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**CONTAMINATION OF ATMOSPHERE
WITH VOLATILE HYDROCARBONS
DURING HANDLING OIL PRODUCTS OF PETROL
AND DIESEL FUEL TYPES**

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The paper describes monitoring of contamination of atmosphere with organic substances during ordinary operation of a petrol station, namely during pumping of fuel by a consumer. The measurements were performed by means of a portable analyser ECOPROBE 5 equipped with an IR detector. The analyser was calibrated using standard mixtures of petrol vapours and air as well as by means of gaseous standards of volatile portions of Diesel fuel. The calibration curves obtained were used for determination of real concentrations of the analysed substances in the units of mg m^{-3} . The practical measurements have shown that the reverse exhaust of petrol vapours cannot prevent contamination of the atmosphere unless the dispensing nozzle is properly inserted during filling the tank.

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Introduction

Volatile organic compounds (VOC) are air pollutants whose importance has been increasing recently. These substances play an important part in physico-chemical processes in troposphere because they significantly contribute to formation of ozone and other photochemical oxidants. They can also represent a serious health hazard to population and to the environment because of the toxicity of some of them (e.g., benzene and buta-1,3-diene) [1]. In particular, VOC include the crude oil products, i.e. substances and preparations containing aliphatic, alicyclic and aromatic hydrocarbons possessing low viscosity and low surface-tension values. Besides the crude oil itself they include the products of crude oil treatment, such as petrol, kerosene oil, Diesel fuel, and mineral oils. Nowadays, in connection with development of industry, agriculture and transport, it is impossible to avoid situations that introduce VOC into the environment. In particular, such situations are connected with:

- escape during handling crude oil products in the cases of their transport, pumping, storage, filling into tanks of machinery, repairs of machinery, exchanges of filling, application of crude oil products as solvents, cleaning aids, grease removers etc.,
- escapes of emergency nature, such as damage of tanks in machinery, rupture of hosepipes and pressure pipelines in machinery, rupture of crude oil pipelines, during traffic accidents of vehicles transporting these products, accidents of storage and handling equipment and their pipe manifolds and fittings, during criminal acts and sabotages concerning these types of equipment etc.,
- escapes connected with improper disposal of used packaging materials and containers of crude oil products.

Suitable methods for determination of pollution of the atmosphere with VOC include the gas chromatography combined with, e.g., flame-ionization detector, thermal conductivity detector, or photo-ionization detector and, in particular, mass detector [2]. Automatic portable analysers for direct quick and/or continuous field analyses of air quality are subject of significant development because of the necessity of obtaining — as rapidly as possible — the most accurate data possible about the actual situation of contamination of the atmosphere with VOC, the necessity of taking proper measures in situations of emergency escape of VOC into the atmosphere or, on the other hand, long-term monitoring of the air quality, e.g., near potential sources of pollution. The most widespread variant of portable analysers are gas chromatographs developed as a scaled-down simpler alternative to laboratory models [3-6]. Although various types of detectors are applied, the most frequent combination is GC + mass detector [7-11]. New types of mass spectrometers were also developed for the purposes of on-line analysis. One of them is the method of Membrane introduction mass spectrometry (MIMS),

which adopts an entry membrane (made of, e.g., poly(dimethylsiloxane)) for concentrating the sample: the membrane is much more pervious for the organic analysed substance than for the matrix, which allows reaching of a very low detection limit [12]. Another possibility is the so-called Selected ion flow tube mass spectrometry (SIFT-MS), which makes use of reactions of analysed substance with precursors (e.g., H_3O^+ , O_2^+ , NO^+), the products of these reactions being subsequently analyzed by means of the differentially pumped quadruple MS-ion-counting system [13]. However, the field analysers based on the principle of gas chromatography and/or mass spectrometry may suffer from the drawback of the necessity of relatively demanding instrumentation: in particular, they may need various carrier gases and a source of vacuum, which makes the manipulation more difficult. An important point also is the way of collecting and concentrating of samples before the analysis proper [14].

A significant role in the determination of contamination of the atmosphere with VOC also belongs to the portable analysers based of spectrophotometric methods. Apart from the mass spectrometers [15-20], which have already been mentioned above in the context of gas chromatography, literature describes, e.g., an analyser working on the principle of UV spectrophotometry, namely with application of various adsorbents, e.g., powdered amorphous SiO_2 [21,22] or finely porous silicate powder [23,24]. Further possibility is offered by the IR analysers, which allow reaching of very low detection limits (less than mg m^{-3}) and are also suitable for long-term continuous monitoring of contamination of the atmosphere with VOC [25,26]. This group of analysers also includes the mobile analyser ECOPROBE 5 [27], which was used for analysis of the atmosphere in the present work. A large advantage of these instruments can be seen in the fact that the sample is sucked directly into the cell volume, where the measurement takes place, and no additional special equipment for collecting and concentrating of analysed substance is needed.

The aim of this work was to calibrate the portable analyser ECOPROBE 5 by means of gas chromatography and then monitor contamination of the atmosphere with VOC from fuels for motor vehicles.

Experimental

Refinery Products Used. Preparation of Gaseous Mixtures

The portable VOC analyser was calibrated using model standard gaseous mixtures of air with the following types of petrol: Natural 95, Natural 98, Special 91 (Paramo, Pardubice, the Czech Republic), Special 100 (OMV Refining, Wien, Austria), and Shell V-Power Racing (Shell Chemicals, Hamburg, Germany), and also a mixture of air with Diesel fuel (Slovnaft, Bratislava, Slovakia). The

mixtures were prepared by addition of a defined amount of the liquid fuel into a gas-tight bag (Linde Gas, Praque, the Czech Republic) whose inner surface was covered with aluminium foil. The addition was carried out by means of a 500- μl hypodermic syringe (Hamilton), whereupon a defined volume of air was pumped into the bag by means of membrane pump M 401. The mixture obtained was heated for a short time period and then left to homogenize at room temperature ($(25 \pm 2)^\circ\text{C}$). Formation of homogeneous mixture was checked by means of gas chromatography: if homogeneous, the gaseous sample gave a constant response, expressed by the height of the representative peak dominating in the sample; subsequently, the concentration of the component was determined by the same method. The standard serving for quantification of unknown petrol samples was the gaseous sample prepared by adding 5 μl liquid substance into a gas-tight glass container of defined volume, which was closed by means of silicone septum. Perfect vaporization of the liquid phase was ensured by short heating with hot air. The concentration of this mixture was determined by calculation. In the case of preparation of standards of volatile hydrocarbons from Diesel fuel, which is a varied mixture of substances with boiling points in the range of 180-370 $^\circ\text{C}$, it was not possible to calculate the concentration on the basis of the whole amount of the liquid sample added, because less volatile components remain in liquid phase at room temperature or slightly above. The content of volatile components in Diesel fuel (hereinafter TSN) was determined experimentally in the following way: an open glass vessel was charged with 200 μl Diesel fuel having the density of 0.8299 g/cm^3 , whereupon the vessel was kept at the temperature of 80-85 $^\circ\text{C}$, and the decrease in the mass of liquid phase was determined by weighing at regular time intervals. Figure 1 shows the time dependence of the mass decrease determined in three repeated experiments.

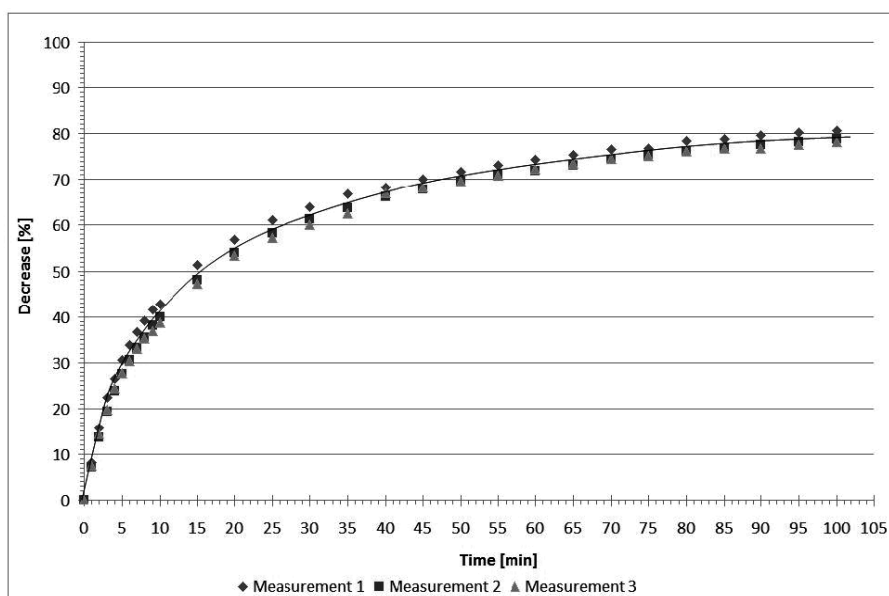


Fig. 1 Time dependence of mass decrease of Diesel fuel at the temperature of 80-85 $^\circ\text{C}$

From Fig. 1 it is obvious, that in the 15-min period from the beginning of heating the decrease in volatile components is considerable, about 50 % TSN being released. The residual mass is stabilized after ca 100 min. Then the whole decrease in volatile components reaches 80 % of the initial amount of Diesel fuel. These findings were used in preparation of standards and calculation of concentrations of gaseous components of Diesel fuel, which then served for quantitative evaluation of both the model and unknown gaseous mixtures by means of gas chromatography.

Instruments and Apparatus Used

The field analyses of gaseous mixtures of air with volatile crude oil products were performed with the portable analyser ECOPROBE 5 (RS Dynamics, Prague) equipped with IR detector. The scheme of this instrument is presented in Fig. 2. The detector contains a source of IR radiation, whose rays are directed into the through-flow cell, where the IR radiation is absorbed in accordance with the absorption bands of the given components. The remaining radiation passes through four optical filters and reaches four sensors. Three filters transmit only specific wavelengths of the radiation characteristic of carbon dioxide, methane and hydrocarbons. The fourth sensor and its optical filter have reference function. The measuring range of the indication sensors lies in the range of 0-500,000 ppm with the detection limit of 50 ppm. The sensor providing information about the total content of hydrocarbons has been calibrated for methane by the manufacturer.

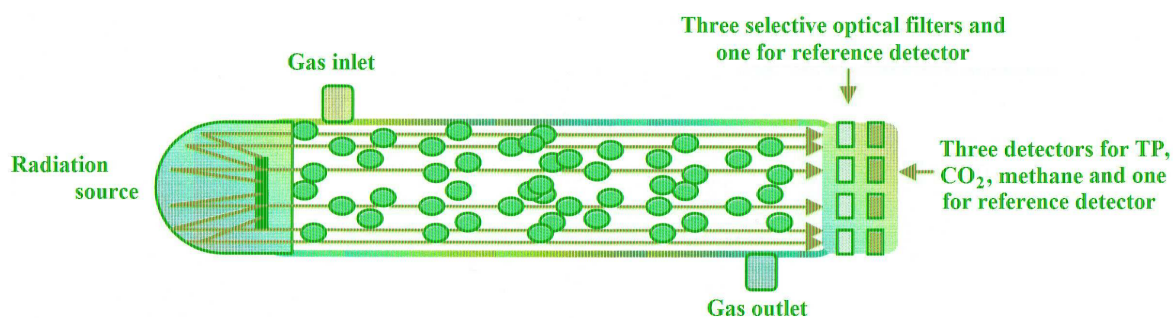


Fig. 2 Scheme of IR detector in portable analyser ECOPROBE 5

The concentrations of model gaseous mixtures of air with crude oil hydrocarbons were also determined by means of gas chromatography using a Chrom 5 apparatus equipped with a flame-ionization detector (Laboratorní přístroje, Prague). Argon was used as carrier gas. Separations were performed on packed column (DC 200). For analysis of petrols the temperature of injector was 160 °C, temperature of oven was 150 °C and temperature of detection was 120 °C.

Analysis of Diesel Fuel was performed at the temperature of injector 180 °C, temperature of oven 180 °C and temperature of detection 150 °C.

Results and Discussion

Calibration of Analyser ECOPROBE 5 for Gaseous Mixtures of Motor Fuels

Since the IR detector channel that measures the total content of hydrocarbons had been calibrated with methane by the manufacturer, it was necessary before practical measurements to calibrate this sensor with a real mixture of hydrocarbons which are to be monitored in the field measurements. Therefore, the calibration curves were determined for both petrol and volatile substances present in Diesel fuel in order to represent the dependence of values provided by ECOPROBE 5 in ppm regime upon the real concentration of analyzed substance in mg m^{-3} . In the cases of the petrol types Natural 95, Natural 98, Special 91, Special 100 and Shell V-Power Racing, the gaseous mixtures of various concentrations of hydrocarbons were prepared by addition of 200 μl liquid substances into a bag which contained a small amount of pure air. After subsequent short heating, air was added into the bag, and the mixture was left to homogenize for a period of 5 min, the temperature being adjusted at (25 ± 2) °C. The mixture prepared was analysed quantitatively by means of gas chromatography, whereupon the bag content was analyzed with the ECOPROBE 5 apparatus. Further gaseous mixtures were prepared by diluting the gas in the bag with pure air, and then they were analyzed by both above-mentioned methods. Plotting of the dependence between the response of IR detector in ppm regime and the real concentration of petrol in the gaseous mixture provided the calibration curves given in Fig. 3.

Figure 3 shows that there are only small differences between the individual regression curves; these differences may be due to experimental error of the two analytical methods adopted. Therefore, it was decided to create a single calibration curve taking into account all the experimental points and apply it to evaluation of concentrations of petrol vapours of all the petrol types examined. The equation of this summary calibration curve reads as follows

$$y = 0.3767x^{1.246} \quad R^2 = 0.975$$

where y stands for the IR detector response presenting the total content of hydrocarbons in ppm units on the basis of the manufacturer's calibration using methane, x is the real concentration of petrol in mg m^{-3} and R is the regression coefficient.

In order to verify correctness of the above-mentioned equation, a series of model gaseous samples of individual sorts of petrol was prepared; also prepared

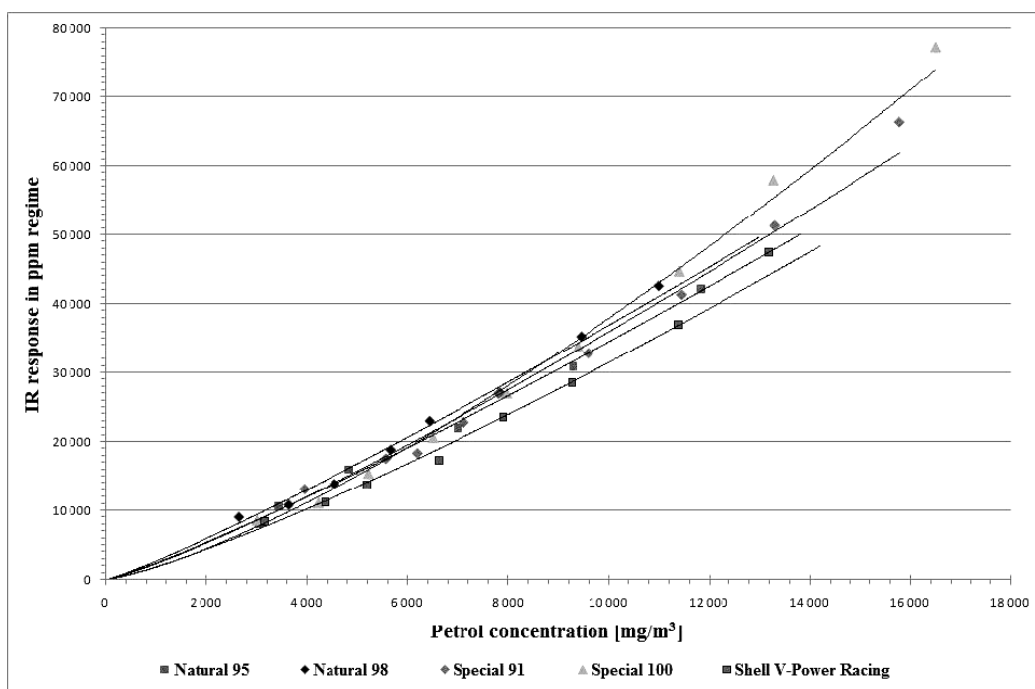


Fig. 3 Calibration dependence between values obtained from ECOPROBE 5 in ppm units and real concentration of petrol vapours in mg m^{-3} units

was a mixture of Natural 95 and Special 91 in the ratio of 94.2 : 5.8 chosen on the basis of statistical data about consumption of petrol in the first half of 2007 [28]. First, their concentration was determined by means of gas chromatography in the range of $3\,051\text{--}13\,578\text{ mg m}^{-3}$ and then by means of the portable analyser giving the readings in ppm units (calibrated with methane); the later data were transformed into real concentrations of petrol in mg m^{-3} units using the above-given calibration equation. The results are presented in Table I, where it can be seen that the concentrations determined by means of the analyser ECOPROBE 5 differ from those obtained by means of gas chromatography by less than 10 rel. percent, which can be considered as acceptable in gas analysis.

The model gaseous mixtures of air with volatile components of Diesel fuel to be analyzed with ECOPROBE 5 were prepared by adding various amounts (100-300 μl) of Diesel fuel into a bag containing a certain volume of air, whereupon the volume of bag was made up with air. Since the formation of equilibrium concentration of volatile components is very lengthy at room temperature, the actually formed mixtures were analyzed by both methods: always 0.5 ml was withdrawn from the sample sucked by the analyzer, and this aliquot was submitted to gas chromatography. The graphical record produced by the analyzer (see Fig. 4) shows that the gaseous mixture has a constant composition throughout the period of measurements (tens of seconds). Plotting of the data obtained from ECOPROBE 5 against the real TSN concentrations [mg m^{-3}] obtained from gas chromatography gave the calibration curve whose equation reads as follows

Table I Comparison of results of petrol vapour concentrations obtained from gas chromatography with those measured by means of analyser ECOPROBE 5 and transformed using above given regression equation

Petrol sort	Sample No.	Concentration determined by means of GC mg m ⁻³	Concentration determined by means of analyzer mg m ⁻³	Error %
Natural 95	1	9280	8791	-5.28
	2	6992	6683	-4.41
	3	3051	2989	-2.03
Natural 98	1	7756	8362	7.81
	2	5654	6103	7.93
	3	4132	4296	3.96
Special 91	1	8830	8146	-7.74
	2	7811	7172	-8.18
	3	5604	5635	0.56
Special 100	1	9840	10699	8.73
	2	7741	7908	2.15
	3	5183	5478	5.70
Shell V-Power racing	1	13578	13197	-2.81
	2	8147	7802	-4.24
	3	5356	4945	-7.68

Note: Results are calculated from three repeated analyses

$$y = 3.348x^{0.716} \quad R^2 = 0.960$$

where y stands for the IR detector response giving the total content of hydrocarbons in ppm on the basis of the manufacturer's calibration using methane, x is the real concentration of TSN in mg m⁻³.

This relationship enables transformation of the analyzer ECOPROBE 5 readings into correct estimation of contamination of the atmosphere with volatile components of Diesel fuel, which can be seen in the results presented in Table II. The table shows that the results obtained from ECOPROBE 5 and the above-given calibration equation differ from those obtained from gas chromatography by less than 12 rel. percent, which can be considered satisfactory in gas analysis.

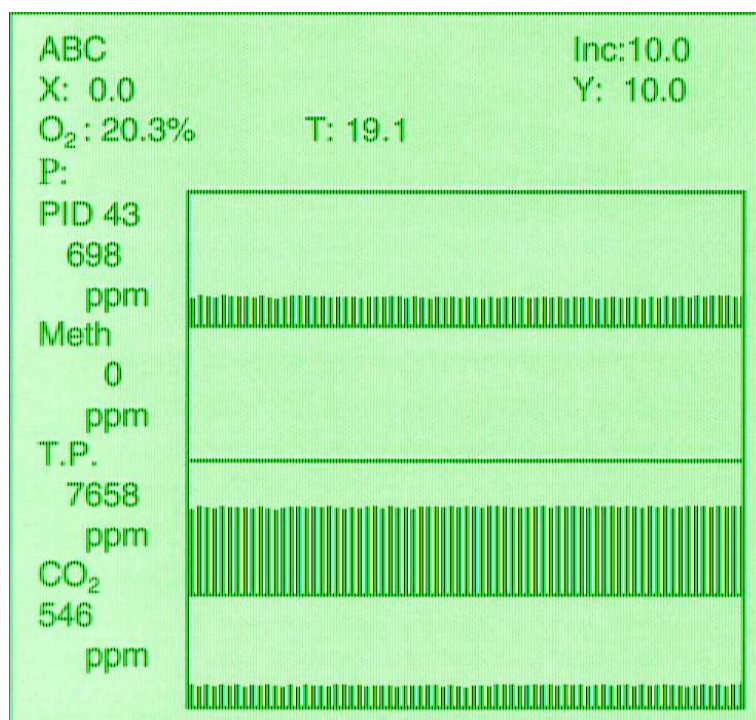


Fig. 4 Graphical record showing constant composition of mixture of air and Diesel fuel in bag during analysis with ECOPROBE 5. ABC – the name of Locality; Inc, X, Y – GPS parameters; O₂ – oxygen concentration; T – temperature; P – absolute ambient pressure; PID – result of photoionization detector, concentration (units ppm); Meth – result of IR Methane channel, concentration (units ppm); T.P. – IR Total Petroleum channel, concentration (units ppm); CO₂ – IR CO₂ channel, concentration (units ppm)

Table II Comparison of concentrations of volatile components of Diesel fuel determined by means of gas chromatography with those obtained from ECOPROBE 5 and above given calibration equation

Sample No.	Concentration determined by means of GC mg m ⁻³	Concentration determined by means of analyzer mg m ⁻³	Error %
1	7124	6712	-5.79
2	3979	3502	-11.99
3	2842	3021	6.31
4	3032	2915	-3.84
5	2577	2299	-10.79

Note: Results are calculated from three repeated analyses

Practical Applications

After the analyser ECOPROBE 5 had been calibrated, it was used for monitoring of the volatile components escaping from motor fuels, particularly during their pumping into tanks of cars. The samples were collected at the distance of ca 10 cm from the tank opening. The data obtained were automatically stored into the memory, whereupon the analyser ECOPROBE 5 was reset (zeroized) and thus ready for next measurements.

Table III Results of analyses in practical application of analyser ECOPROBE 5 during operation of petrol station

Measurement No.	Site of sample collecting	Atmospheric pressure kPa	Temperature °C	$C_{calibr.eq.}$ mg m ⁻³
1	Background of petrol station	97.57424	25.77	Below LOD
2	b	97.57957	25.21	c
3	a	97.56224	25.55	620
4	a	97.55024	26.00	4457
5	a	97.53691	26.01	8811
6	a	97.55158	26.26	17198
7	a	97.55158	26.34	Below LOD
8	Tank opening	97.67556	20.61	c
9	5 cm from tank opening	97.68890	20.96	14212
10	a	97.67823	20.82	10744
11	15 cm from tank opening	97.67556	20.69	7557
12	a	97.53558	26.01	c
13	a	97.54891	26.11	11254

Notes: Samples from 2 to 11 – petrol Natural 95 and samples from 12 to 13 – diesel fuel; a – 10 cm from tank opening; b – 10 cm from canister opening; c – values exceed range of calibration curves; LOD – limit of detection of device used

The concentrations of petrol and Diesel fuel were evaluated from the data measured in ppm regime and transformed by means of the above-given calibration equations. The results obtained are presented in Table III. Since the dispensing

nozzle of petrol station is equipped with efficient exhaust of petrol vapours, it could be presumed that the escaping of volatile substances during pumping the motor fuel would be negligible. Our measurements have shown that this expectation is only fulfilled if the dispensing nozzle is properly inserted into the car tank opening, which was the case in the measurements No. 3 and No. 7. The concentrations measured here were minimal. In the other cases (Nos. 4-6 and 12), the drivers inserted the dispensing nozzle improperly and the contamination values measured were high. In the measurements Nos. 2, 8, and 12, the concentration values are not given because the IR detector response exceeded the range of calibration curve. The table also shows that during filling of motor fuel into a 5-liter canister (measurement No. 2), when the analyzed gas was sucked at the distance of 10 cm from the canister opening, the amount of escaping vapours of Natural 95 was so high that it exceeded the measuring range of analyser ECOPROBE 5. The reason was probably in the fact that the pumping of motor fuel was not continuous, and the dispensing nozzle did not fit tightly in the canister opening. In this case the exhausting of vapours was almost inefficient.

The measurements Nos. 8-11 simulated the situation when the car tank opening remains open for a certain period of time, and the volatile hydrocarbons escape into the atmosphere. The analyser analysed samples taken directly at the car tank opening and at the distances of 5, 10, and 15 cm from it. The IR detector responses and therefrom subsequently evaluated concentrations decreased with increasing distance, which confirmed the fact that the results measured strongly depend upon the choice of site for collecting the samples.

The measuring instrument ECOPROBE 5 was successfully applied to practical analyses of the atmosphere at petrol stations. On the basis of preceding calibration of the analyser, it was possible to determine real concentrations of refinery products in gaseous samples.

Conclusion

Mobile analytical techniques enable not only checking of quality of the environment, but they also can fulfil preventive tasks and/or help operationally deal with ecological accidents. Their application requires serious attention to be given to the selectivity of measurements and correctness of the results obtained. One of possible ways of calibration is described above: it uses a real mixture and can be performed in advance and used if needed.

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