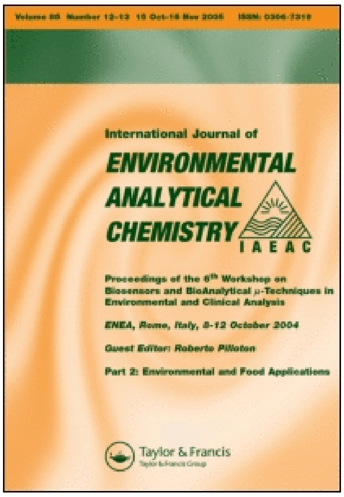

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DETERMINATION OF BENZENE AND TOLUENE IN URBAN AIR WITH DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY

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A recently introduced technique based on differential optical absorption spectroscopy (DOAS) was compared with conventional adsorption sampling and gas chromatography for the determination of aromatic hydrocarbons in air. Measurements were made in Switzerland and Sweden, at sites with benzene and toluene concentrations up to 20 and 40 $\mu g\ m^{-3}$, respectively. The hydrocarbons determined originated mainly from traffic exhaust.

The results demonstrate that the version of DOAS studied is a versatile tool for continuous monitoring of benzene and toluene in air at concentrations higher than 10 $\mu g\ m^{-3}$.

KEY WORDS: Aromatic hydrocarbons, benzene toluene, urban air, differential optical absorption spectroscopy, gas chromatography.

INTRODUCTION

Differential optical absorption spectroscopy (DOAS) is based on the fact that all chemical compounds absorb light at specific wavelengths. The DOAS technique was introduced for real-time monitoring of formaldehyde, ozone and nitrogen dioxide in air about ten years ago[1]. Since then several studies of the method have been carried out[2,3], and today DOAS is commercially available for the continuous measurement of a number of mainly inorganic air pollutants. More than one hundred systems have been installed in Europe.

The aim of this work is to study the potential of the DOAS method for the monitoring of volatile aromatic hydrocarbons in ambient air. The currently accepted method for this purpose is field sampling followed by gas chromatographic determinations. Previous experience of this approach to benzene and alkylbenzenes within the author's research group[4–6] facilitates a comparison with the new DOAS technique. The carcinogenic benzene as well as toluene and other alkylbenzenes have been selected because they are widely present in urban air as a result of petrol-fuelled vehicle emissions[4–6]. In fact, benzene, toluene and *p*-xylene make up approximately 50% of the aromatic hydrocarbon content of emissions from petrol-fuelled vehicles.

EXPERIMENTAL

Differential optical absorption spectroscopy

The DOAS equipment studied consists of an emitter (in this case a xenon lamp), a receptor and an analyzer (spectrophotometer and computer). The emitter and the receptor must be placed on very stable ground. The distance between the emitter and receptor is normally 200–1000 m for applications to ambient air. The absorbance of light from the emitter is continuously measured within the wavelength interval of interest, which is 250–290 nm for benzene and alkylbenzenes. Around 100 spectra per second are collected and each spectrum is transformed to up to 1000 digital values for the wavelength interval. The concentrations of the air pollutants are calculated by the computer from the differential absorbance values at selected wavelengths in accordance with Beer's law. Several specific wavelengths are chosen for each hydrocarbon to be determined. The DOAS instrument must be calibrated for each compound with a known concentration of the compound in air.

The DOAS system used in this study has recently been described in greater detail elsewhere[7]. The instruments, Opsis Analyzer AR 500 and Emitter/Receptor ER 100, were manufactured by Opsis AB (Lund, Sweden). The calibrations were made by Opsis.

Adsorption sampling and gas chromatography

Field sampling with adsorption of hydrocarbons on the Tenax porous polymer, followed by thermal desorption and gas chromatographic (GC) analysis in the laboratory has been described in some detail in previous studies[4,5,6]. In this study, air samples of 0.5–1 litres were taken during approximately one hour. The method permitted determinations of C_6 and higher hydrocarbons down to concentrations less than 1 $\mu g\,m^{-3}$. Above 10 $\mu g\,m^{-3}$, the concentrations recorded were estimated to be within ±20% of the true values.

Sampling sites

Three different sites were used in the study; two in Switzerland (Thun and Worb) and one in Sweden (Göteborg). At all sites, the DOAS light beam ran 3–10 m above the ground, with a distance of 200–550 m between the light emitter and the receptor. The samples for the gas chromatographic determinations were taken as close as possible to the light beam, and in positions where the concentrations were expected to be typical for the beam path.

In *Thun, Switzerland,* the light beam (325 m) ran through the centre of the city through a pedestrian zone along the river Aare and about 10 m above the river. The pedestrian zone was surrounded on both sides by houses and busy streets farther away. All samples for GC except one were taken on a bridge for pedestrians in the middle of the beam path and about 5 m below the light beam. One sample was taken while walking back and forth between the emitter and the receptor. Twelve samples were taken (12/8–9, 1989) during 24 hours. The weather was stable with weak winds and mist, and a temperature of around −2°C.

The study in *Worb, Switzerland* (4/26, 1990) was performed on a plain field outside the village. The air quality was influenced by traffic in Worb and on the main road to Bern at an upwind distance of 0.5 km. The site was chosen as representative of uniformly polluted air, which facilitates a consistent comparison between GC measurements in one point and DOAS measurements all over the beam path (550 m). Four separate DOAS receptors were used in parallel, measuring the light from the same emitter. Eight samples for gas chromatographic determinations were taken 70 m from the receptors and very close to the light beam. To test the uniformity of the polluted air, GC samples were taken at a second point along the beam, close to the emitter. The weather was rainy with intermittent sunshine, and the temperature was 5–10°C.

The measurements in *Göteborg, Sweden* (5/15, 1990) were made in a large parking area (Frölunda Torg) surrounded by houses, shops and busy streets. Exhaust gases from cars below the light path (200 m) and from the traffic on the main road nearby contributed to elevated pollution levels. Samples for gas chromatography were taken at five points along, and less than two meters from the light beam. The weather conditions were windy with sunshine and 15°C.

RESULTS AND DISCUSSION

Thun, Switzerland

The diagram given in Figure 1 summarizes the results of a diurnal study performed in Thun. The measurement periods were about one hour long and centered around the times given along the non-linear time scale. Variations in traffic intensity and air stratification are major factors governing the absolute concentrations recorded.

From Figure 1 it is evident that most results conform well between the gas chromatographic (GC) and DOAS methods. The topography, meteorology and local pattern of traffic emissions may explain certain differences between the point and light beam concentrations. The only GC sample (15.32) taken while walking deviates by higher values than those from DOAS. This is explained by the shorter average distance to the surrounding traffic compared with all other point samples taken on a bridge near to the light beam.

The observed uniform concentration ratio between benzene and toluene is characteristic of exhaust emissions from petrol-fuelled vehicles[4]. The deviating high toluene concentrations obtained around 6 pm might be due to an occasional contribution from another source somewhere along the light beam.

Worb, Switzerland

Outside Worb, the capability of the DOAS instruments was studied by parallel monitoring with four receptors placed close to each other, and more than 500 m

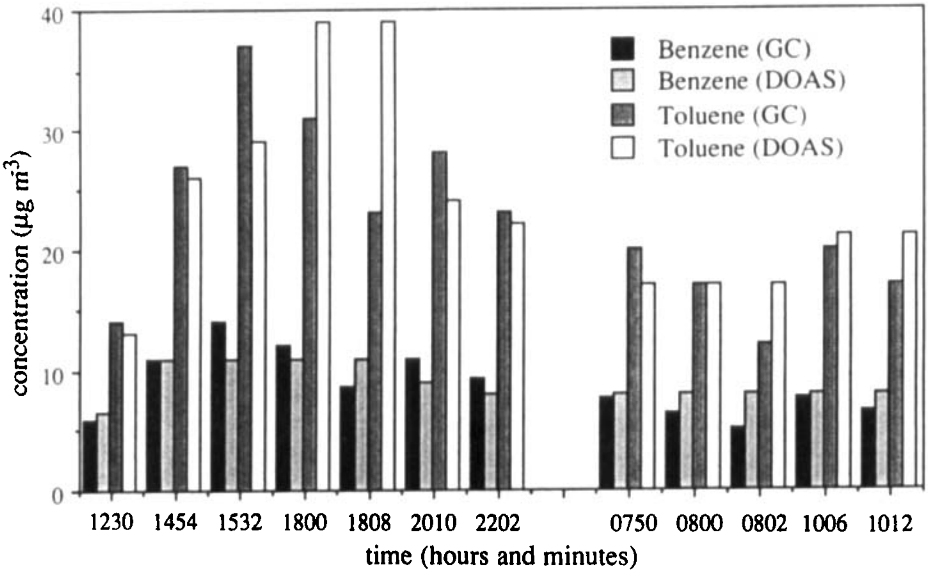

Figure 1 Concentrations of benzene and toluene determined with the DOAS and GC methods in central Thun, Switzerland (12/8–9 1989). The GC point samples were taken below the 325 m long DOAS light path.

from a single light emitter. In Figure 2, results are given for toluene as the major alkylbenzene from traffic emissions. The results reflect morning traffic emissions from Worb and from the upwind main road to Bern. Similar GC reference results from two points along the light path indicated a uniform distribution of the air pollutants.

From Figure 2, it is evident that DOAS results of a good quality are obtained for concentrations exceeding 10 $\mu g\, m^{-3}$. Measurements later in the day demonstrated

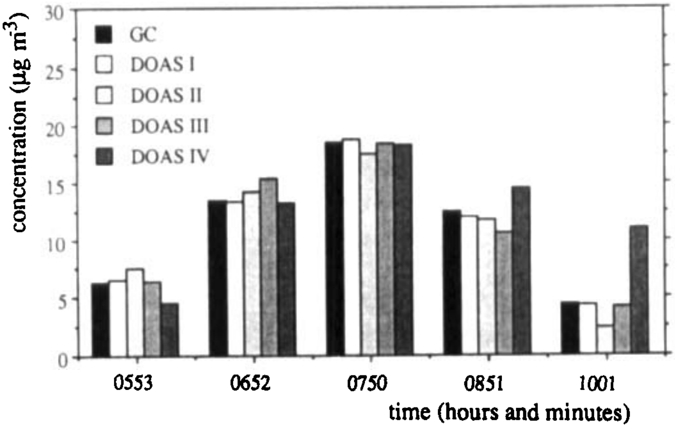

Figure 2 Concentrations of toluene in air outside Worb (4/26 1989), determined with four separate DOAS receptors over a light path of 550 m. Results from GC point samples along the light path are included for comparison.

unsatisfactory accuracy and precision of the DOAS results when GC reference concentrations were below 5 $\mu g\,m^{-3}$.

Comparison with Göteborg, Sweden

Five samples for GC taken with adsorbent tubes along a DOAS light-path in Göteborg demonstrated differing concentrations depending on the distance to petrol-fuelled vehicles. The calculated mean levels were 9.4, 17 and 3.1 $\mu g\,m^{-3}$ for benzene, toluene and *p*-xylene, respectively. The corresponding DOAS levels were 10, 21 and 4.0 $\mu g\,m^{-3}$. The application of DOAS to alkylbenzenes other than toluene suffers from the disadvantages of lower concentrations[6] and similarities between the absorption spectra of several isomers.

Average hydrocarbon ratios from Thun, Worb and Göteborg are given in Table 1. The observed composition is typical of air pollution from petrol-fuelled vehicles[4,6].

CONCLUSIONS

The results demonstrate that presently available DOAS equipment permits reliable continuous monitoring of benzene and toluene at concentrations in air exceeding 10 $\mu g\,m^{-3}$ for distances in the 200–1000 m range. Further instrumental development may extend the applications of DOAS to lower concentrations and to other alkylbenzenes.

A major advantage of the DOAS technique is that the hydrocarbons can be monitored continuously with automatic collection of analytical data. On the other hand, techniques based on adsorbent sampling and gas chromatography permit the determination of a large number of hydrocarbons at lower concentration levels and can also be used for determinations of personal exposure. Clearly, a combination of the two very different analytical approaches is useful for many applications, and particularly for quality control and quality assurance of analysis of urban air samples.

Table 1 Relative composition (%) of three aromatic hydrocarbons from parallel determinations with the DOAS and GC methods at different sites in Switzerland and Sweden

	Thun 12/8–9 1989		*Göteborg 5/15 1990*	
	GC	*DOAS*	*GC*	*DOAS*
Benzene	25	24	32	29
Toluene	63	63	58	60
p-Xylene	12	13	10	11

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