden, many people now deliberately choose stations with vapour recovery to avoid potential health and environmental hazards.

The alkenes of petrol vapours may contribute significantly to health hazards through effects of conversion products which are still not well known. Metabolic conversion of alkenes in man may in part produce genotoxic epoxides (Osterman-Golkar and Ehrenberg, 1982). Atmospheric photo-oxidation of propene has been demonstrated to give other highly mutagenic products (Kleindienst et al., 1985). These health hazards strengthen the arguments for lowering the alkene content of petrol and the arguments for vapour recovery.

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