

KUOPION YLIOPISTON JULKAISUJA C. LUONNONTIETEET JA YMPÄRISTÖTIETEET 224
KUOPIO UNIVERSITY PUBLICATIONS C. NATURAL AND ENVIRONMENTAL SCIENCES 224

JOUNI RÄISÄNEN

Fourier Transform Infrared (FTIR) Spectroscopy for Monitoring of Solvent Emission Rates from Industrial Processes

Doctoral dissertation

To be presented by permission of the Faculty of Natural and Environmental Sciences
of the University of Kuopio for public examination in Auditorium L22,
Snellmania building, University of Kuopio,
on Saturday 15th December 2007, at 12 noon

Department of Environmental Science
University of Kuopio



KUOPION YLIOPISTO

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ISBN 978-951-27-0962-5
ISBN 978-951-27-0797-3 (PDF)
ISSN 1235-0486

Kopijyvä
Kuopio 2007
Finland

Räisänen, Jouni. Fourier Transform Infrared (FTIR) Spectroscopy for Monitoring of Solvent Emission Rates from Industrial Processes. Kuopio University Publications C. Natural and Environmental Sciences 224. 2007. 75 p.
ISBN 978-951-27-0962-5
ISBN 978-951-27-0797-3 (PDF)
ISSN 1235-0486

ABSTRACT

The aim of this work was to develop a measurement strategy for monitoring space average concentrations of solvents in workplace conditions in order to determine emission rates in the workplace air and into the outdoor air. Another aim was to produce data on solvent emissions from different types of industrial processes. The measurements were made in the following processes: ink, paint and resin manufacturing, dry cleaning, plastic lamination, fresh wood sawing, offset printing and rotogravure printing. Open path (OP) and closed cell Fourier transform infrared (FTIR) analyzers were used for on-line monitoring of solvents in the air (workplace air or exhaust air).

The solvent emission rate into a working room was determined by multiplying the room average concentration by the total airflow rate or the concentration in the general exhaust air by the exhaust flow rate. The room average concentration was estimated in terms of the concentrations at fixed points (closed cell FTIR) or in the measurement lines (OP FTIR). The emission rate outdoors was determined as a sum of individual emissions.

The solvent emissions varied strongly due to their production rates and the process phase, as expected. The plant mean indoor solvent emissions ranged from 0.02-21.0 kg h⁻¹ with outdoor emissions of between 0.02 to 9.98 kg h⁻¹. The temporal variation in the solvent concentrations was rather high, up to four orders of magnitude. The dynamic ranges of both FTIR- instruments were wide enough to measure the highest concentration peaks, which occurred in the exhaust air (closed cell FTIR) and workplace air (OP FTIR). According to laboratory tests, the detection limits were 0.4 ppm-m or less for the open path instrument and 1 ppm or less for the closed cell instrument, depending on which solvent was being measured. Both instruments were sensitive enough for monitoring concentrations in plants using high volume of solvents in their processes. The solvent mixtures in the work and exhaust air were complex, but concentrations of the dominant contaminants could be detected and quantified with advanced spectra analysis software (Calcomet®). Based on the laboratory test, the measurement uncertainty of the open path instrument for the studied solvents in field conditions was estimated to be less than 15 % and for the closed cell instrument less than 10 %. At concentrations close to the detection limit (LOD), the measurement uncertainty was higher. With the exceptions of the concentrations close to the detection limit, the accuracy of both instruments meets the requirements of the European Standard EN482 for the measurement of solvent concentrations in workplace air.

The open path and closed cell FTIR spectrophotometers were transportable and simple to operate even in a hostile industrial environment. Both instruments facilitate rapid identification of solvent components, real-time display of concentration data relevant to workroom air and environmental monitoring, as well as process control. Furthermore, no sample handling and storing are required. One considerable benefit of the open path instruments is that no sampling lines, pumps, or sample cells are needed. The simultaneous monitoring of solvent concentration and a tracer gas enables also airflow rate determination. The challenges in FTIR-monitoring are related to the calibration procedures (especially OP FTIR), the selection of the measurement configuration as well as operating the analyzers in a hostile industrial environment.

These field measurements demonstrated the advantages of the open path and the closed cell FTIR analyzers for monitoring solvent mixture concentrations in work air as well as for determining the solvent emission rates. The emission data can be used in exposure and risk assessments processes, and in design procedure of industrial ventilation and in development of exposure models. The FTIR technique should be considered as a standard technique both in industrial hygiene as well as environmental gas phase monitoring tasks, even though advanced skills are required. In addition, further data and research on solvent emissions from different industrial processes are needed.

Universal Decimal Classification: 331.436, 331.471, 543.422.3-74, 667.629.2

National Library of Medicine Classification: WA 450, WA 754, QV 633

Medical Subject Headings: Air Pollutants; Occupational/analysis; Solvents/analysis; Environmental Monitoring; Industry; Workplace; Spectroscopy, Fourier Transform Infrared; Air Pollution; Occupational Exposure; Ventilation; Risk Assessment



Räisänen, Jouni. Fourier Transform Infrared (FTIR) Spectroscopy for Monitoring of Solvent Emission Rates from Industrial Processes. Kuopio University Publications C. Natural and Environmental Sciences 224. 2007. 75 p.
ISBN 978-951-27-0962-5
ISBN 978-951-27-0797-3 (PDF)
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YHTEENVETO (FINNISH SUMMARY)

Tutkimuksen tavoitteena oli kehittää mittausstrategia työtilan liuotainkeskipitoisuuden määrittämiseksi. Keskipitoisuustiedon avulla on mahdollista määrittää epäpuhtauspäästövirtoja työtilaan ja ulkoilmaan. Toissijainen tavoite oli määrittää liuotinpäästövirtoja erityyppisistä teollisuusprosesseista. Mittaukset tehtiin seuraavissa prosesseissa: painovärin, maalin ja hartsin valmistus, kemiallinen pesu, muovin laminointi, tuoreen puun sahaus sekä offset- ja syväpaino. Työilman ja poistoilman pitoisuusmittauksissa käytettiin jatkuvatoimisia avoimen ja suljetun kyvetin Fourier Transform InfraRed (FTIR) analysaattoreita.

Liuotainepäästövirta työtilaan laskettiin liuotimen sisätilan tai poistoilman keskipitoisuuden ja poistoilmamäärän tulona. Sisätilan keskipitoisuus määritettiin kiinteiden mittauspisteiden (suljetun kyvetin FTIR) tai mittauslinjan (avoimen kyvetin FTIR) pitoisuuksien avulla. Ulkoilmaan vapautuva päästö laskettiin yksittäisistä poistoilmakanavista vapautuvien päästöjen summana.

Liuotainepäästöt vaihtelivat voimakkaasti tuotantomääristä ja prosessivaiheesta riippuen. Tehdaskohtaiset keskimääräiset liuotinpäästövirrat sisätiloihin ja ulkoilmaan vaihtelivat välillä 0.02- 21 kg h⁻¹ ja 0.02 – 9.98 kg h⁻¹. Liuotinpitoisuuksien ajallinen vaihtelu oli kohtalaisen suurta, suurimmillaan tuhatkertaista. Molempien FTIR-analysaattoreiden mittausalue oli kuitenkin riittävän laaja kattamaan pitoisuusvaihtelun. Laboratoriotestien perusteella avoimen ja suljetin kyvetin FTIR-analysaattoreiden määrittämisrajat liuotainaineille olivat ≤ 0.4 ppm-m ja ≤ 1 ppm. Näin ollen molemmat analysaattorit olivat riittävän herkkiä liuotinpitoisuusmittauksiin tuotantolaitoksissa, jotka käyttävät suuria määriä liuotainaineita prosesseissaan. Eräissä mittauspaikoissa työilman sisältämä liuotainainesos oli monimutkainen, mutta kehittyneen spektrianalyysiohjelman (Calmet[®]) avulla merkittävämpien epäpuhtauksien pitoisuudet saatiin määritettyä. Laboratoriotestien perusteella mittausepävarmuudet kenttäolosuhteissa olivat < 15 % suljetun kyvetin FTIR-analysaattorille ja < 10 % avoimen kyvetin FTIR-analysaattorille. Määrittämisrajojen tuntumassa mittausepävarmuudet ovat kuitenkin suurempia. Lukuun ottamatta pitoisuuksia lähellä määrittämisrajaa molempien FTIR-analysaattorien tarkkuus täyttää EN482 mittausstandardin ”liuotinpitoisuuden mittaaminen työpaikan sisäilmasta” vaatimukset.

Tutkimus osoitti, että avoimen ja suljetun kyvetin analysaattorit olivat kohtalaisen helppoja kuljettaa ja käsitellä myös vaativissa työpaikkaolosuhteissa. Molemmat analysaattorit mahdollistavat jatkuvatoimisen ja lähes suoraan osoittavan pitoisuuden mittaamisen. Nämä ominaisuudet ovat hyödyllisiä sekä sisäilman että ulkoilman epäpuhtauksien monitoroinnissa sekä arvioitaessa prosessikohtaisten torjuntatoimenpiteiden tarvetta ja tehokkuutta. Avoimen kyvetin FTIR-mittausmenetelmän eräs etu on myös se, että pumppuja, näytteenottoletkuja tai kiinteitä näytekyvettä ei tarvita. FTIR-menetelmä mahdollistaa myös yhtäaikaisen merkkiaineen ja epäpuhtauspitoisuuden mittaamisen. Merkkiainemenetelmällä avulla voidaan määrittää tilan yleisilmavirta. FTIR-mittausmenetelmän haasteet liittyvät lähinnä laitteiden kalibrointiin, edustavien mittauspisteiden tai linjojen valintaan sekä laitteiden käyttämiseen vaativissa tehdasolosuhteissa.

Tutkimus osoitti, että avoimen ja suljetun kyvetin FTIR-mittausmenetelmät soveltuvat työtilan liuotinkeskipitoisuuden määrittämiseen. Keskipitoisuustiedon avulla on mahdollista määrittää epäpuhtauspäästövirtoja sisätilaan ja ulkoilmaan. Epäpuhtauspäästötiedot ovat hyödyllisiä altistumisen- ja riskinarvioinnissa, mitoitettaessa ilmanvaihdon suuruutta sekä toisaalta myös päästötietoihin pohjautuvien altistumismallien kehittämisessä. FTIR-mittaustekniikka tulisikin olla standardimenetelmä sekä työhygieenisissä- että ympäristömittauksissa vaikka käyttäjävaatimukset FTIR-menetelmälle ovat varsin korkeat. Myös tietoa liuotinpäästövirroista eri teollisuusprosesseista tarvitaan lisää.



ACKNOWLEDGEMENTS

The experimental part of this work was carried out in the Finnish Institute of Occupational Health in 1995-2001.

I want to express my deepest gratitude to my two supervisors. I am grateful to Docent Raimo Niemelä Ph.D., who employed this young scientist from Kuopio in his inspiring projects over twelve years ago, placed such excellent facilities at his disposal and kept this research work on track. I would like to thank Professor Pertti Pasanen Ph.D., for his patience, encouraging attitude and constructive comments.

The reviewers of the thesis, Docent Matti Vartiainen Ph.D., from the National Product Control Agency for Welfare and Health, and Senior Research Scientist Arto Säämänen Ph.D. from the Technical Research Centre of Finland, deserve my sincerest appreciation. They provided many valuable comments and advice that clarified and condensed several sections in this thesis.

I express my thanks to all my co-authors and co-workers. Especially, I wish to mention Christina Rosenberg Ph.D. and Kaarina Rantala M.Sc. Very special thanks belong to Director Irma Welling Ph.D. from the Finnish Institute of Occupational Health. One of the experiments was done in co-operation with a Swedish researcher, which gives me the opportunity to thank Urban Svedberg Ph.D., who introduced me to the interesting world of open path FTIR-systems.

Financial support was provided by the National Technology Agency, TEKES, for which I am very grateful.

I want to thank my parents Matti and Irmeli Räisänen; without their tender support, this would never have come to fruition.

The most important thanks are due to my family. My son Elias for providing me with activities, joy and nowadays also challenges in sports, my daughter Elli whose smile and laughter lighten my world and Sari who has loved and encouraged me for over sixteen years.

Kuopio, December 2007

Jouni Räisänen



ABBREVIATIONS

CLS	Classical Least-Squares
CSA	Chemical Safety Assessment
EC	European Community
EMC	Emission Measurement Center
EN	Norme Européenne (European standard)
ES	Exposure Scenario
ESD	Emission Scenario Document
FTIR	Fourier Transform Infrared
HAP	Hazardous Air Pollutant
IR	Infrared
ISO	International Organization for Standardization
LOD	Limit of Detection
LOQ	Limit of Quantification
MCT	Mercury-Cadmium-Tellurium
NIOSH	National Institute of Occupational Safety and Health
OECD	Organization for Economic Co-operation and Development
OH&S	Occupational Health and Safety
OEL	Occupational Exposure Limit
OPD	Optical Path Difference
OP-FTIR	Open Path Fourier Transform Infrared
MSD	Mass Selective Detector
PID	Photo Ionizing Detector
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SNR	Signal to Noise Ratio
STM	Sosiaali- ja terveystieteiden ministeriö
TCE	Tetrachloroethylene
USEPA	U.S. Environmental Protection Agency
VOC	Volatile Organic Compound
ZPD	Zero Path Difference



LIST OF ORIGINAL PUBLICATIONS

This thesis is based on data presented in six articles. In the text, these sources are referred to by their Roman numerals:

Articles:

- I. Räsänen J. and Niemelä R. (1999) The evaluation of a low resolution Fourier transform infrared (FTIR) gas analyzer for monitoring of solvent emission rates under field conditions. *Journal of Environmental Monitoring*. 1: 549-522.
- II. Räsänen J., Niemelä R. and Rosenberg C. (2001) Tetrachloroethylene emissions and exposure in dry cleaning. *Journal of Air & Waste Management Association*. 51: 174-185.
- III. Welling I., Mielo T., Räsänen J., Hyvärinen M., Liukkonen T., Nurkka T., Lonka P., Rosenberg C., Peltonen Y., Svedberg U. and Jäppinen P. (2001) Characterization and control of terpene emissions in Finnish sawmills. *American Industrial Hygiene Association Journal*. 62:172-175.
- IV. Räsänen J. and Niemelä R. (2002) On-line monitoring of solvent emission rates using an open path FTIR analyser. *Annals of Occupational Hygiene*. 46(5):501-506.
- V. Räsänen J., Niemelä R. and Rantala K. (2000) Organic solvent emissions in some industrial processes. Proceedings of the 6th International Symposium on Ventilation for Contaminant Control, Helsinki, Finland.
- VI. Räsänen J., Niemelä R., Pasanen P. (2006) Applying open path and closed cell Fourier transform infrared analyzers for determining solvent emissions from offset and rotogravure printing processes. Submitted to *Annals of Occupational Hygiene*.

In addition, some unpublished data are presented.



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1. INTRODUCTION

Quantitative information of solvent emission rates are key parameters to be taken into consideration when designing control measures *e.g.* ventilation systems and source control actions in work places. Furthermore, solvent emissions from indoor sources are the most significant determinant of workers exposures to these contaminants. Currently, several European Union occupational health and safety (OH&S) directives, particularly 88/642/EEC, 89/931/EC and 98/24/EC, set out criteria and demands for assessing and controlling the exposure and risks in workplaces. In addition to the OH&S-regulations, the new European Union chemical law called REACH (EC Regulation No. 1907/2006; Registration, Evaluation, Authorisation and Restriction of Chemicals) is expected to have a major impact on chemical exposure and risk assessment. Several methods for determination of contaminant emissions from work machines are provided in the European Standard EN 1093-3, safety of machinery – evaluation of emission of airborne hazardous substance – test bench method.

Information about solvent emissions is important also from the point of view of the outdoor environment. At the moment, the outdoor emissions are even more strictly regulated than the air quality in workplaces. Two European Union directives, EC/13/1999 and 2004/42/EC, define outdoor organic solvent emission limits for several types of premises using solvents. Directive 96/61/EC integrated pollution prevention and control (IPPC directive) deals with minimising pollution to air, soil and water from various industrial sources. These directives are targeted at those industrial sectors using high volumes of solvents.

The solvent emissions from industrial processes can be estimated by concentration and airflow measurements, by using mathematical models (*i.e.* mass balance models, physical models) or by material balance calculations. Material balance information is often quite crude, but readily available from consumption volumes, and may therefore be used in certain situations. The mathematical models often suffer problems with accuracy due to insufficient validation in the process conditions. More reliable emission estimates can be obtained by performing concentration and ventilation measurements in workplaces. This kind of emission information is useful if one wishes to express the result as an emissions factor, which relates the emission rate to production rate (Conroy et al., 1995; Wadden et al., 1989; Wadden et al., 1991; Wadden et al., 2001). The determination of emission factors provides an

estimate of the emissions from the same type of source at some other site and this information can represent the basis for designing control measures or assessing exposures.

At the moment, there is a lack of reliable emission information about industrial processes. The reason for this is that there are a limited number of feasible measurement methods and strategies available for workplace conditions. In the emission rate determination, the key parameter is the room average concentration. The room average concentrations can be determined from exhaust air or from work air in terms of local concentrations (Wadden et al., 1995; Wadden et al., 2001). In practice, industrial premises have usually complicated exhaust air ductwork and many openings, and therefore taking meaningful measurements from the exhaust air may not be feasible. The open path FTIR (OP FTIR) instruments have been utilized for the determination of space or room average concentrations to some extent, but currently only one Swedish research group has used the OP FTIR technique for determining solvent and gas emissions determinations in the workplace conditions (Svedberg et al., 2004). A closed cell FTIR instrument equipped with a multipoint sampling unit may also be used in workrooms, where the spatial variation of concentration is not too excessive. The Fourier Transform Infrared Spectroscopy combines the beneficial elements from the integrative and direct reading sampling methods *i.e.* capability of on-line monitoring of multiple compounds. In this work, the FTIR-measurement strategy for determining space average concentrations was further developed, involving laboratory and field calibration tasks as well as field measurement situations. The FTIR concentration data was used for determining solvent emission rates as well as for revealing the temporal variation of emissions to the work space and to the outdoor environment.

2. REVIEW OF THE LITERATURE

Contaminant mass that emits from a process is rapidly transported into the work space air due to the initial velocity of the emission and the free air flow patterns in the work space. The contaminant emission rate and dilution air flow rate are the key factors which determine concentrations levels to which workers will be exposed. These concentrations may vary extensively in time and space. The magnitude of exposure depends on source characteristics such as geometry, strength, initial velocity, control actions at source (process modification, isolation, local ventilation), dilution air flow rates and work practices. Near the source, workers orientation may also have a significant effect on the level of exposure (Johnson et al., 1996, Säämänen et al., 1998). The amount that gains access to the body *i.e.* the systemic dose can be reduced by personal protective equipment. A diagram showing the relationships between source, emission rate, transportation, exposure, systemic dose and health effect is in Figure 1.

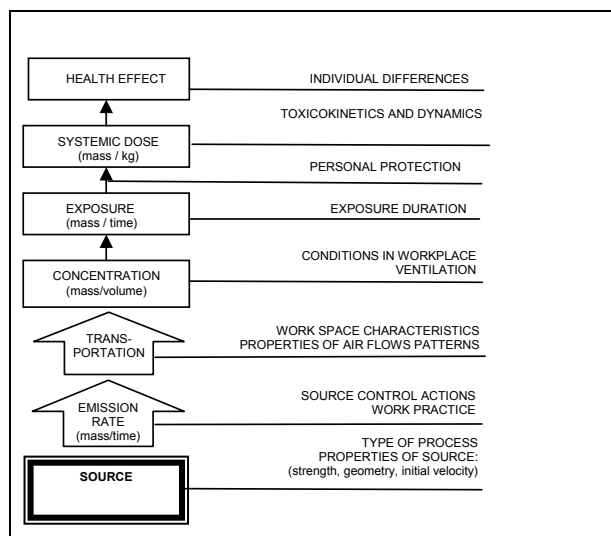


Figure 1. A diagram of the relationships between source, emission rate, transportation, exposure, systemic dose and effects on health.

2.1 Emission rate measurement strategies

Traditionally, industrial hygiene measurements have been focused on the determination of contaminant concentrations in work air or in a worker's breathing zone, while there is only a limited number of studies which have reported emission data. At the present, only a few research groups have published studies on solvent emissions from industrial processes (Herget et al., 1986; Strang et al., 1989; Wadden et al., 1989; Säämänen et al., 1991; Conroy et al., 1995; Wadden et al., 1995; Keil et al., 1997; Wadden et al., 2001; Svedberg et al., 2004). However, contaminant emissions from indoor sources are the most significant determinant of workers' exposures as well as environmental pollution. Reliable, quantitative, information about emission rates are key parameters when designing control measures or predicting exposures both in work places and to the environment.

Emissions from industrial processes can be determined using the following methods: mass balance estimations based on consumption of the chemical in question (e.g. paints), measurements of concentration and air flow rates and or model calculations based on measured data or physical parameters (e.g. temperature, surface area, diffusion coefficients). The emission rates may be estimated also by the tracer gas method. In this test method, the emission can be calculated from a tracer gas emission rate and the correlation of concentrations of contaminants and tracer at the same points near to the source (Antonsson, 1990). A prerequisite is that the releasing mechanism of the actual contaminant and tracer gas are similar. Emission determination methods can also be divided into direct and indirect methods. Concentration and air flow measurements are direct methods, while tracer gas methods, theoretical calculations and modelling are often referred as indirect methods .

The contaminant emission rate (m) can be defined by contaminant concentration (c) and airflow rate (Q) (equation 1):

$$\text{Equation 1.} \quad m = Q * t^{-1} \int_0^t C (dt)$$

Where:

- m = Contaminant emission rate (mass / time)
Q = Air flow rate through the room or in the exhaust duct (volume / time)
t = Time
C = Contaminant concentration in the exhaust air or in the room (mass / volume)

If the cleaned return air is used, the emission from supply air should be extracted from the total indoor emission. The emission in air inlet is proportional to the air flow rate, cleaning efficiency of the filter in return air unit and contaminant concentration (equation 1).

In the case of emissions to the environment, the contaminant concentration and airflow rate can often be measured from the exhaust air ducts. The exhaust air can include process, local and general exhaust or ceiling exhaust fans. The total outdoor emission release is a sum of emissions from the individual exhausts. In determinations of indoor emissions, an estimate is required both of the room average concentration and total airflow rate through the room. In some cases, an estimate of the average workroom concentration and total airflow rate can be obtained by measurements conducted in general exhaust air duct(s). This, however, presumes that general exhaust air duct is not connected to closed process emissions or local exhaust systems and furthermore that there is no significant uncontrolled leakage through windows, doors or other openings. Another way to obtain an estimate of the workroom average concentration is to conduct the measurements within the workroom air (Wadden et al., 2001). Usually, multipoint sampling is utilized for this task. In this approach, each sample is assumed to represent the area where the concentration is homogeneously distributed. This is likely to be an approximation, because there may be notable spatial variations in the solvent concentrations. In workplaces with high spatial concentration variations, a more reliable space average estimate is needed.

A schematic diagram illustrating the principles of indoor and outdoor emission determination is shown in Figure 2.

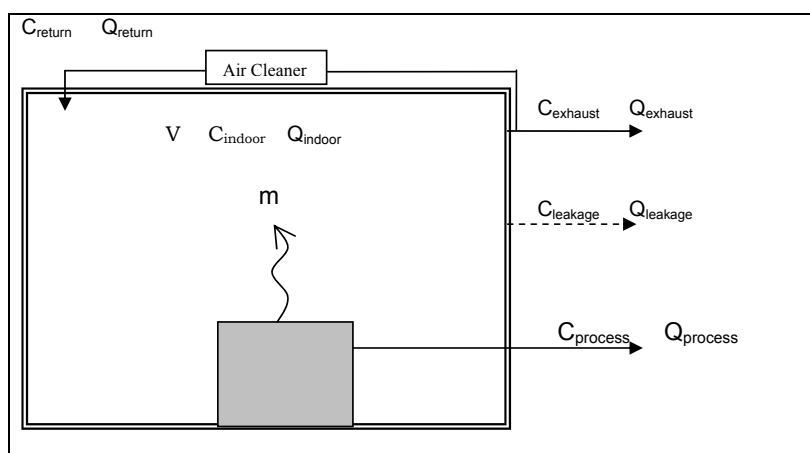


Figure 2. Basic model of a mass balance system used in emission rate calculation between emission rate (m), indoor average solvent concentration (C_{indoor}), room volume (V), average air flow rate (Q_{indoor}), average contaminant concentration in exhaust air (C_{exhaust}), exhaust air flow rate (Q_{exhaust}), average contaminant concentration in leakage air (C_{leakage}), leakage air flow rate (Q_{leakage}), average contaminant concentration in local / process exhaust air (C_{process}) and local / process exhaust air flow rate (Q_{process}). In case of recirculated air, the emission from inlet air should be taken into account, return air flow rate (Q_{return}), average concentration in return air (C_{return}). Emissions from the outdoors to the workroom are assumed to be negligible with respect to high-volume solvents such as those used in industrial processes.

The contaminant concentration in air can be measured by using integrative methods or direct reading (or on-line) instruments. In integrative methods, e.g. charcoal tube sampling, the air sample is collected onto an adsorbent, a filter or a closure, which is then analysed in the laboratory. The advantage of this method is that it can identify and quantify compounds in mixtures, but one clear drawback is its poor temporal resolution. In direct reading or on-line instruments, the concentration information is available instantly, in real time, which makes these kinds of measurements very useful when identifying peak exposures or when revealing concentration variations in time. The major disadvantage of most direct reading instruments is their poor ability to identify compounds in mixtures. However, the Fourier

Transform Infrared Spectroscopy technique combines the beneficial elements of both integrative and direct reading sampling methods *i.e.* it possesses the ability for on-line monitoring of multiple compounds.

Studies on emissions from industrial processes from a standpoint of industrial hygiene have been reported, particularly by two research groups led by Conroy and Wadden from the United States (Wadden et al., 1989; Wadden et al., 1991; Conroy et al., 1995; Wadden et al., 1995; Wadden et al., 2001). In these studies, lead, chromium and cadmium emission rates during abrasive blasting operations, emissions during trichloroethylene degreasing and solvent emission rates in rotogravure and offset printing were determined. The concentration data were obtained by using the charcoal tube method. In the study of Wadden et al. (1989) the trichloroethylene emission rate from a vapour degreaser was determined from point concentration data by using an approach based on Fick's law of diffusion. Solvent and gas emission rates have been determined also by the tracer gas method (Antonsson, 1990). In that study, the emission rate was calculated from the tracer gas (nitrous oxide) emission rate and the correlation of the concentrations of contaminant (carbon dioxide, trichloroethylene) and the trace gas measured at the same points, near to the source. The method was tested both under laboratory and field conditions. In the field measurements (an electroplating process) a mean trichloroethylene emission of 3.2 g min⁻¹ was obtained (Antonsson, 1990). One research group from Finland (Säämänen et al., 1991) has studied styrene emissions during hand lay-up moulding of reinforced polyester. The concentration of styrene was measured by Miran® IR-analyzer under laboratory conditions. Recently, in the study of Svedberg et al. (2004), an OP FTIR technique was utilized for measuring emissions of carbon monoxide and hexanal from storage of wood pellets. The contaminant emissions from work machines, such as spray guns and sanding machines have been determined to some extent using a laboratory test chambers method. This method is described in the European Standard EN 1093-3, safety of machinery – evaluation of emission of airborne hazardous substance – test bench method. A Finnish research group has recently constructed an emission test chamber that fulfils European Standard EN 1093-3 requirements for determining emissions from machines (Rautio et al., 2007). This test chamber has mainly used for the determination of dust emissions.

A summary of previously reported solvent emission measurements are presented in Table 1.

Table 1. Summary of previously reported solvent emission measurements from some industrial processes.

Process	Mean solvent conc. in air	Emission	Control technology	Concentration measurement method	Reference
Vapor Degreaser	3.9-140 ppm	0.67-2.6 g/min	Enclosed system, local exhausts	Point sampling Charcoal tube & Tedlar bags and Miran IR-analyzer)	Wadden et al. (1989)
Electroplating	67 mg m ⁻³	3.2 mg min ⁻¹	General ventilation	IR-analyzer: Laboratory tests and field tests / tracer gas method	Antonsson (1990)
Plastic Lamination	n.a.	0.43-0.55 kg h ⁻¹	n.a.	IR-analyzer: Laboratory chamber	Säämänen et. al. (1991)
Dry Cleaning	35-110 mg m ⁻³	n.a.	Closed type machines	Point sampling (charcoal tube)	Moschandreas & O'Dea (1995) and Solet et al. (1990)
Offset Printing	50-109 mg m ⁻³	0.16 -1.1 kg h ⁻¹	General ventilation	Point sampling (charcoal tube)	Wadden et al. (1995)
Fresh wood sawing	166 mg m ⁻³	n.a.	General ventilation, local exhausts	OP-FTIR monitoring	Svedberg & Galle (2000)
Rotogravure Printing	36-464 mg m ⁻³	222 kg h ⁻¹	Local exhausts	Point sampling (charcoal tube)	Wadden et al. (2001)
Wood pellet storage	21-89 mg m ⁻³	96-703 mg/ton/day	n.a.	OP-FTIR monitoring	Svedberg et al.(2004)

n.a. No information available

In addition to the workplace air quality, the solvent emissions are important also from the point of view of the outdoor atmosphere. Most solvents and gases, often called as volatile organic compounds (VOCs), are released both by natural and anthropogenic sources. The natural VOC emissions predominate on the global scale but in industrial regions, anthropogenic sources are often the most important contributors to the ambient air quality. All VOC-compounds present in the ambient air can absorb heat radiation from the earth's surface, but their most important effect is indirect: VOCs may contribute to tropospheric ozone formation through photochemical processes in the presence of nitrous

oxides (NO_x) and hydroxyl radicals (OH) (Finlayson-Pitts and Pitts, 1986). Furthermore, exposure to ozone can cause acute respiratory health effects, asthma and impair the body's immune system defences (Schwela, 2000; Lagorio et al., 2006). In the European Union, several directives intended to regulate outdoor solvent emissions are in force. The directive 96/61/EC concerning integrated pollution prevention and control (the IPPC directive) is targeted at minimising pollution to air, soil and water from various industrial sources. This directive is aimed at those industrial sectors using high volumes of solvents *e.g.* oil refineries and the chemical industry. The European Union directives EC/13/1999 and 2004/42/EC define outdoor organic solvent emission limits for several types of premises using solvents. Currently these directives are the main policy instruments for the reduction of industrial emissions of volatile organic compounds (VOCs) in the European Community. The directives cover a wide range of activities involving solvents, *e.g.* printing, surface cleaning, vehicle coating, dry cleaning and manufacture of footwear and pharmaceutical products. The VOC directive establishes the emission limit values for VOCs in exhaust air and maximum levels for fugitive emissions (expressed as a percentage of solvent input) for solvent using processes. The VOC directive does allow industrial premises the possibility to seek exemption from the limit values, provided that they achieve by other means the same reduction as would be made by applying the regulation. For example, alternative reductions could be achieved by substituting products with a high content of solvents for low-solvent or solvent-free products and changing to solvent free production processes. The OECD and EU has also established Emission Scenario Documents (ESD) that describe the sources, production processes, pathways and use patterns with the aim of quantifying the emissions (or releases) of a chemical into water, air, soil and/or solid waste. The ESDs are accessible in the Internet at <http://appli1.oecd.org/ehs/urchem.nsf>. The US EPA has also developed a number of generic scenarios to be used as default release scenarios in environmental risk assessment. EPA's emission scenarios can be found at: <http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/index.html>.

2.2 Exposure assessment approaches

Traditionally, OH&S measurements have been focused on the determination of exposure concentration levels, while there is only a limited number of emission data available. Emission, however, is the key factor that determines concentration level for which workers are exposed.

Exposure can be defined as a contact over time and space between a person and one or more biological, chemical or physical agents (US NRC, 1991a). An occupational exposure assessment is needed when characterizing health risks of a chemical(s) or when designing or evaluating exposure control strategies or techniques. In order to assess the total exposure to solvents, it is necessary to take all exposure routes into account (inhalation, dermal and ingestion). For industrial solvents, exposure via inhalation is usually the most significant route, however, for certain work tasks and for certain solvents also exposure through skin may play a significant role. Exposure via ingestion is usually considered to be negligible in industrial environments. At the moment, several European Union occupational health and safety directives *e.g.* 89/931/EC and 98/24/EC (Chemical Agents Directive) set out criteria and demands for assessing and controlling exposure and risks in workplaces. In addition to the occupational health and safety regulations, the new European Union chemical law called REACH (EC No 1907/2006, Registration, Evaluation, Authorisation and Restriction of Chemicals) will have a major impact on chemical exposure and risk assessment. The REACH-regulation has been in force since 1st June 2007. According to REACH, enterprises that manufacture or import more than 10 tons per year chemical substance classified as dangerous, are obligated to register into the central database (European Chemical Agency, ECHA) and to conduct a chemical safety assessment (CSA) in order to justify safe use of the chemical. A key concept in Chemical Safety Assessment is a development of an Exposure Scenario (ES) that requires that an exposure assessment should be conducted. By definition, the Exposure Scenario is a the set of conditions that describe how the substance is manufactured or used during its life-cycle and how the manufacturer or importer controls, or recommends downstream users to control, exposures or to humans and to the environment (REACH-regulation EC No 1907/2006, Annex I).

The exposure to airborne contaminants e.g. solvents and other gases can be estimated by conducting measurements of the work air (IPSC EHC 214, 2000). In principle, there are two approaches which can be utilized for air quality measurements in the work place air: personal or stationary (fixed point) sampling. Usually the most reliable information of exposure levels of the worker (personal exposure) can be obtained by using personal sampling. In this method, an air sample is collected from the worker's breathing zone using charcoal tube sampling or passive monitors. The breathing zone is considered to have an airborne contaminant concentration equivalent to the concentration inhaled by worker. The European Committee of Standardization (EN 1450) has defined a breathing zone as a hemisphere in the front of the worker's face with a radius of 0.3 m. One way of assessing inhalation exposure is to compare the breathing zone contaminant concentrations to the occupational exposure limit (OEL) value given for that contaminant. In Finland, the Ministry of Social Affairs and Health has established the degree on Concentrations Known to be Hazardous (4/2007) where a list of indicative concentration limit values is given.

In the stationary sampling, air samples are collected from fixed points. These samples reflect the concentration within a certain space or area and they are normally used for estimating the concentration distribution in a work room or in verifying the effectiveness of the control measures (IPSC EHC 214, 2000). When the contaminant concentration is equally or nearly equally distributed within a sampled area or space where a worker is situated, the concentrations may be used as an estimate of personal exposure. In the study of Mäkinen et al. (2000), the breathing zone and the stationary sampling approaches were compared with respect to the occupational chemical exposure assessment described in European Standard EN 689. The study results suggested that the stationary sampling may be used for exposure assessment purposes in process tasks where workers do not have manual work tasks. In manual tasks, stationary sampling may not reflect personal exposure levels very well.

Biomonitoring is one method which can be used to characterize internal exposure (Fenske R.A., 1993; IPSC EHC 214, 2000). In the simplest case, the systemic dose is determined from urine levels of chemical that is rapidly absorbed, but not metabolized and excreted within 24 h. Biomonitoring, however, is usually applied to those contaminants where exposure through dermal route is dominant. Although biomonitoring enables determination of the internal dose for an individual worker, the methods have some limitations. In biomonitoring, the causes of exposure cannot be identified.

Likewise, the routes of exposure (if more than one) can not be distinguished (van Hemmen et al, 1995). This kind of information, however, is essential when designing exposure control strategies in workplace. At the moment, there is also limited number of validated methods and biological reference values available.

In addition to direct measurements, the exposure can be estimated by using indirect methods *e.g.* by different kinds of models or by using epidemiological data, questionnaires or health surveys. Epidemiological data as well as some of the models often include measured exposure values from past.

2.2 Principles of FTIR spectroscopy

The theory of FTIR spectroscopy in this chapter is based mainly on the textbook written by Griffiths & Haseth, 1986.

Infrared spectroscopy is an analytical technique which can be used to identify organic and inorganic gases and vapours. The IR-spectroscopy utilises the absorption of electromagnetic radiation into a material, for example vapour or gas molecules: When a beam of IR-radiation with intensity I^0 passes through a substance, it can be absorbed or transmitted, depending upon its frequency and the structure of the molecule it encounters. The wavelength of the absorbed radiation is related to the energy of the transition expressed by Planck's law (Equation 2):

Equation 2.	$E_{\text{final}} - E_{\text{initial}} = hc/\lambda$
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where:

E_{final}	=	higher energy level
E_{initial}	=	lower energy level
h	=	Plank's constant
λ	=	wavelength
c	=	speed of light.

In IR-spectroscopy, the wavelength is often expressed as a wave number W ($W = 1/\lambda$). The energy absorption in molecules is due to electrical, rotational or vibrational transitions that are specific for certain bonds and functional groups. For example, carbon-carbon double bond stretching occurs always in the region around $1650\text{-}1600\text{ cm}^{-1}$. IR- spectroscopy can be used for identification with the specific energy absorption attributable to the functional groups. The amount of absorbed energy can be used for quantification. The infrared spectrum lies in wave number region between $14\ 000 - 10\ \text{cm}^{-1}$. Most IR-analysers operate in the mid-IR region *i.e.* $4000 - 400\ \text{cm}^{-1}$.

The transmittance spectrum illustrates the transmitted IR radiation as a function of wavelength. The transmittance (T) is defined as the ratio of the transmitted energy to the incident energy (Equation 3):

Equation 3.	$T = E' / E''$
--------------------	----------------

Where:

$T =$ Transmittance
 $E' =$ Transmitted energy
 $E'' =$ Incident energy.

When no energy is absorbed into the sample, the transmittance value is unity (or 100 %). The transmittance value is, however, not directly proportional to the concentration and therefore the quantification (concentration determination) is based on the Lambert - Beers' law, which defines the sample gas concentration's relation to the absorbance (Equation 4):

$$\text{Equation 4.} \quad A = \log (1 / T) = abC,$$

Where:

A= absorbance

T= Transmittance

a= absorptivity constant of a substance

b= path length

C= concentration.

An example of an absorption spectrum with four compounds (water vapour, carbon dioxide, dinitrogen oxide [N₂O] and tetrachloroethylene [TCE]) is shown in Figure 3.

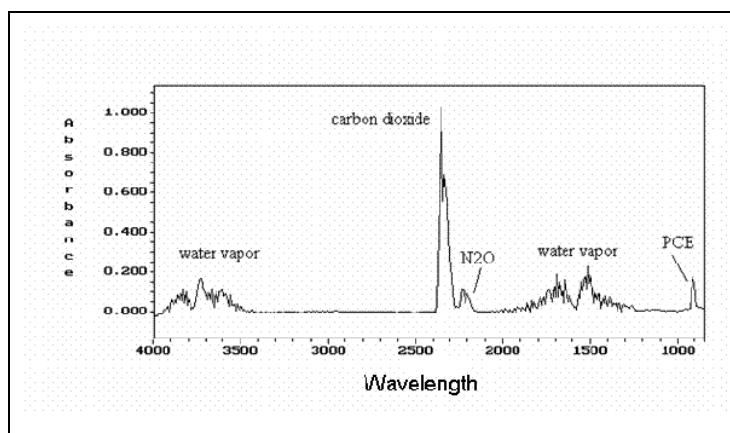


Figure 3. An example of an IR-absorption spectrum with four compounds (water vapour, carbon dioxide, dinitrogen oxide [N₂O] and tetrachloroethylene [PCE]) (II).

The IR-absorption spectra can be collected using an IR-spectrometer. Traditional IR-spectrometers, like Miran®, utilised monochromatic light and therefore their ability to identify several compounds simultaneously was limited. The FTIR- spectrometers were developed to fulfil the need of identifying

and quantifying mixtures of several compounds. The basic theory of FTIR-analysis will now be summarized.

The FTIR-instrument consists of the three following main elements: broadband IR-source, interferometer and detector. The IR-source emits IR-light in a broad mid-IR wavelength region. The IR-light is divided into two separate beams in the interferometer's beam splitter (see Fig. 4). One half of the beam is reflected from the splitter but the other half is transmitted. The transmitted light beam travels to a fixed mirror and the reflected half to a moving mirror. The light beams from both mirrors are then recombined in the beam splitter. If the moving mirror and the fixed mirror are at an equal distance from the beam splitter (ZPD, Zero Path Difference) the recombined beams will be at the same phase and constructive interference is introduced. In this case, the intensity of waves will be additive. If the moving mirror and fixed mirror are at a different distance (Optical Path Difference occurs, OPD) the two light waves in the beam splitter can be at different phases and destructive interference occurs. The constructive interference is introduced when the OPD equals some multiple of the wavelength ($2x\lambda$, $3x\lambda$, etc.). On the other hand, two waves will compensate for each other if the OPD is half of the wavelength ($\lambda / 2$). Due to movement of the mirror and the resulting intensity of the light, the light beam is considered as being modulated. From the beam splitter, the modulated light travels through the sample to the detector yielding an electronic signal. This signal is then processed to form a spectrum.

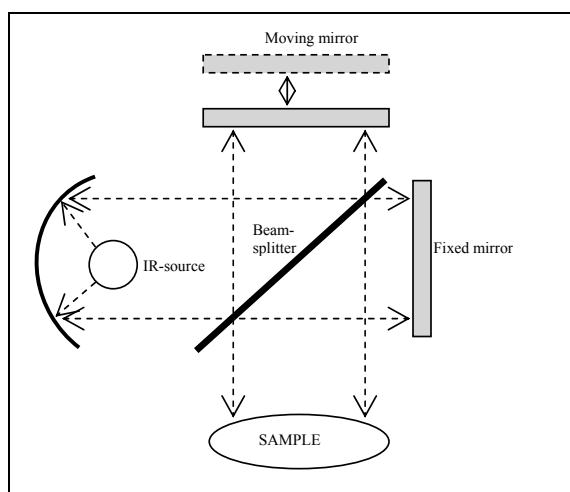


Figure 4. Michelson interferometer

Fourier's theorem states that any mathematical function can be expressed as a sum of sinusoidal waves. In FTIR spectroscopy, the broad band IR-light is modulated and the sum of all waves is expressed in the form of an interferogram. An interferogram is obtained when a moving mirror travels once from the start position to its end position and back again. This process is called a scan. The interferogram is converted to a single beam spectrum by a Fourier transformation. The Fourier Transform mathematics, however, will not be discussed in detail in this thesis, since an understanding of its principles is not necessarily required for the use of FTIR instrument.

The infrared detector transforms the incoming infrared light into a form of an electronic signal. Infrared detectors can be divided into two types: thermal detectors and quantum detectors (Griffiths and De Haseth, 1986). In modern FTIR-spectrometers most commonly quantum type mercury cadmium telluride (MCT) detectors are used. These detectors can be cooled either electronically or by liquid nitrogen.

A single beam spectrum without the sample compounds is called the background spectrum (or sometimes as the reference spectrum). Usually, a background spectrum must be collected before sample spectra collection. The sample spectra are then collected from an atmosphere where compounds of interest are present. In the field measurements, water vapour and carbon dioxide are always present in the background spectrum, but in laboratory conditions, a pure background spectrum, for example a nitrogen atmosphere, can be collected.

The sample identification and quantification is made using the reference spectrum (or calibration spectrum). A reference spectrum is a spectrum of one component (or sometimes a mixture of components) with known concentrations. The reference spectrum can be obtained by using commercial library spectra, or by creating spectra by laboratory calibrations (a more detailed description of a laboratory calibration is given in the materials and methods section). The identification and quantification procedure in many FTIR applications is based on the classical least-squares (CLS) analysis algorithm. The CLS technique uses the linear relationship between the component absorbance and concentration (Haaland & Easterling, 1982; Haaland et al., 1985). At present, there are several types of commercial CLS analysis software available.

A measurement resolution defines how accurately the absorption wavelengths can be separated from each other. The higher the resolution, the better the ability to resolve spectral features. On the other

hand, the high spectral resolution increases the signal to noise ratio (SNR), and that will increase the measurement's detection limit(s) (LOD) and its ability to detect low concentrations. The lower sensitivity of the instrument can be increased by increasing the number of scans (N), but then also the spectrum analysis time (t) increases. The relation between resolution, SNR, number of scans, and spectra analyses time is defined as follows:

$$\text{Resolution} \approx \text{SNR}$$

$$\text{SNR} \approx N^{1/2}$$

$$t \approx N$$

There is no general rule for selecting the proper resolution and spectra collection times, since the selection depends on the needs of each individual measurement.

In principle, FTIR instruments can be subdivided according to their sampling techniques into two categories: Closed cell or open path spectrometers. In the closed cell spectrometers, the sample air is pumped into a gas cell where the IR-beam travels and into where the sample is analyzed. Thus, each measurement result reflects the conditions surrounding the point from where the sample air was taken. In open path spectrometers, the IR-beam is transmitted through an open space, e.g. a production hall. The measurement result is considered to be the integrated gas or vapor concentration in the path along that beam.

Closed cell FTIR-spectrometers

In the closed cell FTIR analyzers the sample air is pumped into an internal cell where it is analyzed. Before the development of FTIR spectrometers, a MIRAN 1 A was widely used closed cell type IR-analyzer in various industrial hygiene applications. Since the 80's considerable efforts have been made to evaluate closed cell FTIR analyzers applicability to monitor concentrations of solvents and gases in workplaces (Herget and Levine 1986, Strang et.al 1989, Strang and Levine 1989, Ying et.al 1989, Ying and Levine, 1989). At that time, the FTIR technique was found to be valuable, especially with least square fit spectral software that enabled quantification of compounds in mixtures, but the instruments were not easily transportable or useable in workplace conditions. In many of these studies both in field and in laboratory, the FTIR instruments have had a relatively long absorption path length with a high

measurement resolution. Therefore, the focus of many studies has been set on the instrument's applicability to measure very low concentrations (sub- ppm levels) (Herget and Levine, 1986; Strang and Levine, 1989; Levine et.al 1989).

In the 90's, more compact and transportable closed cell FTIR analyzers were developed (Franzblau et.al, 1992; Larjava et.al, 1997). Also more powerful software for FTIR multicomponent analysis was introduced (Saarinen and Kauppinen, 1991). A similar type of low-resolution closed cell FTIR spectrometer and multicomponent analysis software as used in this work was applied for the measurements of combustion fuel gases from three industrial boilers and stack gases from wood and oil burning boilers (Larjava et.al, 1997; Jaakkola et al., 1998). In the study of Ahonen et.al (1996), solvent mixture concentrations in workplaces were measured using low resolution closed cell FTIR together with multicomponent analysis in order to determine combined exposures to solvents.

Open path FTIR-spectrometers

Open path FTIR (OP FTIR) spectroscopy is used for the remote measurement of gases and vapours. This technique eliminates the closed cell and allows the infrared beam to pass directly through ambient air *e.g.* through a work room. Likewise, no sampling lines or pumps are needed. The IR source can be integrated to the spectrometer or it can be located at the other end of the IR beam, where it is sent through the air to the detector. If the IR source is integrated into the spectrometer, the IR-beam is directed back to the spectrometer's detector by a remote retroreflector (field mirror). Furthermore, the open path systems can be as active or passive types. An active system uses electrically heated, internal or external, IR source, while a passive system uses a heat source located in the measurement atmosphere, such as stack gas plumes, sun etc.

Previously, the OP FTIR-technique has been used in several environmental and occupational hygiene applications. Most commonly, open path (OP) FTIR-analyzers have been used in environmental air monitoring tasks. Initially, large open path systems were used to monitor fugitive emissions from chemical processes, and gas emissions from stacks (Herget et.al, 1982; Malachowski et al., 1994). In the late 1980's, OP FTIR spectrometers were used at a hazardous waste site with beam path length of over kilometer (Levin et al 1989). The OP FTIR technique has been used also for monitoring emissions along plant fence lines (Russwurm et.al, 1991).

The open path FTIR-spectroscopy has been found to be useful also in buildings and work places for monitoring air contaminants along the beam path, detecting either single compounds or complex mixtures. (Russwurm et al., 1991; Xiao et. al., 1991; Xiao et al., 1993; Malachwski et al., 1994; Svedberg & Galle, 2000; Ross & Todd, 2002; Ross & Todd, 2002; Simpson, 2003; Swedberg et al., 2004).

The FTIR technique has also been used in other industrial hygiene applications, for instance, in computed topography (concentration mapping) though only under laboratory conditions (Yost et al., 1992; Samanta & Todd, 1995, Todd 1996, Todd 2000). In this application, the OP FTIR spectrometer and computed tomography were used for measuring and mapping pollutants in air in real time which can be used for visualizing the flow of gases and vapors both indoor and outdoor environment applications. These maps may be used to evaluate human exposures, source emissions and air dispersion models (Samanta & Todd, 1995). The computed tomography coupled with OP-FTIR measurements have also been used for estimating personal exposures (Wu et al., 2003; Wu et al., 2005).

The OP FTIR technique is an attractive choice especially for indoor emission determinations, because IR beam-average concentration data can be used for estimating space average concentration. However, the OP FTIR measurement technique has rarely been used for determining emission from indoor sources. Recently, the OP-FTIR technique was utilized successfully in solvent and gas emission determinations (Svedberg et al., 2004). In the studies of Svedberg et al. emissions of hexanal and carbon dioxide during wood pellet storage and emission of terpenes during fresh wood sawing were determined. The Emission Measurement Center (EMC) in the Environmental Protection Agency in the USA (US EPA) has also evaluated the application of open path Fourier Transform Infrared Spectroscopy (FTIR), for emissions monitoring. From the EPA's point of view, the technique is promising since it has the capability to measure more than 100 of the 189 Hazardous Air Pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990.

3. AIM OF THE STUDY

The aim of this work was to develop a measurement strategy for monitoring space average concentrations of solvents under workplace conditions in order to determine solvent emission rates to work rooms and to the outdoor air. Another aim was to produce data on solvent emissions from different types of industrial processes.

The detailed objectives of this study were:

- To describe the applicability of FTIR spectroscopy for monitoring concentrations of single solvent in the workplace atmosphere (tetrachloroethylene, toluene, monoterpenes, isopropanol) **(II, III, IV)**.
- To describe the applicability of FTIR spectroscopy for monitoring concentrations of complex solvent mixtures in the workplace atmosphere **(I, IV, V, VI)**.
- To describe the applicability of FTIR spectroscopy for detecting solvent concentration variations in time (single compound and mixtures) in work air **(I, II, V, VI)**.
- To develop a calibration method for field applications of OP FTIR and closed cell FTIR spectrometers **(I-VI)**.

4. MATERIALS AND METHODS

4.1 Measurement sites

The measurements were made between the years 1995 – 2001 in the following processes: Ink, solvent and resin manufacturing, dry cleaning, plastic lamination, fresh wood sawing, offset printing and rotogravure printing. All of the above mentioned processes use high volumes of solvents and have therefore major potential to release solvent vapors into workroom air and outdoor environment. These processes can have multiple sources for releasing solvent mixtures. Often the solvent concentrations vary considerably both in time and in space. The solvent concentration measurements were conducted by using low resolution closed cell and open path FTIR analyzers. A summary of measurement methods and monitored solvents is presented in Table 2.

Table 2. The summary of studied processes, measurement methods and compounds monitored

Process	Method	Solvents / vapours	Other compounds	Article in the thesis
Dry cleaning (n=11)	Closed cell FTIR	Tetrachloroethylene	Nitrous oxide, Carbon dioxide, Water vapour	II
Ink manufacturing (n=1)	Closed cell FTIR	Ethyl alcohol, propan-2-ol, 1-methyl-2-propan-2-ol, ethyl acetate	Carbon dioxide, Water vapour	I, IV
Paint manufacturing (n=2)	Open path FTIR	Ethyl alcohol, Isobutyl alcohol, xylenes	Nitrous oxide, Carbon dioxide, Water vapour	I, IV
Resin manufacturing (n=1)	Open path FTIR	Styrene Acetone	Carbon dioxide, Water vapour	V
Laminating of plastic (n=2)	Open path FTIR	Styrene Acetone	Carbon dioxide, Water vapour	V
Fresh wood sawing (n=3)	Closed cell FTIR Open path FTIR	Monoterpenes	Carbon dioxide, Water vapour	III
Offset printing (n=2)	Closed cell FTIR Open path FTIR	Isopropanol	Carbon dioxide, Water vapour	VI
Rotogravure printing (n=1)	Open Path FTIR	Toluene	Carbon dioxide, Water vapour	VI

n= number of processes / work places

A short description of the measurement strategies and conditions in sampling sites and processes used is now provided:

4.1.1 Dry Cleaning (II)

In Finland, tetrachloroethylene is the primary solvent in dry cleaning processes. The dry cleaning equipment can be either transfer type or dry-to-dry type. The transfer type equipment has separate washing and drying units, while the dry-to-dry equipment consists of a single unit that performs both washing and drying in one cycle. Traditionally the dry cleaning equipment, both transfer and dry-to-dry types, have been vented and are therefore considered as being open systems. The dry cleaning can be considered as a continuous process more than batch process. The main TCE emissions to work air are related to situations when washing machines are unloaded, or when there are TCE leaks from the machines.

In our experiments, six commercial shops and three industrial dry cleaning establishments that use vented or nonvented "dry to dry" machines were selected for the study. Tetrachloroethylene was used as a primary solvent in all establishments. The number of machines in the establishments varied between 1 to 4 with maximum cleaning capacities of 12 - 60 kg. All but two of the establishments, used the nonvented machines. The cleaning rates varied in commercial shops between 4-20 kg/h and in industrial establishments between 30-88 kg/h.

Five establishments were equipped with a mechanical air supply and exhaust ventilation systems, while three had mechanical exhausts only. In one industrial establishment, the supply air was distributed into the dry cleaning room by a displacement system, while in the other establishments, the dilution ventilation was applied. In four of the shops, underpressurized washing drums were used in order to avoid TCE emissions gaining access to the workroom air during unloading. The local exhaust hoods were installed at the spotting and pressing boards in seven establishments.

4.1.2 Paint and ink manufacturing (I, IV, V)

Paint and ink manufacturing can be classified as a batch process, consisting of four major processes phases: mixing, dispersing, blending and packaging. The types of paints can include a variety of different kind of coatings such as for goods, wood and metal furniture and marine paints. Inks currently manufactured in Finland include letterpress, lithographic, offset, and gravure and flexographic inks. The paints and inks can be either water or solvent based.

Solvent emission measurements in this work were conducted in a paint manufacturing plant, which produces approximately 1000 tons of paint per year, consisting mainly of xylenes, ethyl alcohol, butyl alcohol, and solvent naphtha. The measurements were conducted in a working area (500 m²) of a manufacturing department (floor area of 2200 m², height 3.5 m). The department was equipped with a mechanical supply and exhaust ventilation. In addition to the general exhaust ventilation, the mixing and weighing stations were equipped with local exhaust hoods. During the 4.5-h morning shift, 1600 kg of paint was manufactured.

Solvent emissions were determined during the manufacture of flexographic ink. The plant manufactures approximately 2000 t of flexographic ink per year and consumes ethanol 400 t, propan-2-ol 150 t, 1-methoxy-propan-2-ol 180 t, and ethyl acetate 100 t. The production rate varied from 100 kg h⁻¹ to 300 kg h⁻¹ during the study. The ink manufacturing plant (floor area 4700 m², height 7 m) was equipped with a mechanical ventilation system with two exhaust fans. The air from the departments was exhausted at floor level through ductwork. The supply air diffusers were mounted in the middle of the departments at a height of 4 m. In addition to the general ventilation, all departments were equipped with their own local exhausts.

4.1.3 Resin manufacturing (V)

Similar to the manufacture of paints and inks, also the manufacture process of unsaturated polyester resins (gel coat) can be considered as a batch process. The resin manufacturing plant produces 7600 tons of resins consisting of styrene and acetone. Styrene vapors are released from the blending and packing operations, while acetone evaporates from short term washing and cleaning tasks. The

production hall's supply air (hall area 390 m², height 4 m) was introduced through the grills from one side of the hall, and mixed with several high impulse air jets. The air was removed through the local exhaust ducts from several locations in the hall. During the shifts when the measurements were being done (one workday, 7 h), 18 000 kg of resin was manufactured.

4.1.4 Fresh wood sawing (III)

The terpene concentrations were measured in three sawmills (A, B and C) during winter and summer seasons in pine and spruce sawing. The fresh wood sawing can be considered as continuous process, where the terpenes are released as a by-product. The main saws in use in sawmill A were band saws and frame saws, in sawmill B there were band saws and reduce circular saws and in sawmill C there were band saws. The production rates in pine and spruce sawing in winter and summer season from sawmills A, B and C are summarized in Table 3.

Table 3. Production of sawmills A, B and C during measurements (III).

Process	Production rate
	m ³ /h
Pine sawing	
winter	72
summer	72-117
Spruce sawing	
winter	71-77
summer	68-77

In sawmill A, general ventilation was used. Sawmills B and C had also general ventilation, but in sawmill B the main band saw and in sawmill C all band saws were equipped with local exhaust systems. During the winter time, part of the exhaust air was returned after cleaning in a particle filter.

4.1.5 Offset and rotogravure printing (VI)

Offset and rotogravure printing are continuously on-going processes. The presses are operating nearly 24 hour per day for seven days per week.

Solvent emissions were determined in two offset printing houses located in Finland. The offset printing houses (volumes 27 000 m³ and 30 000 m³) were equipped with 7 and 12 offset printing machines. All printing houses were equipped with a mechanical supply and exhaust ventilation. The supply air was distributed from the ceiling level by diffusers and /or jets and removed from the sides of the halls. In addition to the general exhaust ventilation, the printing machines were equipped with local exhaust systems. The local exhaust air from printing machines was cleaned before it was released to outdoor air. Printing houses A and B circulated approximately 70 % of the general exhaust air back to the printing chambers. The circulated air was directed through particle filters and a fumigation system before releasing it to indoor air. The part of the general exhaust air that was led outdoors (30 % of the total air flow) was not cleaned.

The solvent emission measurements were conducted in one rotogravure printing house in Finland. The printing hall (volume 12 100 m³) was housed a single 5-color 10-print press. The printing hall was equipped with a mechanical supply and exhaust ventilation. The press workers stay most of the workday in an isolated control room. The exhaust air (via general ventilation and local exhausts) from the rotogravure printing house was cleaned by catalytic incineration before it was released outdoors. The efficiency of the catalytic incineration is estimated to be 99 %.

4.2 Closed cell FTIR monitoring & calibration

The measurements of solvents in dry cleaning, ink manufacturing and saw mills were carried out using a portable low-resolution (8 cm⁻¹) FTIR gas analyser (Gasmeter, Temet Inc.), equipped with a Peltier-cooled MCT detector ($D^* = 0.3 \times 10^9$) and a 1.1 l gas cell with an absorption path length of 3 m. The spectral response range of the analyser is 4000–950 cm⁻¹. The low frequency end is limited by the cut-off frequency of a Peltier-cooled detector. The analyser has a spectral scanning rate of 10 scans s⁻¹ and a data acquisition rate of 20 kHz. The interferograms are collected as double-sided. The identification and quantification procedure of solvents was performed by CALCMET[®] multicomponent analysis software provided with the analyser. The procedure is based on the modified classical least-squares (CLS) analysis algorithm. In this procedure, the maximum amount of precomputed information is utilised for making the spectra analysis as simple and as fast as possible. The basic difference compared to the common CLS algorithms is that the algorithm fits the measured unknown spectrum

using a set of single component calibration library spectra (Saarinen & Kauppinen, 1991). Likewise, there is no need to define specific analytical spectral regions for each component where it is analysed. If necessary, all the data points in the spectra can be used for fitting the response curve. The typical data processing and transfer time is 2–3 s. The closed cell FTIR analyser was equipped with the computer-controlled multipoint-sampling unit (Fig. 5). The air samples were taken continuously over work shifts / days. A sampling time for each line was 30 seconds to 5 minutes including spectral scanning time of 15 - 30 seconds. The time constant of analyzer was three seconds at a sampling flow rate of 24 l min^{-1} and a cell volume of 1.1 liter.

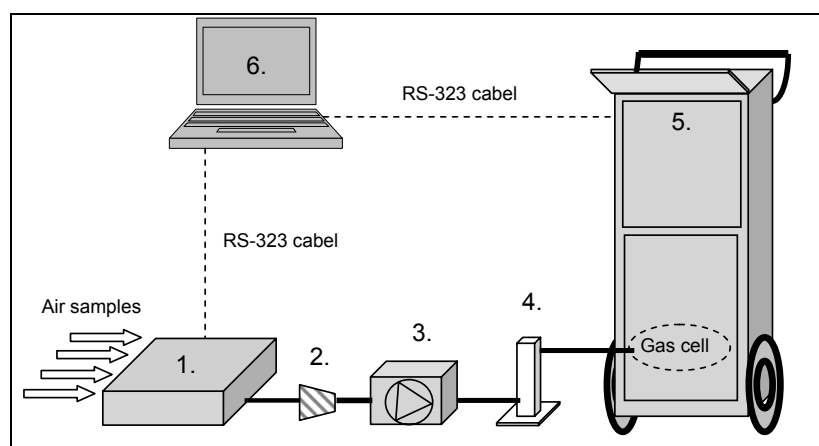


Figure 5. The multipoint sampling system. (1= multipoint sampling unit; 2= particle filter; 3= pump; 4= flowmeter ; 5= closed cell FTIR analyser ; 6= computer).

The closed cell gas analyzer was calibrated in the laboratory under a nitrogen atmosphere by using the dilution method. The closed loop calibration system had a volume of 10.4 l and contained a dilution glass cell and a gas analyser cell, and a membrane pump, Teflon tube and stainless-steel valves. The valves were used for connecting the system either to a closed loop circulation (calibration mode) or to an opened circulation (flushing mode). The reference spectrum was produced by injecting a known mass of liquid analyte into the system. The complete evaporation of analyte was confirmed by heating the injector up to $60 \text{ }^\circ\text{C}$. After the solvent concentration in the system was equally distributed, the IR spectrum was collected and stored onto the reference library on the hard disk of the analyzer, together with the concentration information. The reference was then checked by analyzing pure samples under a

nitrogen atmosphere at five different concentrations, which covered the expected range to be measured. The references were also checked under the laboratory air atmosphere (air temperature 20–22 °C, relative humidity 25–35%, concentration of CO₂ 300–500 ppm) by analyzing mixtures of the compounds at five different concentrations. The limit of detection (LOD) for the solvents was determined in two cases, that of the individual compounds under a nitrogen atmosphere and that of the mixtures under an air atmosphere. In addition to the laboratory calibration, the performance of the analyzer was also checked in the field in a closed loop calibration system (loop volume 1.2 l). The checking was performed both at the beginning and at the end of the measurement period at solvent mixture concentrations of 70–90 mg m⁻³. For and LOD determinations in the laboratory calibrations, 30 spectra were collected using a 20 s spectra averaging time. Spectral overlap from water vapor and carbon dioxide was reduced by including the references of both compounds in the analysis procedure. A background spectrum of the field conditions was obtained by extracting the workroom air through a charcoal filter. The detection limits for the solvents monitored were less than 6 mg m⁻³ and for tracer gas (N₂O) 2 ppm (Table 4.). An example of a reference calibration spectrum of tetrachloroethylene is shown in Figure 6.

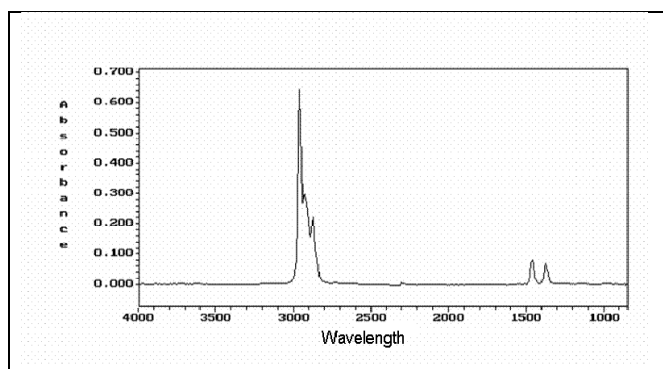


Figure 6. Reference spectrum of tetrachloroethylene (closed cell FTIR analyzer).

The solvent concentrations were on-line monitored from fixed points in working zones and, when possible, from exhaust air ducts. The air samples were taken continuously over work shifts or workdays by using a computer-controlled multipoint-sampling unit (Fig 5.) from two to six sampling points. The spectral data were collected at the resolution of 8 cm⁻¹ using the spectra averaging times of 15-30

seconds. A sampling time for each line was 30 to 180 seconds resulting in the total cycle time for all sampling lines of two to fifteen minutes (I-III)

4.3 Open path FTIR monitoring & calibration

The measurements of solvent concentration in resin and plastic lamination plants, saw mills as well as offset and rotogravure printing houses were conducted by using an open path FTIR analyzer (Bomem MR100 LP, Bomem Inc. Quebec, Canada) (Figure 7). The analyzer transmits the infrared beam (with an IR-source temperature of 1300 K) through a telescopic system to the remote retroreflector (with an area of 0.25 m²) consisting of gold-coated, corner cube mirrors. A liquid nitrogen-cooled *Hg-Cd-Te* detector (detector value *D= 5.2 x 10¹⁰) detects the returned beam. The interferograms were collected double-sided from a spectral region between 7000–450 cm⁻¹. Depending on the resolution (1, 2, 4, 8, 16 or 32 cm⁻¹), the scanning rate varies between 0.5 - 3.6 scans s⁻¹. The interferograms were converted to the spectra by the Grams/32 software (Galactic Inc., New Hampshire, USA) installed in the 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⁽⁸⁾.

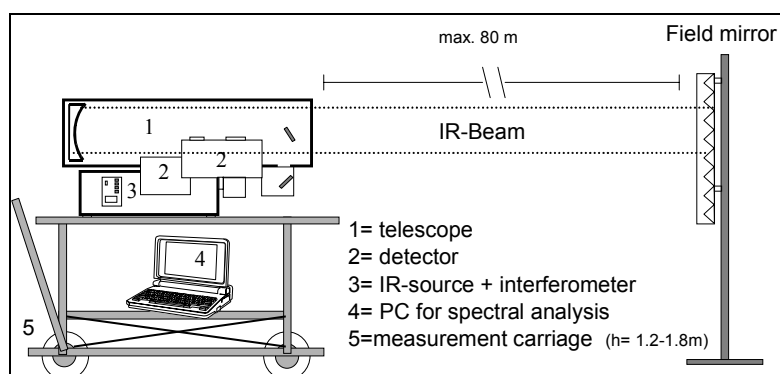


Figure 7. The open path FTIR measurement system

Unlike conventional FTIR analyzers there is no general accepted procedure for the calibration of OP FTIR analyzers. The difficulty of the calibration arises from the fact that the beam is open to the

atmosphere. The commercial calibration spectra data bases are used quite often (Svedberg et.al, 2002). Another way is to use measurement chambers with known concentrations. Our calibration system consisted of a solvent evaporation system, a mixing chamber (volume of 40 m³), and a calibrated closed gas cell FTIR-analyzer (Figure 8). The closed cell analyzer has a measurement uncertainty of less than 10% at the concentration range of 8 - 15 000 mg m⁻³. During the calibration, the solvent concentration was measured in the middle of the chamber. The solvent vapor was generated by bubbling air (2 l/min) through liquid solvent in a 250 ml glass bottle kept at 40°C temperature. The evaporated solvent-air mixture was lead through a Teflon tube (id 4.7 mm) into the chamber's supply air duct. 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 completing the solvent mixing with the air. The homogeneity of the solvent concentration in the chamber was checked by a photoionization detector (MiniRAE Plus, RAE System Inc., California, USA).

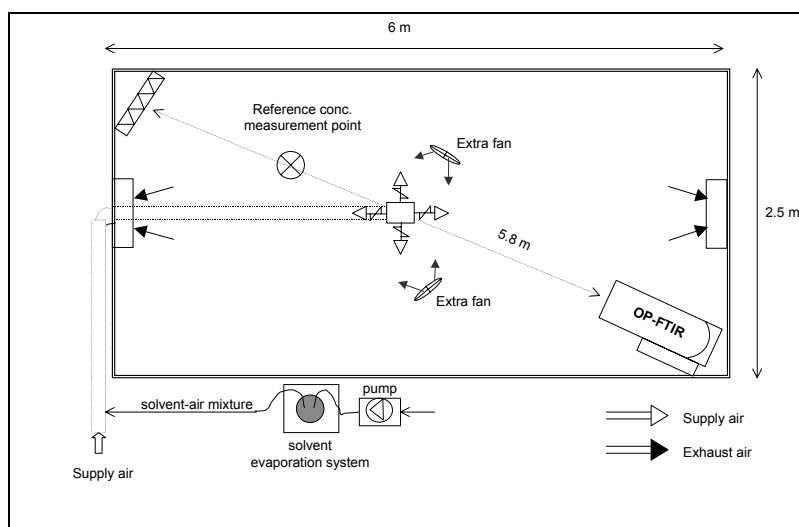


Figure 8. Calibration system for open path FTIR (IV)

The open path FTIR-system's optical path length in the chamber was 11.6 m. After the solvent concentration reached steady-state, the IR spectrum was collected and stored onto the computer's hard disk with the concentration information. The background spectra were taken from the ambient air (air temperature 18-22 °C, relative humidity 10 - 35 %, CO₂ concentration 390-410 ppm) in the chamber prior to the solvent evaporation. In the calibrations, spectral data were collected at the resolution of 8

cm^{-1} with the spectra averaging time of 160 sec. The detection limits (LODs) for solvents monitored were less than 0.4 ppm-m (see Table 5).

The open path FTIR (Bomem) measurements were accomplished by setting the IR-beam so that it passed through the working areas at a height of 1.5 m. The optical path lengths of 10 -32 m were used. An example of an open-path FTIR measurement configuration is shown in Figure 9. The spectral data were collected at the resolution of 8 cm^{-1} using the spectra averaging times of 40-60 sec. The background spectra were obtained from the workroom air early in the morning before the production started (III-VI). At one sawmill, the open path measurements were made using BOMEM MB 100 instruments instead of Bomem MR100 LP. This instrument was used by Swedish researcher, Urban Svedberg and its details are described elsewhere (III).

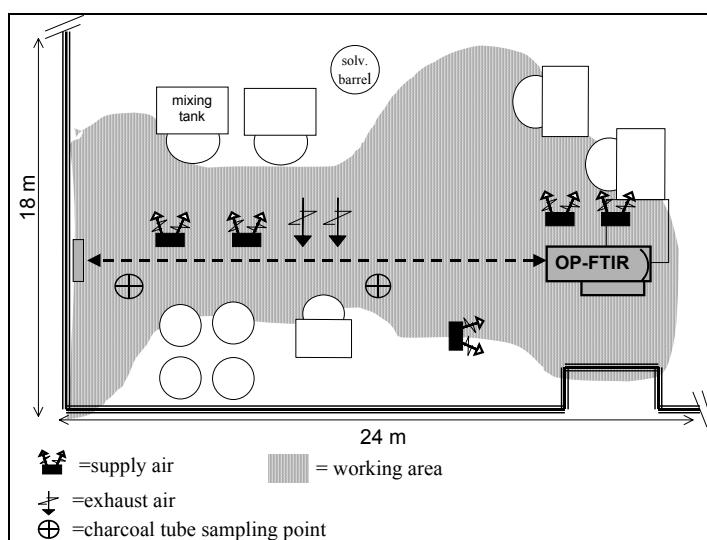


Figure 9. The open path measurement configuration in a paint manufacturing plant (IV).

4.4 Limits of detection

The limit of the detection (LOD) may be defined as the concentration of analyte that provides a detector response that exceeds the instrument noise level by three standard deviations (SD) above the mean of the instrument noise. The detection limits for the target compounds analysed for the closed cell FTIR and OP FTIR analyzers are presented in Tables 4 and 5.

Table 4. The analytical spectral regions, the detection limits and the reference spectra concentrations for closed cell FTIR analyzer.

Compound	Analytical region (cm ⁻¹)	LOD (mg m ⁻³)	Reference concentration in the sample cell (mg m ⁻³)
Tetrachloroethylene	950-3000	6.0	450
Ethyl alcohol	950-3000	1.3	433
Propan-2-ol	950-3000	1.8	304
1-methyl-2-propan-2-ol	950-3000	0.3	354
Ethyl acetate	950-3000	0.6	433
Monoterpenes	950-3000	1.0	361

LOD= limit of detection

Table 5. The analytical spectral regions, the detection limits and the reference spectra concentrations for OP FTIR analyzer.

Compound	Analytical region (cm ⁻¹)	LOD (ppm-m)	Reference concentration in the chamber (mg m ⁻³)
Ethyl alcohol	950-1500	0.05	360
Isobutyl alcohol	950-1500	0.15	284
Xylenes	1315-1670 2690-2800	0.4	310
Styrene	890-1100	0.4	208
Acetone	1600-1900	0.04	340
Isopropanol	950-1500	0.1	400
Toluene	950-3200	0.2	90

LOD= limit of detection, normalised concentration to a 1-m path length (path length in calibration was 11.6 m)

4.5 Charcoal tube and passive monitor sampling

The FTIR measurement results were compared with charcoal tube samples taken at the IR- beam or at the FTIR-sampling points. The charcoal tubes were sampled and analysed according to the procedure standardized in Finland (SFS Standard 3861).

In dry cleaning shops, the general area samples were also collected at 3-6 points in working zones depending on the size of the establishment using charcoal tubes and passive monitors (3M organic vapor monitors 3500). The quantitative determination of dry cleaning solvent concentration followed the standard procedure outlined in the NIOSH method 1003 for halogenated hydrocarbons (NIOSH 1003 method).

4.6 Checking of the spatial distribution of solvent concentration

The short-term photoionization detector (PID) measurements were performed in order to obtain an estimate of the solvent concentration stratification within the production room. The PID measurements revealed that no notable concentration stratification occurred in the studied workrooms. Consequently, the measured mean FTIR-concentrations in working areas could be used as estimates of room-average concentrations in the emission calculations

4.7 Air flow rate measurements

The total air flow rate in a work room was measured by using the tracer gas or pitot tube technique. In the tracer gas technique, the concentration-decay method was used (Kalliokoski et. al 1980, Niemelä et al., 1984). The tracer gas (dinitrogen oxide or sulphur hexafluoride) was released at the center part of the room with the mixing fan or into the inlet air duct in order to obtain perfect mixing. The concentration was measured using FTIR analyzer simultaneously with the solvent monitoring. The air change rate (n) was determined from the slope of concentration decay curve using equation 5.

$$\text{Equation 5.} \quad n = (\ln C_0 - \ln C_t) / t$$

where:

- n = air change rate ($1h^{-1}$)
 C_0 = concentration at the time when the decay starts
 C_t = concentration at time t
t = time interval between C_0 and C_t .

An example of tracer gas concentration curve is shown in Figure 10. As an alternative, the exhaust airflow rates were measured from the exhaust ducts according to the ISO 3966 standard.

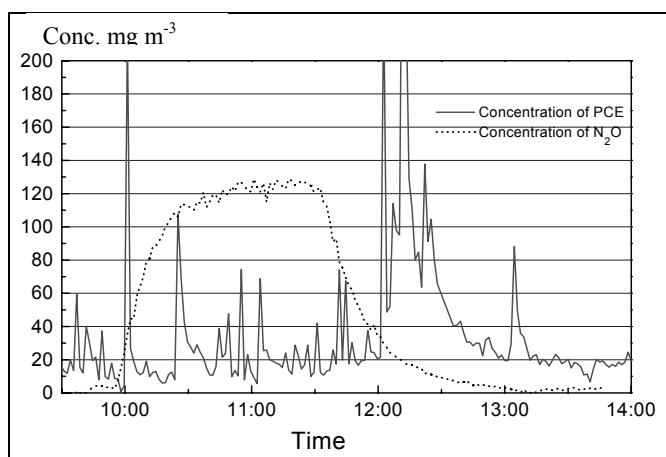


Figure 10. An example of a tracer gas (N_2O) decay curve and temporal variation of a tetrachloroethylene (TCE) concentration in a dry cleaning shop (II).

4.8 Emission rate calculation

The solvent emission rate into a workroom was determined by multiplying the room average concentration by the total airflow rate or the concentration in general exhaust air by the exhaust flow

rate. The room average vapour concentration was estimated in terms of the concentrations at the fixed points (closed cell FTIR) or in the measurement lines (OP FTIR).

The outdoor emission rate was determined by summing the product of the exhaust air flow rate and the average concentration in exhaust air or in the nearest suction area of a ceiling exhaust fan.

When possible, the emission rates were also related to production or use rates, and thus the results were comparable among similar processes.

5. RESULTS

5.1 Dry cleaning

Data obtained from dry cleaning processes are presented in article (II).

The shop-mean TCE emission rates were higher in industrial plants (39.8 g h^{-1}) compared to that of the shops (15.7 g h^{-1}). The emission factors, i.e. evaporated mass of TCE per cleaned mass of cloths, varied between $0.3\text{-}2.8 \text{ g kg}^{-1}$ in the industrial establishments and between $4\text{-}3.6 \text{ g kg}^{-1}$ in commercial shops. The lowest TCE emissions were observed from the processes that used underpressurized drums and extended drying times. The mean emission (0.3 g / kg of cleaned clothes) was nearly 90% less than the emissions in the other shops (mean 2.6 g / kg). It seems that this kind of control technique is suitable for reducing TCE emissions and exposures in dry cleaning processes. The highest emission (3.6 g/kg) was observed in the establishment in which a TCE leak from the machine occurred. Slightly increased emissions were observed also in the industrial plant (2.8 g/kg) that had an underpressurized washing drum, but where short drying times were used. The mean TCE emission rate versus dry cleaning rate is shown in figure 11. The data in this study yielded a relationship between the TCE emission rate m (g h^{-1}) and cleaning rate cr (kg h^{-1}): m (g h^{-1}) = 2.2 ± 0.3 (g kg^{-1}) * cr (kg h^{-1}).

The shop-mean indoor air TCE concentrations were in the range $5\text{-}36 \text{ mg m}^{-3}$ and the total air flow rates varied between $180 - 4100 \text{ l s}^{-1}$, corresponding to air change rates at 2.4 to 14.6 h^{-1} . The cleaning rates ($30\text{-}88 \text{ kg/h}$) were clearly higher in the industrial plants than in the commercial shops ($4\text{-}20 \text{ kg/h}$).

In dry cleaning shops, the general area samples were also collected at 3-6 points in working zones depending on the size of the establishment using charcoal tubes and passive monitors. The parallel charcoal tube /passive monitor and FTIR sampling showed a good agreement, taking into account the fact that the comparison was made under field conditions.

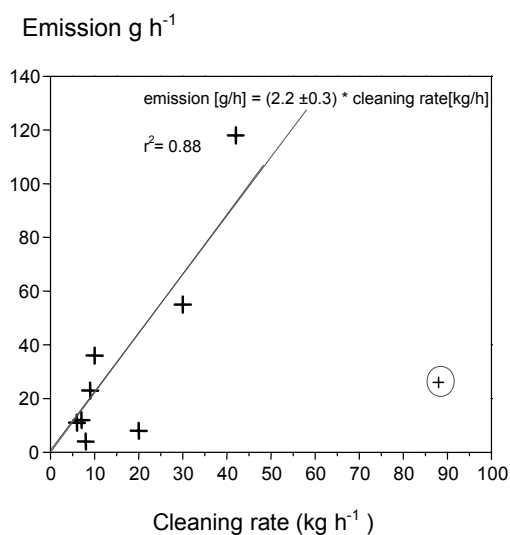


Figure 11. The mean TCE emission rate (m) to room versus cleaning rates (cr). The circled data point is not included in regression analysis since this was obtained from the site with effective control of TCE-emissions (II).

5.2 Ink manufacturing

Original data is published in article I.

The mean total solvent emission over a 48 h measurement period was 1.8 kg h⁻¹. However, a notable temporal variation of emission occurred with the peak value of 10 kg h⁻¹. The strongest emissions were released from the blending department.

The ethanol, ethyl acetate and propan-2-ol concentrations varied in the exhaust air widely, by up to three decades, while the concentration of 1-methoxy-propan-2-ol was below the detection limit for most of the time. The widest variation was observed for ethanol from a concentration level of a few mg m⁻³ up to 1800 mg m⁻³. The peak concentrations of solvents were 3–26 times higher than the

corresponding mean values. The highest concentration peaks in the exhaust air were observed during the ink blending and weighing operations.

The total volumetric exhaust air flow rate, $18\,000\text{ m}^3\text{ h}^{-1}$, consisted of $4700\text{ m}^3\text{ h}^{-1}$ in the mixing department, $3300\text{ m}^3\text{ h}^{-1}$ in the dispersing department, $9300\text{ m}^3\text{ h}^{-1}$ in the blending department and $700\text{ m}^3\text{ h}^{-1}$ in the weighing department, respectively.

5.3 Paint manufacturing

Original data is presented in article **IV**.

The mean total solvent emission into the workroom during paint manufacturing was 0.47 kg h^{-1} .

The main compounds found and analysed from the IR-spectra were xylenes, ethyl alcohol and isobutyl alcohol. The charcoal tube samples revealed traces of ethyl benzene, butyl acetate, ethyl acetate, and solvent naphta but they were not included in the quantitative spectral analysis. The mean xylene, ethyl alcohol, and isobutyl alcohol concentrations along the beam path were 37 , 11 and 10 mg m^{-3} , respectively. The open path FTIR monitoring showed that the solvent concentrations rose during the morning shift (Fig. 12). During the highest production rate (three simultaneous blending operations being done), the maximum concentrations of 128 mg m^{-3} for xylenes and 68 mg m^{-3} for ethyl alcohol were observed. The exhaust airflow rate from the production room of the paint manufacturing plant was $8\,000\text{ m}^3\text{ h}^{-1}$. The temporal variation of solvent concentrations at the paint manufacturing plant monitored by open path FTIR-system is shown in Figure 12.

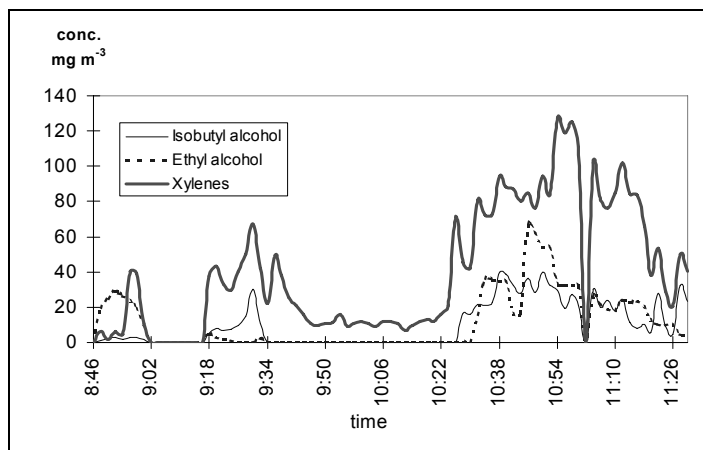


Figure 12. An example of a temporal variation of solvent concentrations in the work air during paint manufacturing (open path FTIR monitoring) (IV).

5.4 Resin manufacturing

Original data is presented in article IV.

In the resin manufacturing plant, the mean solvent emissions into the workroom during resin manufacturing were 0.34 kg h^{-1} . The beam-average styrene and acetone concentrations over a workday were 8 mg m^{-3} and 10 mg m^{-3} , respectively. The temporal variation of styrene concentration in work air was relatively small. The short-term concentration peak (15 mg m^{-3}) was twice as high as the mean value. The exhaust airflow rates from the production room of the resin manufacturing plants was $19\,300 \text{ m}^3 \text{ h}^{-1}$.

5.5 Fresh wood sawing

Data from fresh wood sawing is presented in article III.

During pine sawing, the mean terpene emissions were 150 and 100 g/hour per unit volume production of sawn material (cubic meters per hour), in summer and in winter, respectively. The higher terpene emissions in the summer period are due to the higher ambient air temperatures. During spruce sawing,

the total mean terpene emissions were 21 and 11 g/h per unit volume production of sawn material (cubic meters per hour), in summer and in winter, respectively. Terpene emissions during pine sawing were approximately 10 times higher than those encountered in spruce sawing.

The mean terpene concentration was calculated for each sawmill from average concentrations measured at one to three points (two samples per point). The summary of mean indoor air terpene concentrations is presented in Table 6.

Table 6. Mean total terpene concentrations between sawing lines (III).

Sawmill	Total terpene concentration(mg/m ³)	
	Spruce sawing	Pine sawing
Sawmill A, Winter (n=4)	12	170
Sawmill B, Winter (n=2)	-	160
Sawmill C, Winter (n=6)	16	-
Sawmill A, Summer (n=4)	26	250
Sawmill B, Summer (n=2)	-	240
Sawmill C, Summer (n=6)	11	-

n= number of samples

- no measurement value

The air exchange rate varied from 1.3 to 1.6 exchanges per hour during wintertime and from 1.8 to 2.7 exchanges per hour in summer. The total exhaust airflow rate (m³/h) per produced m³ sawn material was 518-609 in winter and 369-1267 in summer. In saw mill A, the exhaust air flow rate of the bandsaw was about 30 % of the total exhaust air flow rate and in saw mill C it represented 50-70 %

5.6 Offset printing

Original data is presented in article (VI).

In offset printing houses, isopropanol mean concentrations in exhaust air were 41 and 92 mg m⁻³ and exhaust air flow rates to outdoor air 7 600 and 17 200 m³ h⁻¹ corresponding to outdoor emissions values of 0.24 and 0.71 kg h⁻¹. The solvent emissions released to indoor air were higher compared to those

releasing to outdoor air. This is explained by the fact that 70 % of the general exhaust air was circulated back to the printing hall without cleaning and rest of it (30 %) was released to the outdoor air.

The mean solvent concentrations in work air were 39.8 and 49.8 mg m⁻³ and air flow rates 26 000 and 58 000 m³ h⁻¹ from which the calculated indoor solvent emissions were 1.0 and 2.9 kg h⁻¹. The mean emission through the local exhaust from one offset printing machine was 0.24 kg h⁻¹.

5.7 Rotogravure printing

Original data is presented in article (VI).

In the rotogravure printing house, the mean solvent concentration in work space was 302 mg m⁻³ and the air flow rate was 70 000 m³ h⁻¹. These values correspond to a mean indoor emission rate of 21 kg h⁻¹.

As expected, toluene emissions started when printing started and its indoor air concentration increased during the printing process. The maximum concentration of 490 mg m⁻³ was observed at 12.00 hours. The OP FTIR monitoring results showed that there is no significant concentration peaks.

5.8 Summary of results

A summary of the main results i.e. ventilation and air flow rates, mean solvent concentrations in the work air, the mean indoor and outdoor emission rates as well as emission factors (I-VI) are presented in Tables 7 and 8. The indoor and outdoor solvent emissions were in the range 0.02- 21 kg h⁻¹ and 0.02 – 9.98 kg h⁻¹, respectively. As expected, the solvent emissions varied extensively due to production rate and process phases. The emission factors in the manufacture of paint, ink and resin varied between 0.01-0.1 % of solvent input mass. In dry cleaning shops and in saw mills, the emissions were related to cleaning rates or produced wood mass. In saw mills slightly higher emission factors were observed in summer time than in winter due to the higher ambient air temperatures and possible changes in the composition of wood. In the studied industrial plants, the mean solvent concentrations in work air varied between 10 – 305 mg m⁻³ and the air flow rates were in the range 1 000- 70 000 m³ h⁻¹.

Table 7. Summary of the concentration, air flow rate and emission measurements (I-VI).

Process	Q (m ³ /h)	n (1/h)	Mean total solvent conc. in work air (mg/m ³)	Mean total indoor emission (kg/h)	Mean total outdoor emission (kg/h)	Article in the thesis
Manufacture of Ink	18 000	5.0	100	-	1.80	I
Mixing dept	4 700	4.5	21	0.10	-	
Manufacture of Paint	8 000	1.0	58	0.46	-	IV
Manufacture of resin	19 300	12	18	0.35	-	IV
Dry cleaning						
Ind. establishments	7 400	9.6	10.0	0.04	0.04	II
Commercial shops	1 000	3.9	16.1	0.02	0.02	
Pine sawing						
Winter	26 300	1.6	165	4.51	4.33	III
Summer	40 700	2.6	245	7.42	9.96	
Spruce sawing						
Winter	26 300	1.6	14.0	0.27	0.37	III
Summer	40 700	2.6	18.5	0.67	0.75	
Laminating of plastic	8 000	2.9	120	0.6	-	V
Offset printing						
Printing house A	26 000 ¹	1.0	39.8	1.0	0.52 ¹	VI
Printing house B	58 000 ¹	1.9	49.8	2.9	0.71 ¹	
Rotogravure printing	70 000	5.8	302	21	-	VI

- Not determined

Q = total exhaust air flow rate

n = air exchange rate index

¹ Total air flow rate to outdoor air from the printing hall. 30 % of it was led to outdoor air, with the rest being circulated back to the printing hall as the supply air

Table 8. Emission factors in sampling site processes (I-VI).

Process	Emission factor, indoors	Emission factor, outdoors	Article in the thesis
Manufacture of ink	1 % of solvent mass used	-	I
Manufacture of paint	0.1% of solvent input mass	1 % of solvent input	IV
Manufacture of resin	0.01 % of solvent mass used	-	IV
Dry cleaning			
Industrial establishments	1.7 g per kg of cleaned clothes	1.7 g per kg of cleaned clothes	II
Commercial shops	1.8 g per kg of cleaned clothes	1.8 g per kg of cleaned clothes	
Saw Mills (pine)			
Summer	0.13 kg per m ³ produc. wood	0.16 kg per m ³ produc. wood	III
Winter	0.08 kg per m ³ produc. wood	0.10 kg per m ³ produc. wood	
Saw Mills (spruce)			
Summer	0.02 kg per m ³ produc. wood	0.02 kg per m ³ produc. wood	III
Winter	0.007 kg per m ³ produc. wood	0.02 kg per m ³ produc. wood	
Laminating of Plastic	-	250 g per laminating -m ²	V
- Not determined			

6. DISCUSSION

In this work, solvent mixture concentrations were continuously monitored in on-going industrial processes using open path (OP FTIR) and closed cell FTIR analyzers in order to determine solvent emission rates into work spaces and to the outdoor air. A secondary aim was to collect data on solvent emissions from different kinds of industrial processes.

6.1 The applicability of FTIR analyzers for monitoring solvent concentrations

In the field measurement sites, the temporal variation in the solvent concentration was rather high, up to forty fold difference between the lowest and highest values. The highest concentrations were found in the exhaust air ducts. The dynamic range of the low-resolution closed cell FTIR-instrument with a short absorption path of 3 m was wide enough to detect even the highest concentrations. The dynamic range of open path FTIR with a ten time longer absorption path was also found to be wide enough to cover the concentration peaks in the workplace air. According to laboratory determinations, the detection limits were 0.4 ppm-m or less for the open path instrument and around 1 ppm or less for the closed cell instrument. Similar level of sensitivities of closed cell and OP FTIR analyzers have been previously reported (Herget&Levine, 1986; Levine et al., 1989; Ahonen et al., 1996; Svedberg&Galle, 2000). The sensitivity of both instruments was good enough for concentration monitoring in these types of processes using a high volume of solvents. If necessary, the sensitivity of the FTIR-instruments can be increased by increasing the optical path length (OP-FTIR) or by increasing the number of the scans (Griffiths & Haseeth, 1986).

In saw mills, dry cleaning shops as well as in offset and rotogravure printing houses, there was only one target solvent present in the work air. In the rest of the measurement sites, the solvent mixtures in the work and exhaust air were rather complex, consisting of up to six main compounds. In addition, small amounts of non-target compounds were also present in air, but these had no significant influence on the spectral analysis or the emission results. Some of the main compounds as well as water vapour had a significant spectral overlap, but concentrations of the dominant contaminants could be detected and quantified with sufficient accuracy by applying advanced spectral analysis software (Calcmeter[®]). The parallel charcoal tube and FTIR sampling revealed a

good agreement, taking into account the fact that the comparison was made under field conditions (Fig. 13).

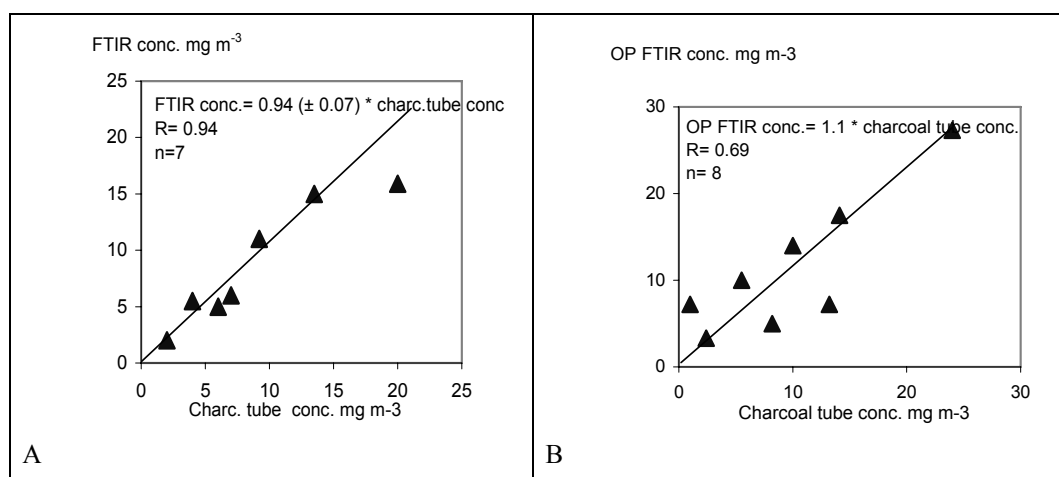


Figure 13 (A, B). Closed cell FTIR (A) and open path (OP) FTIR concentration (B) vs. charcoal tube concentrations, field comparison. Solvents monitored were tetrachloroethylene (closed cell FTIR) and the sum of ethanol, ethyl acetate and propan-2-ol (OP FTIR) (I and IV).

Based on the laboratory tests, the measurement uncertainty of the open path instrument for studied solvents in field conditions was estimated to be less than 15 % and for the closed cell instrument less than 10 % (I-V). At concentrations close to the detection limit (LOD), there was a higher measurement uncertainty. With the exceptions of those concentrations close to the detection limit, the accuracy of both instruments meets the requirements of the European Standard EN482 for the measurement of solvent concentrations in workplace air. Especially in the case of open path FTIR measurements, the instrumental error was negligible compared to possible errors in traditional stationary sampling due to unrepresentative selection of sampling locations.

The field measurements demonstrated that the open path and closed cell FTIR instruments are rather easy to transport and to operate in industrial environments. In the case of open path FTIR, a minimum of two persons was needed for setting up and operating the measurement system. The typical set-up time of the closed cell analyzer was four hours but the open path system required less than one hour. The longer set-up time of closed cell analyzer is due to gas cell temperature

stabilization, which is not required in the open path method. Both the OP FTIR and the closed cell FTIR spectrophotometers facilitate rapid identification of solvent components that are used in the manufacturing processes, near real-time display of concentration data relevant to workroom air and environmental monitoring, as well as process control. Furthermore, the near on-line concentration information from fixed sampling points in working area enables a rapid selection of representative sampling locations, detection of short term concentration peaks and characterization of source activity. Thus, this on-line monitoring feature means that the FTIR-technique has many uses in various kinds of industrial hygiene and environmental applications compared to traditional integrated methods (e.g. charcoal tube sampling). One significant advance with both FTIR instruments is that no sample handling and storing are required. One considerable benefit with the open path instruments is that no sampling lines, pumps, or sample cells are needed.

Although the open path (OP) and closed cell FTIR instruments offer a feasible method for solvent mixture monitoring, some practical issues related to work place measurements and calibrations are discussed here. The selection of the open path FTIR-analyzer's IR-beam orientation becomes an important issue in workplaces. Beam blockage due to the movement of a worker or equipment may cause baseline shifts and decrease the sensitivity. Also vibration may disturb the internal alignment of the FTIR and increase SNR. For the open path FTIR-instrument dust and aerosols in the measurement line can disturb the spectral analyses and increase SNR. In the case of the closed cell instrument, it is essential to ensure that condensation, moisture or dust does not damage the internal gas cell. For this reason, particle filtration is usually applied. With OP FTIR measurements, it is not always easy to collect a clean background spectrum, because significant amounts of target compounds may be present in the air. The background spectrum can be measured in the laboratory atmosphere (Xiao et.al 1994). Another way is to collect the background spectrum from the work place atmosphere before the process is started *i.e.* when the concentration of target contaminants will be negligible. In our experience, the work place atmosphere is a better alternative rather than using a laboratory background. In this way, the spectral analysis errors due to atmospheric water vapor and carbon dioxide can be minimized and errors due to changes in measurement configurations avoided. However, it is important that before one collects a background spectrum to ensure that the atmosphere does not contain any significant amounts of target compounds. This can be done for example by using a photoionization detector with sufficiently low detection limit. For a

closed cell analyzer, a background spectrum can be more easily obtained from the work place atmosphere by directing the air through a charcoal tube filter before spectral analysis in the sample cell. However, even if a clean background can be obtained, instrument fluctuation and changing environmental conditions (*e.g.* humidity) over the measurement period may require the collecting of additional background for a better spectral analysis result. The poor background can be handled also by creating a synthetic background, for example using a background suppression method (Giese-Bogdan et.al, 1999).

The open path FTIR used in these studies was equipped with a liquid nitrogen cooled MCT detector. The liquid nitrogen dewar had to be refilled every four hours, which caused practical problems in long-period monitoring. The closed cell FTIR, on the contrary, had an electronically cooled detector, which enabled also long-term monitoring (no need to refill dewar).

One difficulty with calibrations and validations of OP FTIR systems is that the IR beam is open to the atmosphere. In closed cell FTIR analyzers, the IR beam is enclosed in an internal cell that can be purged with a known concentration of the target compound. A research group from USA has designed a special calibration cell for the OP FTIR (Farah and Todd, 2000). To evaluate the instruments accuracy, the calibration cell can be purged with a known concentration, and compared it with OP FTIR measurement results. In our work, the open-path instrument was calibrated in the laboratory using a dilution method. In principle, the method is similar to that described by Farah and Todd used: instead of a small cell we performed the calibration in a laboratory chamber (III-VI). Although the dilution method calibration in a laboratory chamber is quite laborious, it minimizes the instrumental errors and can therefore be an alternative to commercial calibration library spectra, though these are rather widely used in FTIR-spectroscopy (Ahonen et al., 1996; Svedberg & Galle, 2000; Svedberg et al., 2004). In addition to the laboratory calibration, the field measurement results were checked, by collection of charcoal tube samples from the OP FTIR measurement line. The closed cell spectrometer was checked also in the field, before any actual measurements took place, in order to guarantee that the FTIR instrument was in proper (especially alignment process) condition after its transportation to the measurement site. The checking procedure was relatively simple to conduct even in a hostile industrial environment. No field check of open path FTIR was

done although this could theoretically be possible by using a portable calibration tube through which the IR-beam would travel.

One disadvantage with FTIR systems is that they are usually considered to be a more advanced special technique than the standard method for use in industrial hygiene or environmental measurements. For this reason, very few compact, ready to use, commercial systems have been marketed. Another disadvantage of FTIR systems is the relatively long training period that is needed for novice users. The instrumental costs of FTIR systems, however are not very high e.g. when compared to the costs of gas chromatograph equipped with a mass selective detector (MSD).

6.2 Determination of the space average concentrations

Due to the of rather high complicity of determinations of the space average concentrations in work rooms, some important issues related to the FTIR-measurement strategy will be discussed here.

In work rooms, where solvent concentrations vary widely temporally and spatially, the open path (OP) FTIR monitoring is the preferable technique for determining space average concentrations. The closed cell FTIR together with multipoint sampling may also be used for the estimation of space average concentrations in cases when a spatial concentration variation within the workroom air is not too high or when the concentration can be monitored from the exhaust air.

In the OP-FTIR monitoring, the selection of a measurement line(s) is an important issue. In the resin manufacturing plant, sawmills and in offset and rotogravure printing houses, the estimates of room average concentrations could be obtained from single OP FTIR measurement line with a length of 10 to 35 m. In very large production halls with many sources, it may be necessary to obtain concentrations from several independent lines. In our OP FTIR system, a measurement line up to 80 m can be applied. In principle, OP FTIR measurement configuration with different shapes of lines can also be applied. These kinds of measurement applications, however, require three or more remote field mirrors. In the study of Xiao et.al (1991), for example, M-shaped measurement line was used for the on-line monitoring of methylene chloride, acetone, 2-propanol, methanol and toluene concentrations during furniture stripping. OP FTIR measurement configurations with up to 18 beam

paths have been reported, though only in laboratory test rooms (Todd & Ramachandran, 1994; Todd, 2000).

Before OP FTIR orientation and measurement configuration can be set up, it is essential to obtain an estimate of the spatial concentration distribution, including s stratification of concentrations in the workroom air. In the case where there is a notable stratification, a correction factor may be used in order to transform the beam path average concentration to reflect the average concentration of the room space. Another way is to conduct the OP-FTIR measurements at different heights.

6.3 Solvent emissions

In the determination of the indoor solvent emissions, it is essential to determine the space or room average concentration data together with the ventilation information. The simultaneous monitoring of solvent concentration and a tracer gas in the work space or in the exhaust air enables the determination of the airflow rate. When the tracer gas measurement is conducted in the room space uncontrolled exhaust airflow rates, are also taken into account. In this way, it is also possible to obtain an estimate of the fugitive emissions (VOC-directive demand).

In the studied industrial plants, the indoor and outdoor solvent emissions were in the range 0.02- 21 kg h⁻¹ and 0.02 – 9.98 kg h⁻¹, respectively. As expected, the solvent emissions varied strongly due to production rate and process phases. For instance, in paint manufacturing the highest solvent emissions occurred during the blending operation (I). The outdoor emissions in all studied processes were below the limit values listed in the VOC-directives.

The plant mean solvent concentrations in work air varied between 10 – 305 mg m⁻³. With the exception of rotogravure printing, the mean indoor air solvent concentrations were well below the Finnish OEL-values. In the rotogravure printing hall, the mean solvent concentration in air exceeded the Finnish OEL_{8h}-value by 50 % and the short term OEL by 80 %. These OP FTIR concentrations, however, can only be used as a rough estimate of personal exposures, since the printing workers spend most of their work time in the control room which is isolated from the printing hall. Similarly,

indoor air solvent concentrations in the rest of the studied workplaces do not reliably reflect personal exposure levels, since these processes typically included manual work tasks.

The solvent emission from the paint manufacturing plant to the ambient air was approximately 1.8 kg h⁻¹ yielding an annual average emission of 8600 kg, *i.e.*, 1% of the solvent input volume (I). This finding is in line with previously reported emission estimates of 0.3–2% from the paint manufacturing process (Air Pollution Engineering Manual, 1992). Data obtained from the commercial dry cleaning processes yielded a relationship between the indoor TCE emission rate m (g h⁻¹) and cleaning rate cr (kg h⁻¹) (Equation 6).

$$\text{Equation 6.} \quad m = 2.2 * cr \text{ (II).}$$

Previously, the following relationship has been found for the same variables (Moschandreas et al., 1995) (Equation 7).

$$\text{Equation 7.} \quad m = 0.58 * cr$$

In both studies, the emission rates were obtained by using similar methods, involving the determinations of average indoor solvent concentrations and total airflow rate. The dry cleaning machines in the studies were similar (closed type). Taking into account the measurement uncertainties under field conditions, the results are in fair agreement emphasizing the relatively low emissions from the dry cleaning machines. The FTIR-monitoring demonstrated that underpressurized drums and extended drying times are effective ways to control TCE emissions.

In the offset printing houses, the calculated indoor solvent emissions were 1.0 and 2.9 kg h⁻¹. Previously, indoor solvent emission rates from an offset printing shop have been reported by Wadden et al., 1995. In their study, emission rates were determined during offset printing by combining measured concentrations and ventilation rates with mass balance models. In this process, the solvent emission rate varied between 0.16 – 1.1 kg h⁻¹. These findings are in line with the

values of the emissions found in our study. In offset printing houses, outdoor isopropanol emissions were 0.52 and 0.71 kg h⁻¹. The emission from one offset press was 0.24 kg h⁻¹. The estimate of annual emissions, assuming 20 hours printing / day and 320 printing days per year, would be around 3.3 – 4.5 tons. The solvent emissions released to the indoor air were higher compared to those released into the outdoor air. This is explained by the fact that 70 % of the general exhaust air was circulated back to the printing hall without cleaning and the rest of it (30 %) was released to the outdoor air.

In the rotogravure printing house, the mean indoor emission rate was 21 kg h⁻¹. Previously, a total solvent emission rate of 222 kg h⁻¹ from a rotogravure printing house has been reported (Wadden et al., 2001). In this study, the solvent concentrations were measured from exhaust air ducts using the traditional charcoal tube method. The emission determined in the study of Wadden et al. involved releases via general ventilation and via local exhaust systems, while in our study the emission through local exhausts was not determined. It can be roughly estimated that the local exhaust efficiency of rotogravure press in our study was around 70-90 %. If using these assumptions, then the total emission, via general ventilation and local exhausts, would be between 70 – 210 kg h⁻¹. This is somewhat lower than that found in the study of Wadden et al. Nevertheless, both studies indicate that relatively high solvent emissions can occur from rotogravure printing processes.

In the study of Säämänen et al. (1991) styrene emissions during the hand lay-up moulding of reinforced polyester were determined under the laboratory conditions. Depending on the rolling area, styrene emissions of 0.43 – 0.55 kg/h were detected. In our study, the mean indoor emission in hand lamination process was 0.3 kg/h. This finding is consistent with the findings of Säämänen et al. (1991).

Based on the laboratory test, the measurement uncertainty of the open path FTIR analyzer for the studied solvents and gases under field conditions was estimated to be less than 15 % and for the closed cell FTIR analyzer less than 10 %. The measurement uncertainty for the emission rate, involving FTIR measurements of solvent and tracer gas concentrations is estimated to be 21 % for OP FTIR 14 % for the closed cell FTIR.

In this work, emission factors were determined for manufacture of paint, ink and resins, for dry cleaning, for fresh wood sawing and for plastic lamination (Table 8). The advantage of emission factors for indoor sources is that they remove the effect of the surrounding space from the description of the source. Emission factors can be used for estimating emissions from the same types of processes located at other sites. This kind of information is extremely valuable when designing engineering control measures or when assessing occupational or environmental exposure. The emission factors can be used also in developing exposure models for the assessment of chemical risks in workplaces.

Traditionally, solvent emissions to the outdoor environment have been more strictly regulated (VOC-directive, IPPC-directive) than the emission to work air (OH&S EU-directives). This can lead to a situation where outdoor emissions are reduced at the expense of the work air quality. In theory, the contaminant concentration in process exhaust air can be decreased by circulating part of the contaminant mass released back through the work air. Therefore, it is essential to ensure that the emission control strategies are designed in such a way that they do not impair work air quality or pollute the outdoor environment.

6.4 FTIR in exposure assessment applications

Workplace air is usually composed of mixtures of contaminants and their ambient concentrations can vary both in time and space. Traditionally, time-weighted average concentrations have been determined by using the charcoal tube or passive monitor methods. This type of sampling smoothes concentration fluctuations in time and therefore peak concentrations may not be observed. The temporal variation of concentration can be measured by using direct reading instruments, but they cannot identify compounds in mixtures. The FTIR systems provide near real time concentration information of compound in mixtures. Thus, the FTIR technique can be used for assessing both short and long term exposures to solvent mixtures.

With regard to the OP FTIR system, the ability to monitor contaminant concentrations in open air means that this technique is very attractive for some exposure assessments in a variety of applications: When the OP-FTIR measurements are conducted in the working zone, the beam

average concentrations may be useful generating of task specific exposure data. The beam (space) average information may also be useful in estimating group exposures. However, space average concentrations, however, may not always provide an optimal estimate for breathing zone concentrations if the worker is located near to the emission source.

The space average concentration information is needed when one wish to determine solvent emissions to work air. Reliable emission information can be subsequently used for the development of predictive exposure models. The emission information provides also a good basis for estimating worker's exposure levels in screening types of assessments.

7. CONCLUSIONS

In this work, a measurement strategy was developed for monitoring space average concentrations in workplace conditions in order to determine emission rates. Additionally, data on solvent emissions from different types of industrial processes was gathered. The following paragraphs list the main conclusions associated with the detailed study aims:

- The open path (OP) FTIR monitoring can be successfully used for determining space average concentrations in workplaces with high spatial and temporal variations of a single solvent or of solvent mixture concentrations (e.g. resin manufacture, fresh wood sawing, offset printing and rotogravure printing).
- The low resolution closed cell FTIR analyser with a short absorption path length (3 m) can be beneficially used for the measurements of solvent and solvent mixture concentrations in wide concentration ranges (e.g. manufacturing of paint and ink, fresh wood sawing, plastic lamination, dry cleaning, offset printing). The closed cell FTIR equipped with a multipoint sampling system can also be used for determining the space average concentration when spatial concentration variation is not too high, or when the concentrations can be monitored from the exhaust air.
- The FTIR concentration data can be successfully used for the estimation of space average concentration that is essential in indoor emission determinations
- Laboratory experiments demonstrated that the open path (OP) FTIR spectrometer can be successfully calibrated in the mixing chamber by the dilution method. This provides a preferable alternative to commercial calibration library spectra. The dilution method is suitable for the calibration of the closed cell spectrometer too.
- The simultaneous quantification of solvent mixtures and tracer gas could be done by taking advantage of advanced spectral analysis software (Calcmet ®) even though the air sample

was rather complex. The simultaneous monitoring of solvent concentration and a tracer gas enables airflow rate determination. When the tracer gas measurement is conducted in room space also uncontrolled exhaust airflow rates are taken into account and an estimate of the fugitive emissions may be obtained

- The FTIR-instruments are capable of performing continuous concentration monitoring of compounds in mixtures and also provide a good temporal resolution. These features make the FTIR-technique useful in many kinds of industrial hygiene and environmental applications. The FTIR technique should be considered as a consistent technique to be applied both in industrial hygiene and environmental monitoring tasks, even though advanced skills are required of the operator.
- In order to estimate emission rates from different industrial processes, concentration data together with ventilation information are needed. The development of an emission database is emphasized.

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