On-line Monitoring of Solvent Emission Rates Using an Open Path FTIR Analyser

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Solvent mixture concentrations in paint and resin manufacture were on-line monitored using a portable open path Fourier transform infrared (OP-FTIR) analyser in order to determine solvent emission rates into workplaces. The mean solvent emission rate was 0.46 kg/h in paint production and 0.35 kg/h in resin manufacture. Expressed as emission factor, i.e. evaporated portion of the total solvent mass used, the corresponding values were 0.01% for paint production and 0.1% for resin manufacture. The OP-FTIR instrument together with advanced spectra analysis software facilitated a rapid identification of solvent mixtures and on-line concentration monitoring with good temporal resolution. The analyser seems to be particularly useful in industrial hygiene applications where spatial average concentrations are needed. The further benefit of the open path instrument is that no sampling lines, pumps or sample cells are needed.

Keywords: open path FTIR; on-line monitoring; emission rates; solvent

INTRODUCTION

Fourier transform infrared (FTIR) spectrometers have proved to be powerful instruments in on-line monitoring of solvent vapour mixtures for industrial hygiene applications, as well as for process control (Xiao et al., 1990; Jaakkola et al., 1998; Räisänen and Niemelä, 1999). Most FTIR analysers and other on-line monitoring instruments, such as gas chromatographs and mass spectrometers, are equipped with a closed cell into which the air is sampled prior to analysis. Such samples reflect the conditions surrounding a sampling point. There are, however, measurement needs in which the spatial average concentration of a certain line or area is required. For instance, in evaluating solvent exposures in a specific workroom zone a reliable estimate of the area’s concentration must be obtained. Furthermore, data on the room average concentration together with the ventilation rate enable the determination of solvent emission rate into a workroom or outdoors. Usually, multipoint sampling is utilized for this purpose, assuming that the samples are representative of the unsampled areas. However, if there is a great variation in solvent concentrations in the workplace atmosphere, this assumption may not be valid.

In past decades, open path FTIR (OP-FTIR) analysers have mainly been used in environmental air monitoring tasks (Herget, 1982; Grant et al., 1992), but workroom monitoring applications have been reported (Xiao et al., 1991; Todd, 1996; Svedberg and Galle, 2000). In open path spectroscopy the IR beam is transmitted through an open space, e.g. a production hall. A measurement result is considered to be an integrated gas or vapour concentration along that beam. This feature is utilized in mapping air contaminants by a computed tomography system (Yost et al., 1994; Samanta and Todd, 1996). In addition, the beam average concentrations provide better estimates of space average concentrations. Similarly to the closed cuvette FTIR analyser, the OP-FTIR analyser retains the ability to continuously monitor multiple compounds.

The aim of this study was to describe OP-FTIR analyser applicability in solvent mixture concentration measurement in working areas and to use these concentration data for determining solvent emission rates in the manufacture of paints and resins.
MATERIALS AND METHODS

**OP-FTIR analyser**

The solvent concentration measurements were conducted using an OP-FTIR analyser (Bomem MR100 LP; Bomem Inc., Quebec, Canada) (Fig. 1). The analyser transmits an IR beam (with an IR source temperature of 1300 K) through a telescopic system to a remote retroreflector (0.25 m² area) consisting of gold-coated, corner cube mirrors. A liquid nitrogen-cooled Hg-Cd-Te detector (detector value $D = 5.2 \times 10^{10}$) detects the returned beam. The interferograms are collected double-sided from a spectral region between 7000 and 450 cm⁻¹. Depending on the resolution required (1, 2, 4, 8, 16 or 32 cm⁻¹), the scanning rate varies between 0.5 and 3.6 scans/s. The interferograms are converted to spectra by Grams/32 software (Galactic Inc., NH) installed on a PC. The identification and quantification procedure was performed by CalcmetW 2.02 multicomponent analysis software (Temet Inc., Helsinki, Finland). The procedure was based on the modified classical least squares (CLS) analysis algorithm (Saarinen and Kauppinen, 1991).

**Calibration of the open path instrument**

Unlike conventional FTIR instruments, there is no generally accepted procedure for the calibration of OP-FTIR instruments. The difficulty of calibration arises from the fact that the beam is open to the atmosphere. A way of calibration is to use an exposure chamber with known target concentrations (Samanta and Todd, 1996; Todd, 1996), whereas another is to build a special closed cell for the OP-FTIR system (Farhat and Todd, 2000). Our calibration system consisted of a ventilation test chamber (length 5.3 m, width 3.0 m, height 2.5 m), a solvent evaporation system and a calibrated conventional closed gas cell FTIR analyser (Temet Instruments Inc.) as a reference instrument. The ventilation test room was originally designed to study contaminant dispersion with different air flow patterns. The test room was equipped with a balanced mechanical supply and exhaust system separate from the air conditioning system of the building. The supply air was introduced into the chamber by a ceiling mounted air diffuser and removed through the exhaust grills from both ends of the chamber. Two extra fans were used for complete solvent mixing with the air. The experimental set-up of the ventilation test room is shown in Figure 2. The homogeneity of the solvent concentration in the chamber was checked with a photoionization detector (MiniRAE Plus; RAE System Inc., CA).

The conventional closed cell FTIR analyser which served as a reference instrument was calibrated under a nitrogen atmosphere. The reference spectrum was produced by injecting a known mass of liquid analyte into a closed loop system with a volume of 10.4 l (Räisänen and Niemelä, 1999). The solvent absorbance signal was established to be linear up to concentration levels of several thousand milligrams per cubic metre, depending on the solvent.

In the case of OP-FTIR calibration, the background spectra were taken from the chamber air (temperature 22°C, relative humidity 25%, CO₂ concentration 390 p.p.m.) prior to solvent release into the chamber. The calibration conditions were rather similar to the actual indoor conditions in the factories (air temperature between 20 and 22°C, relative humidity between 20 and 30%). The vapour of each solvent of interest was generated by bubbling air (2 l/min) through liquid solvent in a 250 ml glass bottle kept at 40°C. The evaporated solvent–air mixture was fed through a Teflon tube (i.d. 4.7 mm) into the chamber supply air duct. After the solvent concentration reached steady-state, the IR spectrum was determined and stored on the computer’s hard disk along with the concentration information. The optical path length in the chamber of the OP-FTIR system was 11.6 m. The spectral data of five solvents of interest as well as water vapour and carbon dioxide

![Fig. 1. The open path FTIR measurement system.](image-url)
were collected at a resolution of 8 cm\(^{-1}\) with a spectra averaging time of 160 s (Table 1). Interference by water vapour and carbon dioxide was treated in the same way as any other interfering compound, i.e. by windowing and multicomponent analysis. It is worth noting that the amount of water vapour in the air was relatively low in both the calibration conditions and the factory conditions. A higher water content, e.g. in stack gas emissions, may require special precautions in the analysis.

In terms of this calibration procedure the measurement uncertainty for the OP-FTIR system was estimated to be same as the reference instrument, i.e. <10%. At concentrations close to the detection limit, however, the measurement uncertainty may be higher. Apart from concentrations close to the detection limit, the accuracy of the analyser meets the requirements of European standard EN482 for the measurement of solvent concentrations in workplace air. According to the laboratory tests the detection limits for the solvents typically used in paint and resin manufacture were 0.4 p.p.m.-m (path length adjusted concentration) or less. If necessary, even better sensitivity can be achieved by increasing the optical path length. In the calibration an optical path length of 11.4 m was employed, whereas in the field measurements the length was 30 or 32 m, i.e. about three times as long. The instrument still operated in the linear range, as the mean solvent concentrations were one-tenth or less the concentrations in the calibration chamber. The optical path length of this system can be extended up to 150 m.

### Field Measurements

The paint manufacturing plant produces annually ~1000 tons of paint, consisting mainly of xylenes, ethyl alcohol, butyl alcohol and solvent naphthas. The measurements were conducted in a working area (500 m\(^2\)) of the production department (floor area 2200 m\(^2\), height 3.5 m) (Fig. 3). The process was a typical batch process in which the main solvent sources were mixing and weighing operations. The department was equipped with mechanical supply and exhaust ventilation. In addition to the general

### Table 1. The analytical spectral regions, the detection limits and the reference spectra concentrations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analytical region (cm)</th>
<th>LOD (p.p.m.-m)</th>
<th>Reference concentration in the chamber (mg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl alcohol</td>
<td>950–1500</td>
<td>0.05</td>
<td>360</td>
</tr>
<tr>
<td>Isobutyl alcohol</td>
<td>950–1500</td>
<td>0.15</td>
<td>284</td>
</tr>
<tr>
<td>Xylenes</td>
<td>1315–1670</td>
<td>0.4</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>2690–2800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>890–1100</td>
<td>0.4</td>
<td>208</td>
</tr>
<tr>
<td>Acetone</td>
<td>1600–1900</td>
<td>0.04</td>
<td>340</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>2100–2300</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

LOD, limit of detection; n.d., not determined; p.p.m.-m, path length adjusted concentration.
exhaust ventilation, the mixing and weighing stations were equipped with local exhaust hoods. During the 4.5 h morning shift measurements 1600 kg of paint was manufactured.

The resin plant produces annually 7600 tons of resins consisting of styrene and acetone. Styrene vapours were released from the mixing and packing operations, while acetone evaporated from short-term washing and cleaning tasks. The air supply into the hall (area 390 m², height 4 m) was introduced through grills on one side of the hall and mixed with the hall air by high impulse air jets. The air was removed through local exhaust ducts from several locations in the hall. During the 7 h measurement 18000 kg of resin was manufactured.

The background spectra were obtained from the workroom air early in the morning before production started. The duration of measurement was selected to cover the actual process phases with the main solvent emissions. In the case of paint manufacture the measurements lasted 4.5 h and in resin manufacture 7 h. In the monitoring set-up, the IR beam with an optical path length of 30 m crossed the working areas at a height of 1.5 m (Fig. 3). The spectral data were collected at a resolution of 8 cm⁻¹ using spectra averaging times of 40–60 s, sufficient to detect concentration variations.

Even though the OP-FTIR analyser was calibrated under laboratory conditions the field measurement results were compared with charcoal samples taken in the IR beam in order to ascertain the stability of the calibration under factory conditions (Fig. 4). For the charcoal tube (SKC) sampling periods of 2–3 h were used. The charcoal tube samples were analysed according to the standardized procedure in Finland (SFS 3861; Finnish Standardization Association, 1978). The mean solvent emission rate into a workroom was determined by multiplying the room’s average solvent concentration by the total exhaust airflow rate. The exhaust airflow rates were measured from the exhaust ducts according to the ISO 3966 standard (ISO, 1977). The solvent concentration along the beam path served as an estimate of the average solvent concentration in the workroom. Short-term photoionization detector measurements were performed in order to determine the solvent
concentration spatial distribution in the production room.

RESULTS

In the paint plant the main compounds analysed from the IR spectra were xylenes, ethyl alcohol and isobutyl alcohol. The charcoal tube samples also included traces of ethyl benzene, butyl acetate, ethyl acetate and solvent naphthas. These compounds were, however, not included in the quantitative spectral analysis due to their negligible amounts. The mean xylene, ethyl alcohol and isobutyl alcohol concentrations in the working area over the 4.5 h measurement period were 37, 11 and 10 mg/m$^3$ (Table 2). These values correspond to ~15% of the Finnish occupational exposure limit (OEL, TWA 8 h) (Finnish Ministry of Social Affairs and Health, 1988). At the highest production rate (three simultaneous blendings), maximum concentrations of 128 mg/m$^3$ for xylenes and 68 mg/m$^3$ for ethyl alcohol were observed (Fig. 5). In the resin plant, the average styrene and acetone concentrations over a workday (7 h) were 8 and 10 mg/m$^3$ (9% of the corresponding OEL, TWA 8 h) (Table 2). Excluding two short-term peaks of the concentration of acetone, no notable temporal variations in the acetone and styrene concentrations occurred.

The exhaust airflow rates from the production rooms of the paint and resin manufacturing plants were 8000 and 19300 m$^3$/h. The photoionization detector measurements revealed that no notable solvent concentration stratification occurred in the workrooms studied. Consequently, the measured mean FTIR concentrations in working areas can be used as estimates of average room concentrations in the emission calculations. The mean solvent emissions into the workroom during paint and resin manufacture were 0.46 and 0.35 kg/h (Table 2). Expressed as the emission factor, i.e. evaporated portion of the total solvent mass used, these values correspond to 0.01 and 0.1%, respectively.

DISCUSSION

In this study solvent mixture concentrations in paint and resin manufacture were monitored on-line using an OP-FTIR analyser. The solvent mixture in the workplace air of the paint plant was complex, involving xylenes, ethyl alcohol, isobutyl alcohol and atmospheric water vapour, as well as small amounts

Table 2. Summary of the open path FTIR measurement results

<table>
<thead>
<tr>
<th>Paint manufacturing (optical path length 30 m)</th>
<th>Concentration (mg/m$^3$)</th>
<th>Emission Mean (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylenes</td>
<td>LOD–128</td>
<td>0.31</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>LOD–68</td>
<td>0.09</td>
</tr>
<tr>
<td>Butyl alcohol</td>
<td>LOD–40</td>
<td>0.08</td>
</tr>
<tr>
<td>TVOC</td>
<td>7–191</td>
<td>0.46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Resin manufacturing (optical path length 32 m)</th>
<th>Concentration (mg/m$^3$)</th>
<th>Emission Mean (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>5–15</td>
<td>0.15</td>
</tr>
<tr>
<td>Acetone</td>
<td>2–115</td>
<td>0.20</td>
</tr>
<tr>
<td>TVOC</td>
<td>6–125</td>
<td>0.35</td>
</tr>
</tbody>
</table>

LOD, limit of detection.
of ethyl benzene, butyl acetate, ethyl acetate and solvent naphthas. Although these compounds show spectral overlap, the concentrations of the dominant contaminants could be detected and quantified due to the advanced spectra analysis software.

The field measurements demonstrated that the open path system is easy to transport and operate in industrial environments. In industrial workrooms the typical analyzer set-up time is <1 h. For most closed cuvette FTIR analysers the set-up time is notably longer due to the cuvette temperature stabilization process. The considerable benefit of open path instruments is that no sampling lines, pumps or sample cells are needed. Likewise, sample handling and storage are not required. The OP-FTIR instrument facilitates rapid identification of solvents with concentration data with good temporal variation relevant to workplace air monitoring, as well as process control. In workplace measurements the IR beam orientation should be carefully chosen because beam blockage due to passage of a worker or equipment may cause instantaneous disturbances in monitoring.

Despite many benefits in field measurements, calibration of an OP-FTIR instrument is laborious. In this study, instead of using library spectra we used a ventilation chamber with known concentrations detected by a reference instrument. By this procedure we wanted to eliminate any errors in instrument function. Fairly good agreement between the OP-FTIR and the charcoal tube concentrations was observed, taking into account that the comparison was made under field conditions (Fig. 4).

In both manufacturing plants the mean indoor solvent emission rates were at the same level, 0.46 and 0.35 kg/h. However, the emission factors (the evaporated solvent mass per solvent mass used in production) differed significantly, 0.1% for paint production and 0.01% for resin manufacture. Compared with the Finnish OEL (TWA 8 h) for the combined effect of the solvents the mean values measured in both plants were relatively low, 9–15% of the OEL. It is worth noting that the open path concentrations do not represent personal exposure but illustrate solvent concentration levels in the general workroom air.

Although sampling at one point, in the breathing zone or at a fixed point, has traditionally been the major sampling method in industrial hygiene, information on spatial average concentration offers notable benefits in numerous applications. The average room concentrations needed in estimating the emission rate into a workroom can be determined in terms of the beam average concentrations. In addition, the space average concentration data benefit exposure assessment for a group of persons working in particular areas, as well as performance evaluations of the process and the control systems. As a conclusion, the field measurements demonstrated the advantages of the OP-FTIR analyzer for monitoring solvent mixture concentrations in workroom air as well as for estimating the solvent emission rates.

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REFERENCES