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Measurement of Aromatic Hydrocarbons with the DOAS Technique

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Long-path DOAS (differential optical absorption spectroscopy) in the ultraviolet spectral region has been shown to be applicable for low-concentration measurements of light aromatic hydrocarbons. However, because of spectral interferences among different aromatics as well as with oxygen, ozone, and sulfur dioxide, the application of the DOAS technique for this group of components is not without problems. This project includes a study of the differential absorption characteristics, between 250 and 280 nm, of twelve light aromatic hydrocarbons representing major constituents in technical solvents used in the automobile industry. Spectral overlapping between the different species, including oxygen, ozone, and sulfur dioxide, has been investigated and related to the chemical structure of the different aromatics. Interference effects in the DOAS application due to spectral overlapping have been investigated both in quantitative and in qualitative terms, with data from a field campaign at a major automobile manufacturing plant.

Index Headings: **Differential optical absorption spectroscopy; Aromatic hydrocarbons; Atmospheric measurement.**

INTRODUCTION

The recent growing awareness of the direct and indirect environmental effects of organic solvents has exposed the lack of selective and continuous measurement techniques of these species in ambient air. Fourier transform spectroscopy has been used to detect hydrocarbons in the infrared spectral region,[1] but continuous refinements may extend the practical use of this method into the ultraviolet region[2] where the absorption cross sections are larger. Long-path DOAS (differential optical absorption spectroscopy) in the ultraviolet region has been shown to be applicable for the subgroup of light aromatic hydrocarbons.[3,4] However, the application of the DOAS technique for this group of compounds is not without problems[5,6] because of spectral interference between different aromatics as well as with ozone, oxygen, and sulfur dioxide. The band around 260 nm has also been shown to be feasible for lidar measurements of aromatic hydrocarbons.[7]

This paper examines the differential absorption characteristics, between 250 and 280 nm, of twelve light aromatic hydrocarbons in the group of benzene derivatives (6–11 carbon atoms) that are used as technical solvents in the automobile industry. Spectral overlapping between the different species has been investigated and related to the chemical structure of the different aromatics. Overlapping from oxygen, ozone, and sulfur dioxide has also been considered. The effects of spectral resolution and analytical algorithms in allowing the separation of components are discussed. Interference effects in the DOAS application due to spectral overlapping have been investigated both in quantitative and in qualitative terms, with data from a field campaign at a major automobile manufacturing plant.

Benzene has three absorption bands in the UV region, two stronger ones around 184 and 204 nm plus a weaker one at 256 nm ($^1B_{2u} \rightarrow {}^1A_{1g}$). Since atmospheric attenuation makes only the last band practically useful for long-path absorption spectroscopy, we hereafter refer to this band when discussing spectral signature. The similar structure of the absorption spectra for light aromatic hydrocarbons in this region originates from excitation of the electrons in the unlocalized π bonds in the benzene ring. This band has a characteristic shape with a considerable amount of fine structure due to vibrational transitions. However, the fact that the atoms closest to the ring have the strongest influence on the electron structure of the π bonds has the result that most benzene derivatives have a very similar spectral signature. This similarity is most clearly illustrated by the subgroup of aromatics where one hydrogen atom in the benzene ring is substituted with a shorter or longer hydrocarbon chain. This group of compounds has very similar absorption characteristics because the major perturbation of the π bonds is caused by the first alkyl group in the chain. Adding one more alkyl group to the far end of the hydrocarbon chain (in, for example, propylbenzene to form isobutylbenzene) has virtually no effect at all on the π bonds and, thus, on the spectral signature, as can be seen in Fig. 1. This similarity is obviously a disadvantage when a spectroscopic method is used to identify and quantify the different species. This interference problem will, therefore, be further discussed later in this paper. Although the benzene derivatives show spectral similarities, substitution of hydrogen atoms in benzene with smaller alkyl groups (e.g., methyl or ethyl) changes the spectrum primarily in two ways:

1. A smoothing of the fine structure.
2. A dislocation of the absorption maximum, often towards longer wavelengths.

These phenomena are clearly illustrated in Fig. 2.

EXPERIMENTAL

Experimental Setup. The experimental setup is shown in Fig. 3. A full description of the instruments has been published[8] and will therefore only be briefly discussed in

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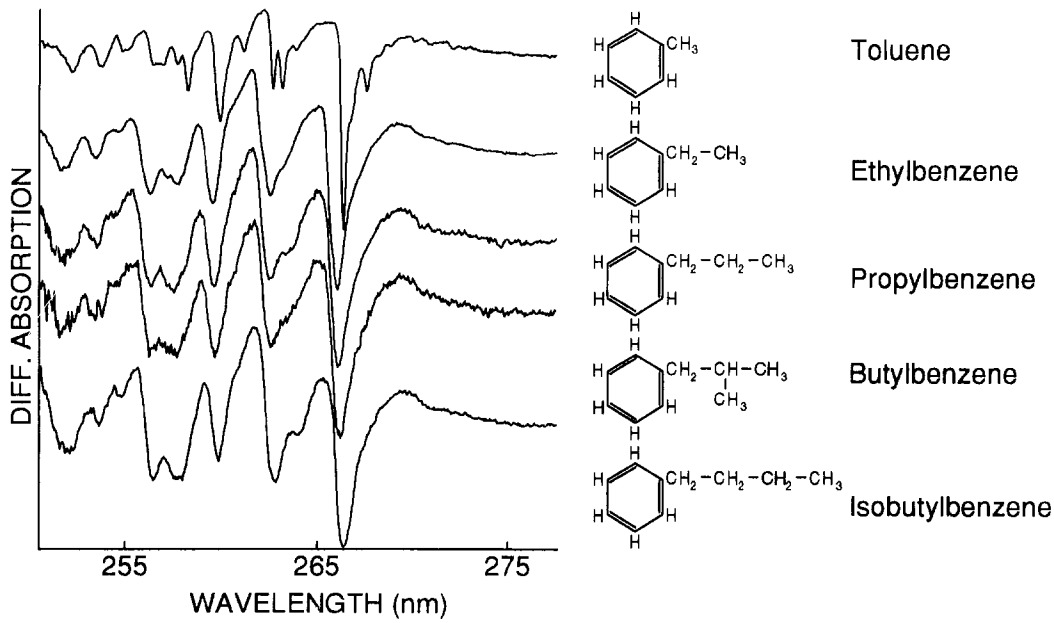

FIG. 1. Differential absorption spectra and chemical structure of toluene, ethylbenzene, propylbenzene, butylbenzene, and isobutylbenzene.

this paper. The lamp used was a 150-W xenon arc lamp (Hamamatsu L 2273) which has a broad emission spectrum that is useful in DOAS applications. The light was sent through a 2-m-long White cell (multiple reflection cell) with a volume of 140 L.[9] The exiting light was focused and fiber-coupled alternatively into two spectrometers (Spex 500 M, *f*/4, 1200 grooves/mm, blaze: 300 nm; and Spex 1870c, *f*/4, 600 grooves/mm, blaze: 300 nm). For rapid scanning (10 ms/scan) the exit slits are replaced with rotating slotted disk setups. A mask in the focal plane limits the spectrum width to approximately 40 and 90 nm, respectively. The slits at the rim of the disk have a width of 100 μm, as the entrance slit, and the spectral resolution is 0.2 and 0.8 nm for the two spectrometers. The wavelength scale for each individual scan was synchronized with a trigger signal generated when the slit passed an infrared light barrier.

The White cell was used in order to be able to record absorption spectra at suitable optical densities at a known measurement path in the cell (40 m). Small amounts of each species in liquid phase were put into the cell. After complete evaporation and equilibrium were established in the cell, the gas concentration was determined by gas chromatography (GC) analysis of two to three samples taken from the cell (500 μL direct to GC). Immediately after the sample was taken, absorption spectra were recorded with the two different DOAS systems. The error in the measured cross sections is estimated to be less than 10%, and the main uncertainty comes from the gas concentration determination.

DOAS is a long-path absorption technique based on the Beer–Lambert law. However, instead of measuring the total absorption at one wavelength, one uses the differential absorption within a wavelength interval. This approach minimizes many sources of error such as aerosol attenuation and spectral transmission of the instruments. The DOAS evaluation algorithm is well described in Ref. 10 and will, therefore, only be summarized in this paper. It starts with subtraction of the "electrical" background, i.e., dark current in the PM tube and preamplifier offset, from the "raw-spectrum". A polynomial is fit to a part of the spectrum and the differential structure is obtained by dividing the spectrum by the polynomial. To use the Beer–Lambert law, one performs a logarithmic transformation of the differential spectrum. Calibration spectra are stored together with information of the optical depth (concentration times pathlength). Each measurement spectrum is then correlated with the calibration spectra according to classical least-squares fit theory, and the corresponding gas concentrations are calculated. The quality of the data an be estimated from the variance and correlations between the calibration and measurement spectra.

RESULTS

Laboratory Studies. *Differential Absorption Characteristics.* We have measured the differential absorption spectra between 258 and 280 nm for twelve aromatic hydrocarbons displayed in Fig. 2. These hydrocarbons are benzene, toluene, *p*-xylene, *m*-xylene, *o*-xylene; ethylbenzene, butylbenzene, isobutylbenzene, propylbenzene; 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. Oxygen, ozone, and sulfur dioxide have absorption spectra in this spectral region and can therefore interfere. Differential spectra for these species are also presented in Fig. 2. We have also found that three hydrocarbons frequent in technical solvents—isopropanol, butylacetat, and butylene glycol—do not have suitable differential absorption structure in the wavelength interval 210–310 nm and are not included in this study. In Table I the theoretical detection limits for pure samples of the aromatics studied are listed (1-km pathlength, least detectable absorption 10^{-3}, 0.2-nm spectral resolution). These detection limits do not include spectral interferences.

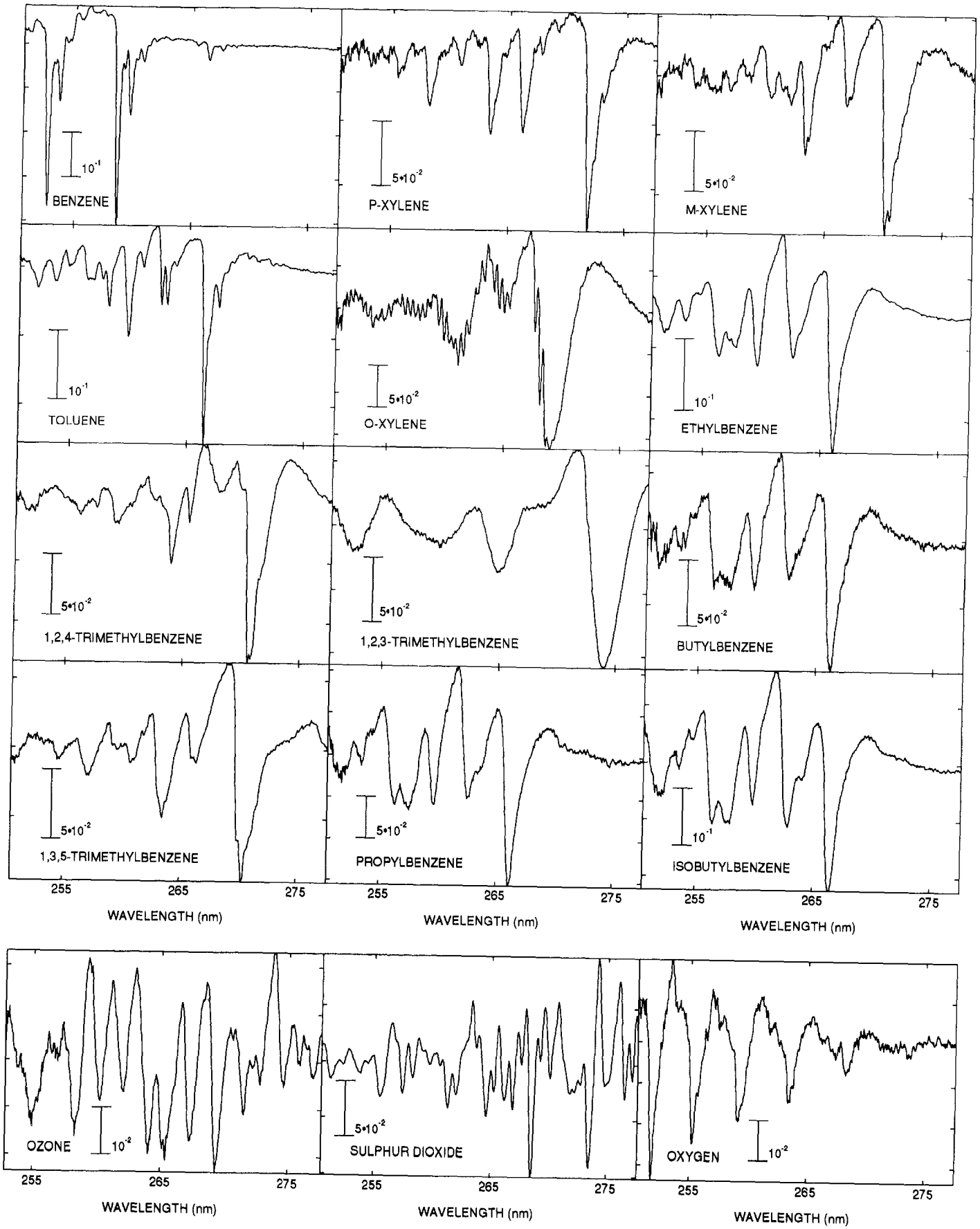

FIG. 2. Differential absorption spectra (40-m path) for: benzene (18.5 mg/m³ in air, 25 C, 1 atm); *p*-xylene (1.2 mg/m³); *m*-xylene (8.4); toluene (10.3); *o*-xylene (31.0); ethylbenzene (12.9); 1,2,3-trimethylbenzene (25.9); 1,2,4-trimethylbenzene (14.2); butyl-benzene (7.9); 1,3,5-trimethylbenzene (20.7); propylbenzene (25.1); isobutylbenzene (48.0); ozone (4.4); sulfur dioxide (20.1); and oxygen (100%).

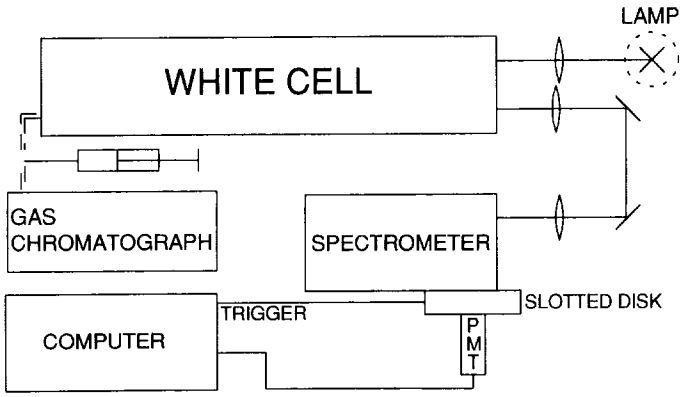

FIG. 3. Experimental setup for the laboratory study.

TABLE I. Theoretical detection limits for pure samples of the studied aromatics (1-km pathlength, least detectable absorption 10^{-3}, 0.2-nm spectral resolution).

Species	Detection limit ($\mu g/m^3$)
Benzene	1.5
Toluene	1.4
p-Xylene	0.3
m-Xylene	1.8
o-Xylene	4.7
Ethylbenzene	2.0
Butylbenzene	2.3
Isobutylbenzene	6.5
Propylbenzene	4.7
1,2,3-Trimethylbenzene	6.2
1,2,4-Trimethylbenzene	3.3
1,3,5-Trimethylbenzene	5.2

Resolution Effects. The spectral overlapping between the different species is, of course, dependent on the spectral resolution. Figure 4 shows the effect of spectral resolution when the toluene spectrum is recorded. Normally, a better resolution improves the possibility of distinguishing the separate constituents from each other. Furthermore, a better resolution improves the sensitivity of the instrument and also the linear range.

Limitations and Error Sources in the DOAS Evaluation Procedure. As mentioned earlier, a polynomial baseline correction is normally used in the DOAS evaluation algorithm. This correction procedure might, however, introduce systematic errors at high absorbance values, especially for poor spectral resolution. A wavelength correction procedure also normally used in the DOAS application is to correct for dislocation of the wavelength scale due to thermal effects and mechanical thrusts. The correlation between the measured spectrum and the reference spectra is repetitively evaluated as the reference spectra are shifted one step within a small interval around the zero position. The concentration is then evaluated at the position of best correlation. This procedure is very useful when only one species is expected to contribute to the signal. It will, on the other hand, reduce the possibility of distinguishing between two species with similarly shaped spectra that have the location of absorption maximum as the main difference. This is the case for some of the hydrocarbons (see, e.g., Fig. 1).

For the identification of the individual components in a mixture, two different algorithms, or a combination of them, can be used. One way is to sequentially correlate the measured spectrum with the different correlation spectra. Because of the interference between different species, enhanced by the wavelength correction procedure, the individually evaluated concentrations are quite likely not to be correct. The other way is to use multiple regression analysis. The measured spectrum is simultaneously correlated with spectra for all possible species that absorb in the wavelength interval. This approach ensures the same wavelength correction for all species. However, if the reference directory of possible species is large, there is a possibility, especially if the correlation coefficients between several species are large, of negative and positive concentrations for species not present in the atmosphere at the time the measured spectrum was recorded, as well as incorrect results for the present species. The algorithm could be used repetitively with exclusion of species with concentrations that are negative or less than two times the standard deviation. In a situation when the reference directory of possible species is so large that the simultaneous correlation algorithm becomes unstable, or the directory is too large for the software, a reduction is needed. With no other information, the sequential correlation algorithm, together with the iteration criteria mentioned above, can be used to select the species for the subsequent multiple regression analysis. A limitation to a maximum of six species at one time was used in the present investigation to exemplify this combined method. The reduced number of evaluated species can, in principle, be handled by correlation of the residual spectrum with another set of reference spectra. A more serious disadvantage is that this approach discriminates species that correlate negatively with species that dominate the absorption signal due to their abundance and/or larger cross section. For example, *p*-xylene has a differential cross section many times larger than that of *o*-xylene, and their spectra correlate negatively. In commercial xylene mixtures, there might be twice as much *p*-xylene as *o*-xylene, and a spectrum of this mixture evaluated only with respect to *o*-xylene will give a negative value. If *o*-xylene is excluded in the multiple regression analysis of the spectrum, the evaluated *p*-xylene concentration will be too low.

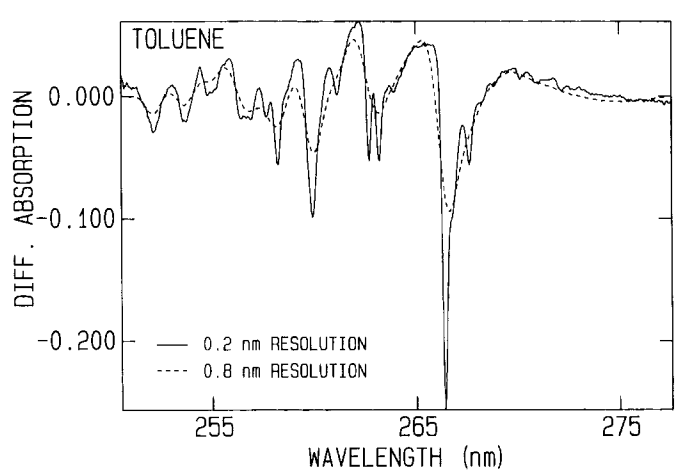

FIG. 4. Differential absorption spectra of toluene; 0.2-nm spectral resolution (solid line) and 0.8-nm spectral resolution (dashed line).

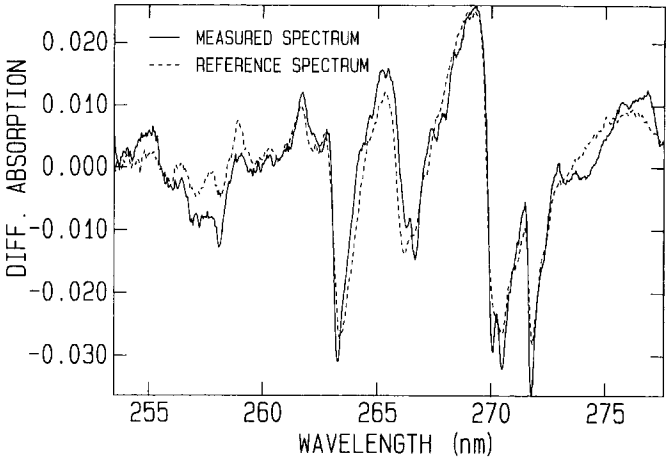

FIG. 5. Measured spectrum from field measurement at paint shop (solid line) correlated with a combination of reference spectra (dashed line). The absorption in the reference spectrum corresponds to: *p*-xylene = 23 $\mu g/m^3$; *m*-xylene = 164 $\mu g/m^3$; ethylbenzene = 76 $\mu g/m^3$; 1,2,3-trimethylbenzene = 65 $\mu g/m^3$; 1,2,4-trimethylbenzene = 79 $\mu g/m^3$; and 1,3,5-trimethylbenzene = 372 $\mu g/m^3$ (350-m measurement path, 0.2-nm spectral resolution).

Interferences from Abundant Atmospheric Gases. Oxygen (O_2) constitutes a fifth of the atmosphere and must always be taken into account as a severe interferent. The evaluation interval can, in principle, be chosen to minimize overlap from the oxygen spectrum. However, the benzene spectrum is almost completely overlapped by oxygen, so that the interference has to be handled actively. The best way is, of course, to incorporate oxygen in the multiple regression algorithm. The disadvantage in our case is that one of the six evaluated species is then wasted in order to give a value known from the start. The oxygen concentration is quite constant in the atmosphere, and a "zero" spectrum could be recorded in clean atmosphere with the same optical pathlength. This spectrum would also contain the specific spectral response of the instrument. By dividing the measured atmospheric spectra with the zero spectrum, one compensates for the influence from oxygen and instrumental features. The disadvantage with this method is that a fixed negative offset is introduced not only for oxygen but for all species represented in the zero spectrum. The quality of the oxygen compensation by a zero spectrum is also influenced by the variations in the atmospheric temperature and pressure.

Ozone (O_3) has a strong absorption band around 260 nm and is one of the most common pollutants. Fortunately, the ozone spectra differ from the spectra of the aromatic hydrocarbons, and the interference effect could be minimized by means of multiple regression.

Sulfur dioxide (SO_2) has a very strong absorption band centered at 300 nm and is also quite abundant, so that its absorption in the region around 265 nm can also be significant. The differential absorption spectrum of SO_2 is, however, like that of ozone, quite different from aromatic hydrocarbon spectra, and the interference from SO_2 can be treated like the one from ozone.

Field Measurements. A field campaign was carried out at the paint shop of a major car factory in Sweden. The same two instruments used in the laboratory were used in parallel along the same open measurement path. The measurement path passed half a meter above the chimneys of a number of painting lines. This arrangement reduced the influence from background sources and fluctuations in the wind direction. In the end of the 175-m path, a retro reflector was mounted to give a total measurement path of 350 m.

The numerous different hydrocarbons in technical solvents make a paint shop a very complex source. The average distribution of the solvents used in the paint shop was known. Because of the limitations in our software, the concentration for only six aromatic hydrocarbons could be evaluated at one time. The best correlation with smallest standard deviation was obtained with the following combination: *p*-xylene, *m*-xylene; ethylbenzene; 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene.

At lower concentrations, the correlation was good between the two systems. At higher concentrations, the low-resolution system showed lower concentrations for *p*-xylene, *m*-xylene, and 1,2,3- and 1,2,4-trimethylbenzene, as an effect of a smaller linear range. For ethylbenzene it was the opposite for almost every level. The explanation for this result could be that the low-resolution system had greater difficulties in separating ethylbenzene from other single-substituted derivatives, e.g., toluene. 1,3,5-Trimethylbenzene was a special case; it could not be identified by the low-resolution system in separate correlation, probably because that system could not reveal any specific signature in the spectrum. 1,3,5-Trimethylbenzene was included in the evaluation algorithm to complete the comparison, but the correlation between the two systems was very poor for this species. Data reported from the field campaign are from the system with 0.2-nm spectral resolution because of the better performance.

A spectrum from the field campaign evaluated with this reference matrix is shown in Fig. 5. *o*-Xylene was known to be present from the xylene mixtures used in the process, which possibly reduced the evaluated *p*-xylene concentration, as discussed earlier. Other single-substituted benzene derivatives are also likely to have interfered, especially with ethylbenzene. In Fig. 6a–6c, the concentrations of the six species are presented for a part of the measurement period. The variations in concentration correlate very well with the production cycle. The increase in the concentrations from the first day to the second is not a result of a change in production, but an effect of different meteorological conditions. The second day a light breeze blew the plumes along the measurement path with the result of a higher average concentration in the path in comparison to the first day, when a stronger wind blew more from the side, producing a less concentrated plume as well as a smaller portion of the plume in the light beam.

Interference Test. All raw spectra were stored during the field campaign, which made it possible to make later evaluations with alternative combinations of reference spectra. From a cross-correlation study of the 12 components, toluene and ethylbenzene were shown to strongly interfere with each other. In order to demonstrate the problem with interference, we evaluated the spectra from the field campaign using two different combinations for the reference matrix, identical except for ethylbenzene:

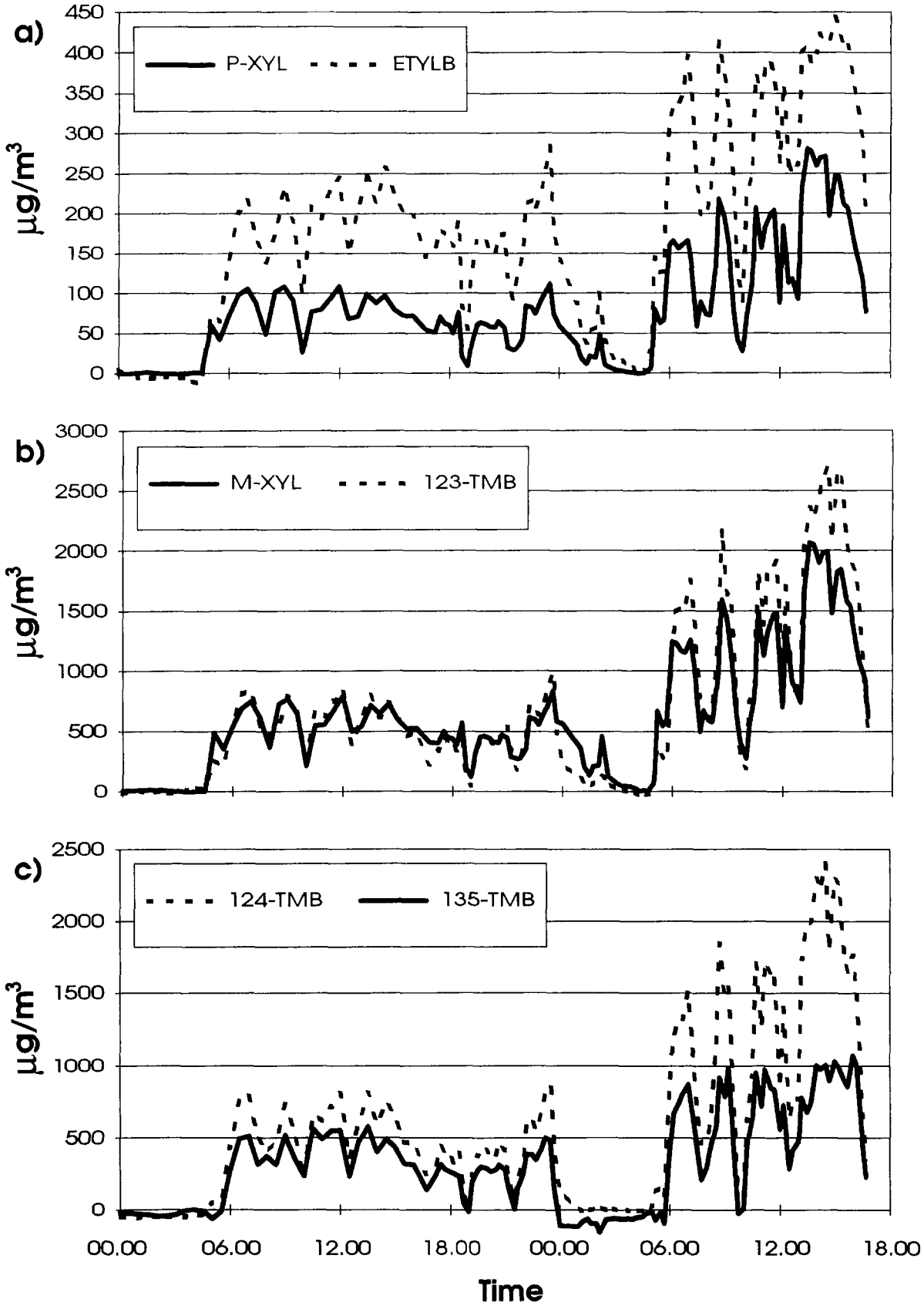

FIG. 6. Measurements at paint shop. (**a**) *p*-xylene and ethylbenzene; (**b**) *m*-xylene and 1,2,3-trimethylbenzene; (**c**) 1,2,4- and 1,3,5-trimethylbenzene.

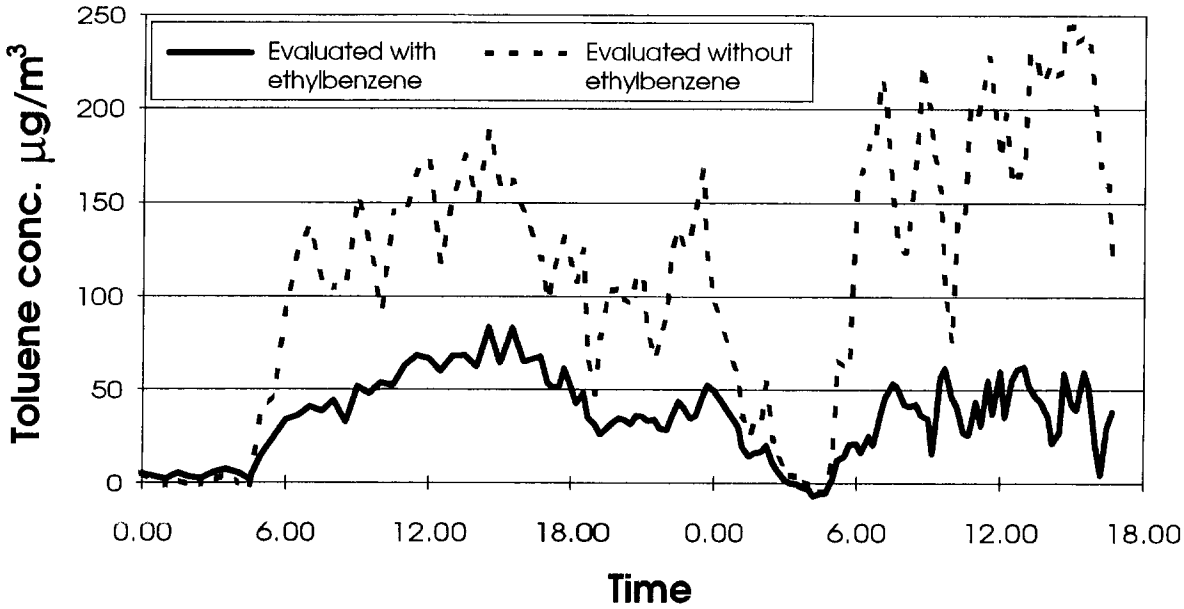

FIG. 7. Comparison of evaluated toluene concentrations with ethylbenzene (solid line) and without ethylbenzene (dotted line) in the reference spectra matrix.

Combination 1	Combination 2
p-Xylene	*p*-Xylene
m-Xylene	*m*-Xylene
1,2,3-Trimethylbenzene	1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene
Toluene	Toluene
	Ethylbenzene

The result is presented in Fig. 7. From this figure the effect of measured toluene concentrations with the use of the different reference matrix is seen and the importance of using a proper set of reference spectra is evident.

CONCLUSION

The DOAS technique is a low-cost, real-time analytical method and has a great potential to become an important tool for continuous measurements of aromatic hydrocarbons. However, the problem with interference effects due to spectral overlapping has to be treated with great care. This problem implies the absolute necessity of a correct set of reference spectra in order to achieve reliable data. A first necessity for the proper choice of reference spectra is a good knowledge of the chemical composition of the air to be studied. Since many hydrocarbon sources are very complex, it is almost impossible to include all contributing components. This complexity promotes the need for intelligent approximations, meaning that only the compounds with the strongest absorption and highest abundance are included. If strong interferences are known to exist between important components, they must be taken into account, in assumptions of the relative distribution of components, and in error estimations. Use of better spectral resolution and improved evaluation algorithms can improve the selectivity of the optical techniques. In practice, for many cases, it would be advisable to supplement the open-path monitoring with a specific point sampling technique (e.g., TENAX and GC) to determine the hydrocarbon profile in the specific measurement situation. The use of alternative techniques combined with knowledge of the emission-generating process (e.g., input) is a good basis for a correct construction of the reference matrix as well as validation of the data.

ACKNOWLEDGMENTS

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