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# SINTEF REPORT

TITLE

**H&E TQP ID1:  
 Establish sampling and analytical procedures for potentially harmful components post combustion amine based CO<sub>2</sub> capture**

**Subtask 3: Online sampling and analysis**

**FM07-AJZ00-Z-RA-0002-03**

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**ABSTRACT**

The major objectives of the project are described in the Tender Invitation of H&ETQPAmine1: "Establishing sampling and analytical procedures for potentially harmful components for post combustion amine based CO<sub>2</sub> capture". The present report covers Subtask 3: Online Sampling.

A status of commercial available online analysers for emission monitoring of wet flue gas from absorbers for carbon capture is given. The response from most of the suppliers of traditional emission monitoring systems has been limited with respect to the requested compounds. This is primarily due to, for the time being, a non-existent market. New technologies have been considered, these are in general available for laboratory purposes. Most progress has been made for dedicated ambient air analysis and monitoring. However, these designs are to date only suitable for non-condensing gases. The instruments will need considerable improvements until continuous operation 24/7 with wet flue gas is possible.

The main challenge for all analysers considered for application is the requirement of non-condensing gas in the analyser for proper function. The heated sampling lines necessary in order to ensure complete evaporation of the gas sample is considered to be a challenge for achieving a representative analysis. Due to the high water content of the sampled gas, the temperature in such sampling lines needs to be relatively high, thus creating a potential for induced degradation and artefact formation in the gas sample.

The effects of heated sampling lines need to be investigated, as limited information is available on the subject. Depending of the outcome of such an investigations, SINTEF recommends two possible approaches for online gas analysis of the gas of interest:

- 1) If heated sampling line does *not* represent a problem for degradation and artefact formation of the gas sample, SINTEF recommends the use of an isokinetically operated sampling unit and a PTR-TOF-MS analyser with heating of the gas sample for the online analysis of the gas of interest.
- 2) If heated sampling line *does* induce degradation and artefact formation in the gas sample, SINTEF recommends the application of an *isokinetically* operated sampling unit, *cooled probe* and *condenser* which generates a dry flue gas that can be analysed by PTR-TOF-MS, IMS or FTIR (in that preferred order) with gentle heating of the gas (60°C). The collected liquid phase condensate can be semi-continuously analysed by an LC-MS and/or GC-MS for speciation and quantification.

A research project investigating the effects of heated sampling lines for a defined set of solvent systems can be completed within 6 months. A proof-of-concept study of SINTEFs suggested alternative setup avoiding heating of the gas can be completed within 6 months.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Process Technology	Prosessteknikk
GROUP 2	Measurement	Måling
SELECTED BY AUTHOR	Flue Gas	Røykgass
	Online Analysis	Online Analyse

## EXECUTIVE SUMMARY

### Challenge:

Online emission monitoring on a CO<sub>2</sub>-capture plant requires analyses which cope with the prevailing conditions (low flue gas temperature and high humidity) and expected low concentrations of trace compounds.

The flue gas contains large amounts of water, organic compounds like solvent amines and their degradation products. The expected high water concentration poses considerable challenges to analyzers with respect to detection limit and function of the analyzer itself.

Heated sampling lines with elevated temperatures in order to fully evaporate the wet gas sample are a potential risk for *degradation* and *artefact formation* in the sample. There is limited knowledge regarding the thermal stability of the compounds present in the gas mixture and today's sampling systems and analyzers require elevated sampling temperature (~180°C) to avoid condensation and to protect analytical equipment. At these temperatures, thermal degradation of MEA has been reported in long sampling lines.

In addition to water and organic compounds, the gas mixture of interest also contains oxygen, NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> among others, and heating of this complex gas mixture in long sampling lines could in theory lead to accelerated artefact formation and induce chemical change of the sample. This should especially be taken into consideration for gas mixtures containing NO<sub>x</sub> and secondary amines or other nitrosamine precursors in order to avoid artefact formation of nitrosamines during sampling.

### Status:

To our knowledge, no commercial analyser system from traditional flue gas monitoring e.g.: from refineries or waste incineration can be adapted to the compounds of interest. Substantial problems for these analysers arise from the type and number of organic compounds, their physical properties and their expected low concentration in sub-ppm range. Therefore a more fundamental investigation for this analysis is needed.

A comprehensive overview of technologies is established and the most promising have been evaluated. New technologies have been considered, these are in general available for laboratory style applications or tailor-made for single or few compounds of a subset of the compounds. Most progress has been made for dedicated ambient air analysis and monitoring, this development is driven by safety considerations. However, the design of the equipment is to date only suitable for non-condensing gases.

Only one commercial application is identified where an analyser operates continuously to monitor MEA emission in a CCS-plant, consisting of a heated sample line and FTIR system. The application of FTIR based analysers is possible; however the heated sampling lines, the accuracy and lower detection limits with off-the-shelf industrial systems are of concern, considering that a *high number of organic compounds* in a wet flue gas need to be analyzed simultaneously. The absorption spectrum of the individual compounds will overlap, making identification and quantification difficult. Further, higher water concentration in the flue gas will have negative influence on the analysis results. Available data are based primarily on laboratory projects and

need verification to ensure accuracy and repeatability also for multi-component mixtures in practice.

MS instruments generally allow specific analysis of a higher number of compounds, but require a non-condensing gas at the inlet and heated inlet is necessary. Instruments with PTR/soft ionization seem promising due to lower detection limits. Ion mobility spectroscopy (IMS) is also considered a possible methodology for the given task, but is regarded as a less generic tool compared to MS as it does not give molecular weights of the compounds analysed. Application of soft ionization MS or IMS analysers is with today's commercial analysers not possible as the appropriate sample transfer systems for gas feed to the analyser need to be developed.

### **Recommendation:**

The effects of heated sampling lines should be investigated, in order to determine possibilities and limitations for heating of the gas sample prior to analysis. SINTEF therefore recommends two possible approaches for online gas analysis of the gas of interest:

- 1) If heated sampling lines do *not* represent a problem for the stability of the sample or artefact formation, SINTEF recommends the use of an isokinetically operated sampling unit and a PTR-TOF-MS analyser with heating of the gas sample for the online analysis of the gas of interest.
- 2) If heated sampling lines *do* represent a problem for the stability of the sample or artefact formation, SINTEF recommends the application of an *isokinetically* operated sampling unit, *cooled probe* and *condenser* which generates a dry flue gas that can be analysed by PTR-TOF-MS or IMS with gentle heating of the gas (60°C). The collected liquid phase condensate can be periodically transferred to an LC-MS and/or GC-MS for speciation and quantification. In order to apply FTIR-analysis of this dry gas downstream the condenser, it is expected that a special gas cell with long optical path length (> 10 m) is required in order to obtain detection limits in the low ppbv range. SINTEF expects difficulties with obtaining detection limits in the low ppbv range by FTIR without lowering the water content of the sample prior to analysis.

### **Future work:**

The *stability* of the gas sample should be investigated regarding the effects of heated sampling lines in relation to sample line temperature, length and residence time of the sampling line together with sampling lines material selected. Further, artefact formation due to reactions with other flue gas components (NO<sub>2</sub> etc.) need consideration. The chemical stability of the gas sample should be studied by a reference method used to analyse a defined realistic gas matrix before and after sample transfer at different conditions by varying these mentioned parameters for the sampling line. From these experiments, it should be possible to determine whether the gas matrix undergoes chemical change due to the sampling procedure.

If the findings of this study show that heated sampling lines represent a problem regarding degradation and/or artefact formation of the sample, SINTEF proposes a proof-of-concept study of the two-analyser scheme with a knock-out-condenser and a subsequent dry-gas analysis downstream the condenser as described above in order to solve the problem.

## Abbreviations

BAT	Best Available Technology
BREF	Best Available Technology Reference Document
CEM	Continuous Emission Monitoring
CI	Chemical Ionization
DOAS	Differential Optical Absorption Spectroscopy
EI	Electron Impacts
IMS	Ion Mobility Spectrometry
IPPC	Integrated Pollution Prevention and Control
IR	Infrared
UV	Ultraviolet
LOD	Lower detection limit
NDIR	Nondispersive infrared
MCERTS	Environments Agency's Monitoring Certification Scheme (Great Britain)
MS	Magnetic Sensor
MS	Mass Spectrometry
NMHC	Non-Methane HydroCarbons
FID	Flame-ionisation detector
PID	Photo-ionisation detector
FPD	Flame-photometric detector
LC	Liquid chromatography
GC	Gas chromatography
TCD	Thermal conductivity detector
RH	Relative Humidity; 100% = dew point @ given temperature
PTR	Proton Transfer
PTR-TOF-MS	Proton Transfer Time of Flight Mass Spectroscopy
FTIR	Fourier transform infrared
CVF	Circular variable filter
UV-Vis	Ultraviolet-visible
GFC	Gas-filter correlation
TDL	Tuneable Diode Laser
TDLAS	Tuneable Diode Laser Absorption Spectroscopy
PTR	Proton Transfer
VOC	Volatile Organic Carbon
TOF	Time of Flight

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## 1 INTRODUCTION

### 1.1 Background

The fundamental objective of the planned CO<sub>2</sub> capture plants is to minimize the emission of CO<sub>2</sub> and contaminants in the treated flue gas released to the atmosphere. For the qualitative and quantitative measurements of the emissions it is crucial to establish appropriate measurement sites, sampling procedures, analytical procedures and subsequently evaluate automated analysers and if possible online-monitoring system. The aim of the present subproject (H&E TQP Amine 1.3) is to present “Automated analyzers” from the sweet gas stream exiting the absorber and water wash section, respectively. Procedures shall be universal applicable for both pilot plant test and full scale.

Further details about the background of the project are given in the tender document H&ETQPAmine1: Attachment A1: “*Scope of Service: Establish sampling and analytical procedures for potential harmful components post combustion amine based CO<sub>2</sub> capture*”.

### 1.2 Scope of work

In order to support the Company in the performance of comprehensive emission measurements both for process operation and required by authorities) procedures for sampling are presented. Literature (international standards and guidelines) is reviewed and appropriate procedures evaluated. The present work is a continuation of

- SINTEF Report F16317: H&E TQP ID1: Establish sampling and analytical procedures for potentially harmful components post combustion amine based CO<sub>2</sub> capture. Subtask 1: Design of Sampling Points in treated flue gas<sup>1</sup>
- SINTEF Report F16586: H&E TQP ID1: Establish sampling and analytical procedures for potentially harmful components post combustion amine based CO<sub>2</sub> capture. Subtask 2: Manual sampling<sup>2</sup>

Further we refer to: SINTEF Report F6335: CO<sub>2</sub>-Kårstø – Concept study no. 9, selection of gas analyser and monitoring system, March 2008<sup>3</sup>.

The objective at hand requires considerable attention to take care of a series of subsequent considerations which arise through the follow-up project within the TQP-Amine project:

- The analysis system shall not generate alterations (degradation) of the species analysed
- Automated operation is a prerequisite
- Analyser systems which are commercially available are preferred

Systems shall be applicable for both pilot and full scale design of a CO<sub>2</sub>-capture plant. Though information on these two systems is still limited, we assume that operation conditions are similar; the principal difference will be the emission cross section.

The present study will list, describe and discuss pros/cons of selected online equipment/techniques which are available commercially at present for emission monitoring including trace component analysis. Further, a validated recommendation on which equipment/technique will be best for overall application shall be given considering installation and reliable operation in an industrial environment.

The main challenges of online sampling and analysis are summarized by the following bullet points:

- **A representative flue gas sample** from both pilot, demo- and later full scale plant needs to be obtained. The flue gas will contain gaseous compounds, aerosols (condensate compounds) and droplets (entrainment from demister) which need to be analyzed together. Sampling for online analysis can be performed in-situ or extractive. In-situ analyzers are directly installed in the live gas stream, for extractive sampling isokinetic (see Reference 1 and 2) sampling and sample transfer to a sensing device is necessary.
- **Sample transfer** (if necessary) need to ensure that samples are not altered. **Thermal decomposition and artefact formation** and **condensation** of flue gas compounds requires a trade-off to find a suitable window of operation. The sample line itself need to be inert to avoid absorption / adsorption in **sample line materials**, further chemical reaction with sample line materials or possible generated deposits (salts and corrosion products). Minimizing effects require stainless steel pipes with frequent monitoring with respect to corrosion. Condensation of water vapor in the sample line would also remove soluble from the gas phase, thus influencing a gas analysis, slugging problems because of liquid plugs will be detrimental to instrumentation.
- **Analysis** of compounds in an analyzer itself. **Interference** between organic compounds and with the flue gas matrix which consists of  $N_2$ ,  $H_2O$ ,  $CO_2$ ,  $O_2$ ,  $CO$ ,  $NH_3$ ,  $SO_x$  and  $NO_x$  needs consideration when analyzers are evaluated. Further, sample treatment in the analyzer is important.

### 1.3 Report outline

Chapter 2 gives the basis for this study, which is a summary of the information given by the Company completed by physical properties of the compounds to analyse. Chapter 3 presents an overview over valid international standards and guidelines for online sampling from stationary sources. In Chapter 4, relevant information on measurement principles for online analysis of wet flue gases is presented. The applicability of these sensors is summarized in Chapter 5. In Chapter 6 the data from the previous chapter are discussed. In Chapter 7 and 8, conclusions and some recommendations are presented, respectively.

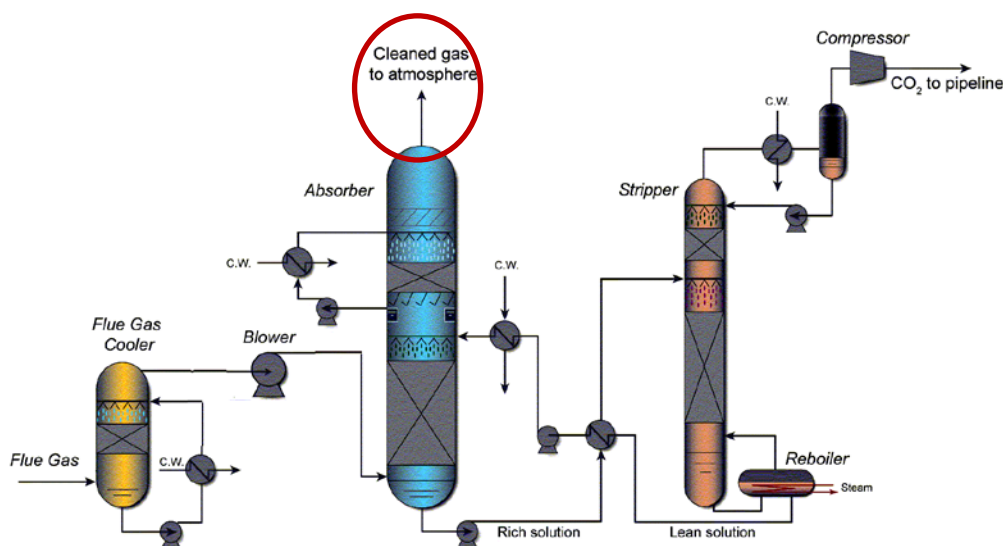
## 2 BASIS FOR THE STUDY

The present objective requires considerable attention to take care of the rather specific and non-standard compounds with respect to emission monitoring. According to IPCC, online emission monitoring is a rather mature field considering waste incineration and industrial (processing and cement) applications<sup>4</sup>. Installation, performance and reliability in demanding environments is proven and complementary regulations<sup>5</sup> are available for operation. However, the compounds considered here are beyond the scope of today's commercial continuous emission monitoring systems. Compounds are rather specific and few to none standard systems for on-line analysis are commercial available for these.

Analysis shall be performed such that continuous emission monitoring of the wet flue gas is performed. The sweet gas temperature is expected to be 25 - 50° C and contain compounds such as absorbents (e.g.: amines) and their degradation products; further water droplets/mist from the water wash section are expected. It is not known a-priori how much water soluble compounds are carried upwards between sections (absorber and wash sections) through entrainment. Flue gas compounds from a combustion process are expected, however these are not topic of the study since analysers for these applications are readily available.

### 2.1 Process design

The basic flowsheet of a CO<sub>2</sub>-capture plant together with mark-up of a specific location of a measurement site is given in Figure 2-1; operational parameters for treated flue gas (sweet gas) are given in Table 2-1. Flue gas entering from the up-stream process will be cooled and enters the absorber from the bottom; distributed over the absorber packing material and get in contact with the absorbent. On top of the absorber section water wash sections will be installed to minimize emissions, treated flue gas exits from the wash section through a stack.



**Figure 2-1: Simplified process diagram, circled part is focus of the study (SINTEF)**

### 2.2 Operational conditions

We assume that operational conditions (both with respect to flue gas compounds as well as flow conditions) in full scale and pilot will be kept as similar as possible. The flue gas conditions and composition, sweet gas (absorber outlet stream) conditions and composition, given here are based on information extracted from the document H&ETQPAmine1: Attachment A1 and given directly



from Company. The treated flue gas from the stack will be saturated with water and the conditions and compositions are given in Table 2-1.

**Table 2-1: Nominal conditions and composition of treated flue gas (sweet gas)**

<b>Conditions</b>	<b>Units</b>	<b>Nominal values Pilot scale</b>	<b>Nominal values Full scale</b>
Flow (Normal)	Sm <sup>3</sup> /h	250 - 1200	0.72 – 2.3 *10 <sup>6</sup>
Temperature (Normal)	°C	25 - 50	
Pressure (a)	bar	1.01325	
Main body velocity	m/s	2.0 – 3.0	
Exit velocity after water wash	m/s	20	20
<b>Composition</b>			
Oxygen (O <sub>2</sub> )	wt-%	15	
Nitrogen (N <sub>2</sub> )	wt-%	80.7	
Carbon Dioxide (CO <sub>2</sub> )	wt-%	0.6	
Water (H <sub>2</sub> O)	wt-%	3.9	
NO <sub>x</sub>	ppm	?	2 – 20 <sup>+</sup>
NH <sub>3</sub>	ppm	?	< 50
SO <sub>2</sub>	ppm	?	0.10 <sup>+</sup>
Amines	ppmv	?	< 5

### 2.3 Compounds

The compounds to be sampled are presented in Table 2-2. The thermal stability of compounds and their boiling points (see also Reference 2 for a more extensive list) together define a range of operation temperatures for sampling and analysis devices; too high temperatures result in decomposition of absorbents and degradation products to CO<sub>2</sub>, NH<sub>3</sub>, HCN and NO<sub>x</sub>. On the contrary too low temperatures will lead to adsorption/absorption, condensation and deposition of compounds in the sampling transfer lines and analyzer system. All these effects will have negative influence on the analysis result and need consideration.

**Table 2-2: Properties of compounds**

	Component Name	Abbreviation	CAS. Nr.	Melting point	Boiling point	Thermally stable <sup>+</sup> / Decomposition °C
N-Nitrosamines	N-Nitrosodimethylamine	NDMA	62-75-9	-28	152	
	N- Nitrosodiethylamin	NDEA	55-18-5	<25	175	
	N-Nitrosomorpholine	NMOR	59-89-2	29	140	
	N-Nitrosopiperidin	NPIP	100-75-4	170	229	
	N-Nitrosodiethanolamin	NDELA	1116-54-7		125	200°C
	N-Nitrosopiperazine	NPZ	5632-47-3		264	
	1,4-Di-Nitrosopiperazine	DNPZ	140-79-4		406	
Alkyl- amines	Methylamine	MMA	74-89-5	-94	-6	
	Ethylamine		75-04-7	-81	16,6	
	Dimethylamine	DMA	124-40-3	-93	7	
	Diethylamine		109-89-7	-50	55	
Amines	Mono-ethanol-amine	MEA	141-43-5	10	171	~180°C /6, 7/
	Di-ethanol-amine	DEA	111-42-2	28	268	
	Piperazine		110-85-0	106	146	
	1,2-Di-amino-ethane		107-15-3	8,5	116	
	2-Amino-2-methyl-1-propanol	AMP	124-68-5	30	165	
	N-Methyl-di-ethanol-amine	MDEA	105-59-9	-21	247	
Amid- es	Formamide		75-12-7	2,5	210	180°C (115°C /8/)
	Acetamide		60-35-5	81	222	
Alde- hydes	Formaldehyde		50-00-0	-92	-19,5	

+ Thermally stable in context of a real flue gas consisting of N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, CO, NO<sub>x</sub> and SO<sub>x</sub>.  
Residence time at that temperature is not considered.

### 3 ONLINE SAMPLING FROM STATIONARY SOURCES

An overview of relevant guidelines and standards which have been used for this work are given in Table 3-1

**Table 3-1: Overview Guideline and Standards relevant for automatized emission monitoring**

<b>Identifier</b>	<b>Title</b>
<b>EN 14181</b>	Stationary Source Emissions – Quality Assurance of automated Measuring Systems /9/
<b>EN 15259</b>	Air quality. Measurement of stationary source emissions. Requirements for measurement sections and sites and for the measurement objective, plan and report /10/
<b>VDI 4200; 2000</b>	Realization of stationary source emission measurements /11/
<b>BREF 07.2003</b>	General Principles of Monitoring /4/
<b>M2</b>	Technical Guidance Note: Monitoring of stack emissions to air /12/
<b>M16</b>	Technical Guidance Note: Monitoring volatile organic compounds in stack gas emissions /13/
<b>M20</b>	Technical Guidance Note: Quality assurance of continuous emission monitoring systems – application of BS EN 14181 and BS EN 13284-2 /14/
<b>M21</b>	Technical Guidance Note: Stationary source emissions – A procedure to use and Alternative Method for measuring emissions of sulphur dioxide, using instrumental techniques /15/
<b>EN 13284</b>	Stationary source emissions. Determination of low range mass concentration of dust. Automated Measuring systems /16/
<b>EPA Method 320</b>	EPA Test Method 320: Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy /6/
<b>EPA Method 321</b>	Test Method 321 - Measurement of Gaseous Hydrogen Chloride Emissions At Portland Cement Kilns by Fourier Transform Infrared (FTIR) Spectroscopy /17/
<b>ASTM 6348-03</b>	Standard Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy /18/
<b>EPA SPEC-15</b>	Performance Specification 15 Performance Specification for extractive FTIR continuous emissions monitoring systems in stationary sources /19/

For the design of a measurement section we refer to H&E TQP ID1 projects: Establish sampling and analytical procedures for potentially harmful compounds post combustion amine based CO<sub>2</sub> capture; specifically Subtask 1: Design of Sampling Points in treated flue gas<sup>1</sup> and for manual operation to Subtask 2: Manual sampling<sup>2</sup>.

## 4 MEASUREMENT PRINCIPLES

Online analysis for emission monitoring is based on the following principles:

- **Extractive gas analyzers**
- **In-situ probe analyzers**
- **Across-stream in-situ analyzers**

Extractive gas analyzers are based on sampling gas at a sampling point and transferring the gas to a measuring device. For extractive sampling, the inlet manifolds and sampling lines of continuous analyzers should be designed from materials that do not affect the integrity of the sample. Extractive methods involve either heating in order to avoid condensation, or drying in order to remove water<sup>12, 13, 14, 15</sup>. A disadvantage of heating the sampled gas can be chemical change in the gas sample caused by thermal reactions in the heated sample lines and analyzer. This can potentially be a critical problem when analyzing a complex gas matrix with compounds of interest present in the low concentration range. For such gases, knowledge on the chemical and thermal stability of the sample upon heating is important. In the case of drying of the gas prior to analysis, this is normally done by cooling. A significant fraction of the water-soluble compounds present in the gas will then be lost in the formed condensate, making the dry gas analysis incomplete and careful attention when a calibration function is needed.

By definition, "in-situ" measurements are made in place directly within the process without changing the state of the sample. In-situ probe analyzers are sensors placed directly into the flue gas stream for measuring single compounds in a flue gas stream. For across the stream in-situ measurements, the presence of droplets and the formation of mist represent a problem. Optical analysis methodologies depend on a clear line of sight and analytes present in droplets and aerosols are not included in the resulting measurements.

### 4.1 Gas chromatography (GC)

Chromatography is a collection of techniques used to analyze and separate mixtures of compound in complex matrices. Chromatography is a system that consists of a stationary phase (usually solid material) and a mobile phase (gas or liquid). The sample is introduced in the mobile phase which passes over the stationary phase. Substances are separated due to their difference in interaction with the stationary phase. Compounds that adhere easily to the stationary phase will move slowly in the chromatographic system, compounds less adherent, will move faster and the different compounds will be separated. At the end of a chromatographic system there is a detector. GC detectors can be of various types, some general (multipurpose) or more specific depending on the compounds to analyze.

In gas chromatography the stationary mobile phase is an inert gas (He, H<sub>2</sub> and N<sub>2</sub>). The stationary phase is embedded in a column and can be of various materials depending on your analytes. The column can be a glass or metal tube that is packed with particles that hold the stationary phase, or more common a silica capillary that has a layer of stationary phase on its inside. The column is placed inside an "oven" that allows control the temperature of the column. The temperature can be held at a certain point, or the temperature can be varied (increased) to allow compounds with high boiling points to pass through the system. The upper limit of operation is given by the combination of thermal stability of compounds and simultaneously the need for vaporization of these with highest boiling points. GC detectors can be of various types, some general (multipurpose) or more specific depending on the compounds to analyze.

#### 4.1.1 GC-Detectors

**Thermal conductivity detector (TCD):** The TCD consists of a temperature controlled cell which holds an electrically heated filament. When mobile phase flows through the cell there is a stable transfer of heat from the filament to the cell body. When an analyte passes through the cell, the thermal conductivity changes and the temperature of the filament change. The change of resistance of the filament generates a time proportional signal for the amount of a substance.

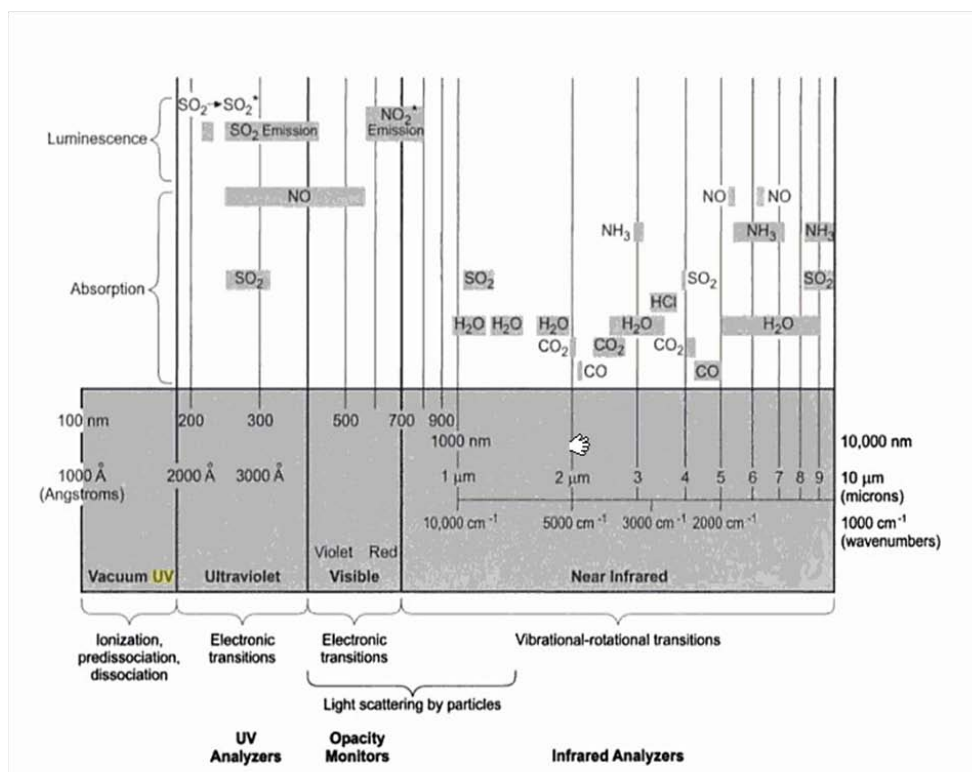
**Flame-ionisation detector (FID):** Hydrocarboneous compounds entering a H<sub>2</sub>-airflame are ionized, the current between electrodes carried by carbon compounds is measured, this current is proportional to the number of combustible carbon of a component. The response of the sensor is linear for homologous compounds (e.g.: alkanes) and over a rather broad concentration range from low ppm-levels upwards. Highly oxygenated/halogenated organic compounds give a poor response and are not suited for analysis with a FID. For FID-detector is water an inert component.

**Photo-ionisation detector (PID):** UV lamps with selectable energies (wavelengths) generate high-energy photons which are used to ionise separated compounds in a microcell. The gas becomes electrically charged and the ions produce an electric current, which is the signal output of the detector. The time-proportional current measured is proportional to the amount. The detector responds to organic and inorganic compounds with an ionisation potential of <12 eV, e.g. O<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, halogens, PH<sub>4</sub>. Detection limits for gaseous compounds of ppb are reported, speciation is strongly dependent on the type of chromatographic pre-treatment. Experiments with Nitrosamines are performed and showed that detection to 50 pg/l are possible<sup>20</sup>.

**Flame-photometric detector (FPD):** The design is similar to a FID, however light tight. Combustion products from compounds containing P and S are burnt in H<sub>2</sub>-air flame and give specific band emissions. Wavelengths (525 nm for P, 355 nm for S) isolated by filters and measured by PMT. Selective for nitrogen and phosphorus compounds.

## 4.2 Spectroscopy

Spectroscopy are optical methods for analysis of gaseous compounds. There are many techniques for gas analysis that involve observations of the electromagnetic radiation spectrum. The relevant part of the spectrum consists of: X-rays, ultraviolet, visible light and infrared. The ultraviolet, visible and IR regions are particularly relevant to gaseous air pollutant analysis, whereas X-ray methods are more relevant to particulate-phase pollutants and will not be discussed here. Figure 4-1 shows the electromagnetic spectrum with absorbance regions for typical combustion gases.



**Figure 4-1: The electromagnetic spectrum for with typical absorbance regions for combustion gas products.**

#### 4.2.1 Infrared Spectrometry

Infrared absorption spectrometry is based on spectra that arise from various changes in energy brought about by transitions of molecules from one vibrational or rotational energy state to another. In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion. As the molecule vibrates, a regular fluctuation in dipole moment occurs, and a field is established that can interact with the electrical field associated with radiation. If the frequency of the radiation exactly matches a natural vibrational or rotational frequency of a molecule, a net transfer of energy takes place that results in a change in the amplitude of the molecular vibration; absorption of the radiation is the consequence. No net change in the dipole moment occurs in homo-nuclear species such as O<sub>2</sub>, N<sub>2</sub> or Cl<sub>2</sub>; consequently, such compounds cannot absorb in the infrared spectrum. With the exception of a few compounds of this type, all other molecular species absorb infrared radiation.

From the standpoint of both application and instrumentation, the infrared spectrum is conveniently divided into near-, mid-, and far-infrared radiation; rough limits of each are shown in Table 4-1.

**Table 4-1** Infrared Spectral Regions<sup>25</sup>

Region	Wavelength ( $\lambda$ ) Range, $\mu\text{m}$	Wavenumber ( $\bar{\nu}$ ) Range, $\text{cm}^{-1}$
Near	0.78 to 2.5	12 800 to 400
Middle	2.5 to 50	4000 to 200
Far	50 to 1000	200 to 10
Most used	2.5 to 15	4000 to 670

Three types of instruments for infrared absorption measurements are available from commercial sources: (1) dispersive grating spectrophotometers (used primarily for qualitative work); (2) multiplex instruments (combining many signals into a single channel), employing the Fourier transform; and (3) non-dispersive photometers. Until the 1980s, the most widely used instruments for infrared measurements were dispersive spectrophotometers<sup>25</sup>. In dispersive instruments, a selected narrow band wavelength of IR energy reaches the detector<sup>21</sup>.

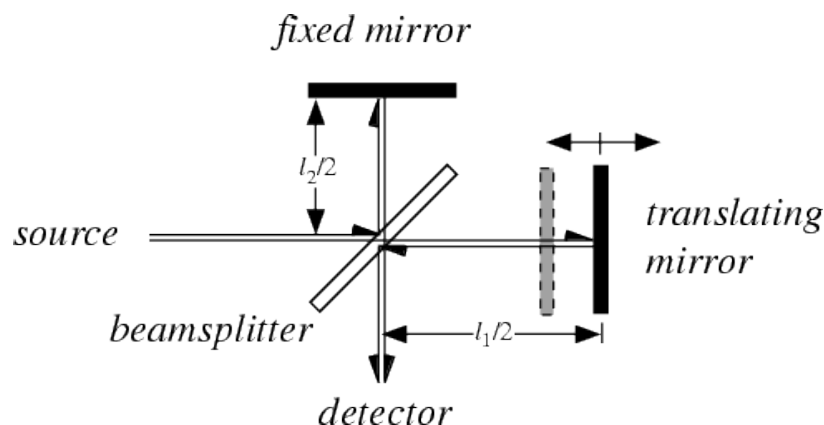
The techniques and the applications of methods based upon the three infrared spectral regions differ considerably. Measurements in the near-infrared region (NIR) are made with photometers and spectrometers similar in design and compounds for ultraviolet (UV)/visible spectrometry. Photometers based upon interference filters are used for measuring the composition of gases and atmospheric contaminants, but today the majority of new instruments are of the Fourier transform type<sup>27</sup>. The appearance of relatively inexpensive Fourier transform spectrometers in the last two decades has markedly increased the number and type of applications of mid-infrared radiation. This increase has come about as a consequence of at least an order of magnitude improvement in signal-to-noise ratio and detection limit that can be realized with interferometric instruments. Fourier transform spectrometers with high throughput also make the far-infrared spectral region more accessible for analysis.

Monitoring of gases with CO<sub>2</sub> and a high content of water, is a challenge for IR based methodologies, due to the strong absorptivity of infrared radiation for these molecules. Water, which absorbs over broad regions of the infrared spectrum, is especially a major challenge for the analysis of compounds present at sub ppm concentrations. In addition, for complex gas matrixes, interference of different compounds makes a good knowledge of the composition of the gas necessary.

#### **4.2.2 Fourier Transform Infrared spectroscopy (FTIR)**

FTIR is an advanced type of IR technique which measures all infrared frequencies simultaneously and can be used for both quantitative and qualitative measurements. Fourier transform infrared (FTIR) spectrometers are cheaper than conventional spectrometers because building of interferometers is easier than the fabrication of a monochromator. Measurement of a single spectrum is faster for the FTIR technique because the information at all frequencies is collected simultaneously. This allows multiple spectral absorption samples to be collected and averaged together resulting in an improvement in sensitivity. Today, virtually all modern IR spectrometers are FTIR instruments favoured for their speed, high resolution, sensitivity, and unparalleled wavelength precision and accuracy.

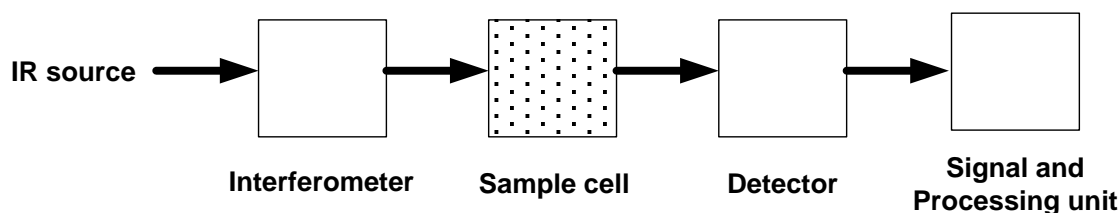
The majority of commercially available Fourier transform infrared instruments are based on the Michelson interferometer shown in Figure 4-2. Michelson interferometers provide a significant sensitivity advantage over grating, prism, and circular variable filter (CVF) spectrometers, as the interferometer is not limited in aperture (slit width or height) as severely as dispersive or CVF instruments, giving a higher light gathering capability and a larger throughput<sup>25</sup>.



**Figure 4-2: Principle of the Michelson interferometer used in Fourier transform spectroscopy<sup>22</sup>.**

Encoding of the infrared spectra is here accomplished by splitting the source into two beams whose path lengths can be varied periodically to give interference patterns. The interferogram is a measurement of the temporal coherence of the light at each different time delay setting. With the use of Fourier transformations it is possible to convert a signal in the time domain to the frequency domain (i.e. the spectrum). The fundamental measurement obtained by an FTIR is made in the time domain, which is Fourier transformed to give a spectrum of absorbance plotted against wavenumbers.

Figure 4-3 shows the basic compounds of an FTIR instrument. After passing through the interferometer, the IR radiation passes through the sample before entering the detector from which the signal can be encoded into the resulting spectrum.



**Figure 4-3: The basic compounds of an FTIR spectrometer; the infrared source, interferometer, sample cell, detector and signal and data processing unit**

The path length of the sample cell is proportional to the measured absorbance of the resulting spectrum. The dependencies of the measured absorbance is:

$$Absorbance, A = \log\left(\frac{1}{T}\right) = a \times b \times l$$

The measured absorbance of the FTIR-spectrum is the logarithm of the inverse transmittance  $T$  and the absorption from a single compound is typically linearly dependent on the concentration  $c$ , the length  $l$ , and the absorption coefficient of the compound, which characterizes the capacity of the sample to absorb infrared radiation. Above absorbance units of 1 (10 % of radiation transmitted through the sample), the compounds in general do not obey Beer-Lambert law as the molar absorptivity is no longer a linear function of concentration<sup>23</sup>.



The most common method for online measurements of gas by FTIR is performed by an extractive method, where gas is sampled through a heated sampling line for gas transfer to a sample cell for analysis. In order to avoid condensation of the gas, the sample line and the gas cell is heated to a temperature of typically 180°C. Non-extractive methods for gas analysis are also possible, like the open-path FTIR method which is an optical remote sensing technique which consists of transmitting an infrared beam from less than 10 and up to several hundred meters across the atmosphere prior to the detector<sup>24</sup>. The principles for an open-path instrument is the same as shown in Figure 4-3, but the closed sample cell is here replaced by a light path through open air, often via a remote reflector. Open path FTIR has the advantage of potentially very low detection limits due to the long path length available for IR absorption. The forming of mist is a limitation for the open path method, as the IR beam depends on a clear line of sight to the detector.

### 4.2.3 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) refers to absorption spectroscopy in the ultraviolet-visible spectral region. Only certain types of electronic transitions in polyatomic molecules provide spectra accessible to conventional instruments. Those of saturated hydrocarbons, C–H bonds, and O–H bonds are not of diagnostic value; UV-visible spectroscopy is of most use for molecules containing multiple bonds, which give rise to electronic transitions having wavelength maxima positions characteristic of the neighbouring atoms<sup>25</sup>. UV spectroscopy is used where strong absorption of ultra-violet radiation occurs in a substance. Such UV-absorbing groups are known as chromophores and include aromatic groups, conjugated system of bonds and carbonyl group among others. The absorption in the visible range directly affects the perceived colour of the chemicals involved. UV has been reported to be used for individual or simultaneous measurement of SO<sub>2</sub>, NO, NO<sub>2</sub>, Cl<sub>2</sub> as well as NH<sub>3</sub>, CS<sub>2</sub>, COS. Cross-sensitivities to CO<sub>2</sub> and H<sub>2</sub>O do not exist because of the spectral range used<sup>26</sup>.

### 4.2.4 Non-dispersive Infrared spectroscopy (NDIR)

Non-dispersive infrared sensors (NDIR) are simple spectroscopic devices often used as gas detectors for air pollution monitoring in the field. The non-dispersive instrument does not scan the spectrum, but instead is designed to look at that portion of the IR spectrum where the pollutant shows peak absorption. Gas concentration is measured electro-optically by its absorption of a specific wavelength in the infrared region. The NDIR detector has an optical filter in front of it that eliminates all light except the wavelength that the selected gas molecules can absorb<sup>26</sup>.

A number of simple, rugged non-dispersive instruments have been designed for quantitative infrared analysis. They can be simple filter- or non-dispersive photometers<sup>26</sup>, or instruments that employ filter wedges in lieu of a dispersing element<sup>27</sup>. Some other instruments do not have wavelength selection device at all<sup>21</sup>. Another type of IR analyser that is popular for analysing carbon monoxide in ambient air uses the gas-filter correlation (GFC) method. With this technique, the IR spectrum from the sample gas is compared with a spectrum engraved on a grating. Two filter chambers are fixed to a rotating filter wheel, one containing pure sample gas and the other containing pure nitrogen. The two filter chambers are alternately brought into the light path from the sample cell. This arrangement is designed to minimise the effects of interfering gases<sup>25</sup>. Disadvantages of non-dispersive instruments are that interference from highly absorbing compounds like water and CO<sub>2</sub> other compounds can reduce their usefulness. In addition, there is limited speciation beyond general classes of hydrocarbons. Therefore, the technique is suited best to single compounds or simple mixtures where there are no interferences.

#### 4.2.5 Tuneable diode laser absorption spectroscopy (TDLAS)

TDLAS is the most common laser based absorption technique for quantitative assessments of species in gas phase<sup>28</sup>, the laser diode allows the instrument to target very specific wavelengths. In the most sensitive instruments the diode laser is repetitively tuned over an absorption line of a target molecule and the absorption spectra are averaged over a specified time interval.

Near room-temperature diode lasers (operating at a temperature accessible with thermoelectric coolers, generally ~250 to 350 K) are presently available over a range of wavelengths extending from about 630 nm in the visible to about 2.2  $\mu\text{m}$  in the mid-IR. Most applications relevant to gas dynamic and combustion flows are based on absorption by low-molecular weight molecules with well resolved absorption transitions such as  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{HF}$ ,  $\text{H}_2\text{S}$ , and  $\text{CH}_4$ . With the exception of visible transitions of  $\text{O}_2$  and  $\text{NO}_2$ , the absorption measurements are performed on vibrational absorption bands. Apart from measurements of concentration, TDLAS can also be applied for determination of temperature, pressure, velocity and mass flux of the gas under observation<sup>29</sup>.

TDLAS can be used detect absorptions as small as 1  $\text{mg}/\text{Nm}^3$  over path lengths up to 200 m through the open air and is frequently used for measurement of trace gas pollutants in the atmosphere<sup>30</sup>. The TDLAS spectrometers usually work with open-path or multi-pass absorption cells to achieve high sensitivity. TDLAS has been applied for in-situ measurements of combustion-generated pollutant emissions. Combined with fiber-optic distribution networks, compact and portable sensors are now appearing for a variety of applications<sup>31</sup>. Mid-IR diode lasers have been applied as monitors for ammonia in coal combustion<sup>32</sup>. Sampling the combustion gases into a low-pressure, low-temperature cell eliminates many of the interference problems associated with in-situ measurements. Using this approach, off-the-shelf commercial instruments have become available for combustion applications such as  $\text{NH}_3$  monitoring in post-combustion  $\text{NO}_x$  cleanup systems for coal-fired utility boilers<sup>33</sup>.

#### 4.2.6 Differential Optical Absorption Spectroscopy (DOAS)

For the retrieval of trace gas amounts, the technique of Differential Optical Absorption Spectroscopy (DOAS) is a well established remote sensing method which has been developed and improved over the last decades. It was first used for measurements conducted with ground-based instruments, but can also be applied when observing the atmosphere from space<sup>34</sup>. The DOAS method makes use of the individual absorption characteristics of molecules on the mathematical basis of Lambert-Beer's absorption law. The technique enables to observe atmospheric trace gases such as ozone and  $\text{NO}_2$ . For this the absorption in visible and near ultraviolet sunlight scattered in the zenith is measured. So called slant columns, that are the column densities along the light path can be derived. The fundamental difference between typical radiative transfer calculations and the point of view in the DOAS method is the way how the light is traced through the atmosphere. DOAS type measurements can be conducted either using an artificial light source (active DOAS, e.g. with xenon or mercury<sup>35</sup> arc lamp) or the sun as natural light source (passive DOAS)<sup>36</sup>.

### 4.3 Mass spectrometry

Mass spectrometry allow us differentiate between different organic molecules due to the relationship between their molecular mass and their net charge<sup>37</sup>. Most organic are molecules have a neutral charge in gas phase and therefore need to be ionized before they can be analyzed in the mass spectrometer. There are mainly two ionization techniques that are used in MS instruments for real time monitoring of gases; electron impact and chemical ionization. Electron impact (EI) is a technique where the organic molecules are bombarded with electrons, the

bombardment causes an electron to be removed from the molecule and the result is a net positive charge of one. This is a very general technique is applicable to a great number of organic compounds. The energy of the electrons is important, due to the fact that some molecules will not only become ionized but will also disrupt into smaller fragments. Fragmentation can in some applications be helpful, and in some applications be a disadvantage.

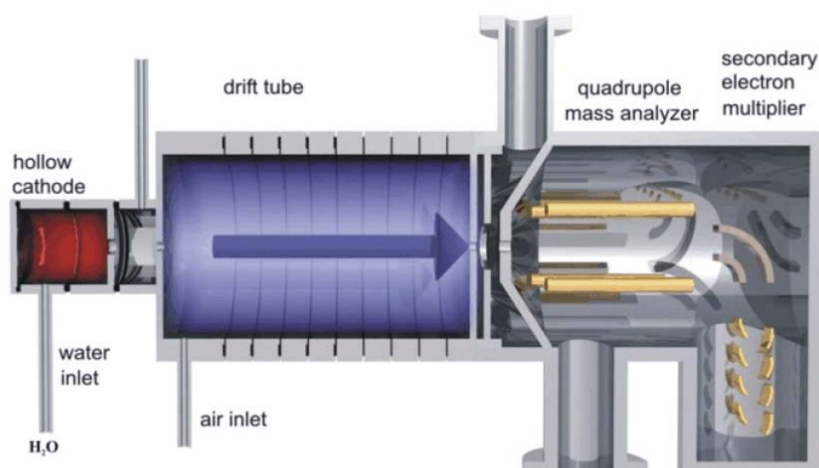
The alternative to EI is chemical ionization (CI) also known as “soft” ionization or Proton Transfer (PTR). To achieve ionization the target molecule; this technique utilizes other charged molecules to ionize the molecules of interest. It can for instance be a charged water molecule  $\text{H}_3\text{O}^+$  that donates its extra proton to the analyte and giving it a positive charge. Molecules that are to be ionized with PTR must have a higher proton affinity than its donor molecules. Mass analyzers are also of different designs, each having some advantages over the other depending on the compound and the analytical problem that needs to be solved. The most common design for process mass spectrometry is a quadrupole instrument, it usually has lower price compared to other designs, good sensitivity and poor resolution. The poor resolution may be a problem if there are compounds with almost similar molecular mass. Quadrupole instruments also come in different sizes, from small portable devices to large stationary instruments. The other designs that offer better resolutions i are: Time of Flight (TOF) and Magnetic Sector (MS). TOF and MS on the other hand do not have same potential regarding low detection limits when compared to a quadrupole design, and are usually more expensive. Mass spectrometry can also be used in combination with both liquid and gas chromatography giving the advantage of both chromatographic separation and mass selective detection. The combination with chromatography makes it possible to analyze much more complex samples than mass spectrometry alone. Mass spectrometry is a very universal technique but it also has some limitations. The thermal stability of the compound is of importance; usually the inlet for a mass spectrometer is between 120-180 °C. Compounds with high boiling points and thermally unstable compounds will be difficult to analyze, and can interfere with other compounds.

#### 4.3.1 GC-MS and LC-MS

Mass spectrometry can be used as detector for both liquid- and gas chromatography, and the combination of the techniques gives higher specificity, cleaner mass spectra due to the separation of the substances and better sensitivity compared with each technique on its own. The combination of liquid chromatography mass spectrometry (LC-MS) is more suitable of water soluble compounds, compounds with high boiling points and thermo labile compounds. Gas chromatography mass spectrometry (GC-MS) has its advantage on volatile compounds that are thermally stable.

#### 4.3.2 PTR-MS

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a highly sensitive, real-time analytical technique for detecting volatile organic compounds (VOCs) in air, which was originally developed in the mid-1990s in the laboratories of the Institute of Ion Physics at the University of Innsbruck, Austria. PTR-MS combines the concepts of soft, non-fragmenting chemical ionization of organic trace gases (via proton transfer reactions with  $\text{H}_3\text{O}^+$  reagent ions) and of highly sensitive and quantitative product ion formation in an ion drift tube. A schematic figure of a conventional PTR-MS instrument is given in Figure 4-4.

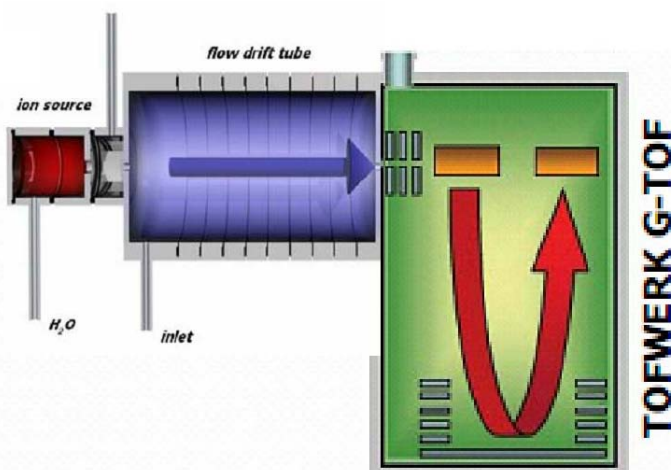


**Figure 4-4: The Proton-Transfer-Reaction Mass Spectrometer<sup>51</sup>.**

The PTR ion source consists of an external hollow cathode discharge in which  $\text{H}_3\text{O}^+$  ions are generated from pure water vapour. The  $\text{H}_3\text{O}^+$  ions are injected into a reaction chamber, an ion drift tube which is continuously flushed with analyte air containing organic trace gases. In the drift tube,  $\text{H}_3\text{O}^+$  ions react with molecules that have a higher proton affinity than water, i.e. the large majority of polyatomic volatile organic molecules especially those containing the heteroatoms O and N. Protons are transferred onto the analyte molecules which are not fragmented as in conventional 70 eV electron ionization mass spectrometry or in on-line mass spectrometric methods based on electron transfer reactions (e.g. from  $\text{Xe}^+$ ,  $\text{Kr}^+$  or  $\text{Hg}^+$  ions). Salient PTR-MS features are: i) direct sampling without sample pre-treatment, < 0.2 s residence time in the inlet), ii) on-line capability (sub-second time response), iii) a ~ 10 pptV-level detection limit, iv) soft, non-fragmenting fragmentation and v) an inherently quantitative character of the ionization process. The latter is particularly important for quantitative detection of organic species for which no external calibration gas-phase standard can be produced (e.g. amines, amides, nitrosamines, nitramines, etc.)<sup>51</sup>.

### 4.3.3 PTR-TOF-MS

In its conventional version, the PTR source is coupled to a quadrupole mass spectrometer (QMS). The use of a low mass resolution QMS often limits the selectivity of the PTR-MS method to identify individual compounds of interest in complex matrices. This limitation is overcome by the recently developed High Mass Resolution Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-TOF). In PTR-TOF-MS, the quadrupole is replaced by a high resolution time-of-flight mass spectrometer. Figure 4-5 shows a schematic figure of a PTR-TOF-MS instrument.



**Figure 4-5: The Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer<sup>51</sup>.**

The PTR-TOF-MS can identify the exact atomic composition of C, H, N and O containing product ions at  $m/z < 250$ . One remaining constraint is that the PTR-TOF does not resolve isomers, i.e. it does not have an MS/MS capability.

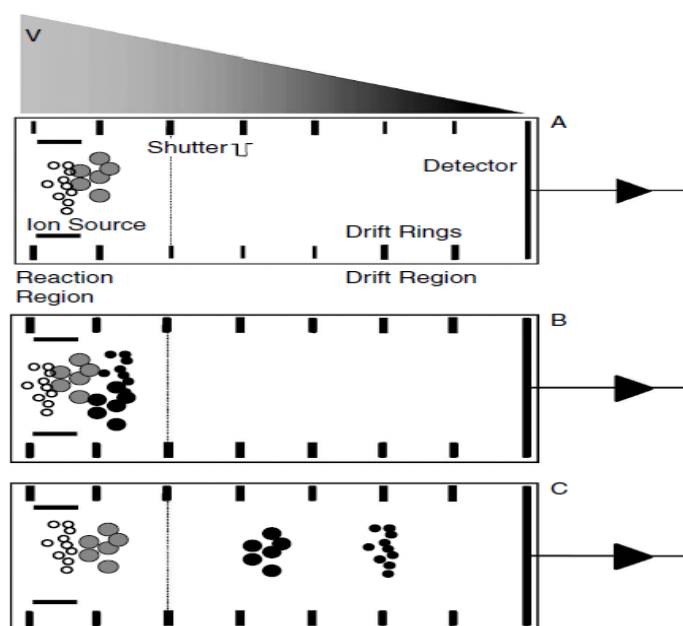
PTR-MS has been successfully applied to measure volatile organics in many different analytically challenging matrices such as car engine emissions, fire emissions, waste incinerator gas, gasified wood, fermentation gas, human breath and others. In general, high humidity levels are not problematic except for the fact that condensation must be prevented by keeping inlet and instrument at elevated temperatures. Ammonia levels may be problematic to analyse if they exceed 100 ppm. At these levels, the primary  $\text{H}_3\text{O}^+$  signal gets significantly depleted. In such events it is necessary to dilute the analyte gas with zero air.

PTR-MS has been used for qualitatively and quantitatively analysis of amines (methylamine, dimethylamine, trimethylamine, monoethanolamine, piperazine), amides (formamide, N-methylformamide, N,N-dimethylformamide), nitrosamines (N-nitrosodimethylamine, N,N-diethylnitrosamine, N-nitrosopiperazine, N-nitrosomorpholine), nitramines (N-nitromethylamine, N,N-dimethylnitramine) and imines (N-methylmethanimine) in ambient air. Detection limits for amines, amides, nitrosamines, nitramines were in the range of 10-50 pptv in these ambient air measurements<sup>52</sup>.

#### 4.4 Ion mobility Spectrometry

IMS is a technique that measures the velocity of ionized substances in an electric field<sup>38, 40</sup>. The instrument consists of an ion source, a drift tube and a detector. Substances that are to be analyzed with IMS have to be ionic, some compound are already on ionic form, and need no further ionization. Neutral compounds however need to be ionized before they can be analyzed. There are different types of ion-sources that can be used with IMS. Traditionally radioactive sources like  $^{63}\text{Ni}$  and  $^{241}\text{Am}$  have been applied. Ionization techniques that have been used with LC-MS (APPI, APCI and ESI) are now also being used with IMS when analyzing liquid samples. The drift tube is the component that separates the different ions, substance ions are drawn in to the drift tube, in the drift tube there is a counter flow of gas known as drift gas or buffer gas. The ions moving through the drift tube are colliding with neutral drift gas molecules that slow them down. How much the velocity is affected depends on the actual size (not mass directly), and conformation. IMS is capable of separation isomers with exact same mass and molecular formula that are structurally different. Ions are detected when they hit the detector at the end of the drift

tube, and the time they have spent in the drift tube is recorded (see Figure 4-6). One clear drawback with IMS is that there exist no commercial available universal spectral libraries that can be used<sup>39</sup>.



**Figure 4-6: Schematic over view of an IMS instrument. A) Substances entering the ion source. B) Substances are ionized. C) Ions are injected into the drift tube, and pass through it with different velocities. Neutral substances do not enter the drift tube**

Most IMS analysers are used in security and military applications. Industrial applications have been developed but suffer from some limitations especially ruggedness and stability. Examples of applications: Acids and corrosive gases<sup>40</sup>, volatile organic compounds, halocarbons, ammonia in water, ammonia in air, contaminants in semiconductor manufacturing, and air quality in recycled or controlled atmospheres<sup>40</sup>. IMS-systems rarely come with a specific inlet system to produce gaseous samples<sup>41</sup>. For two phase samples (gas & liquid) the sample systems consists of an evaporator and a membrane. The commercial availability of sample systems for non-ambient air applications is yet limited, liquid droplets entering the draft tube are detrimental for the instrument.

#### 4.5 Light scattering for particles

We have limited the information search for methodologies to analysis of gaseous compounds. Installation of dust sensors in wet flue gases is rather complicated and to achieve reliable measurement comprehensive maintenance is required<sup>42</sup>. Standard optical instruments can measure the amount of water droplets<sup>43</sup>, however isokinetic gas sampling will ensure representative sampling of entrained droplets in the emission.

#### 4.6 Volume flow

For efficient emission control and reporting the volume flow needs to be measured. For wet flue gases in large stacks ultrasonic based velocity sensors are more suitable<sup>44</sup> than pitot tubes and annubars<sup>45</sup>. The ultrasonic sensor measures diametrical over the stack cross section while pitot tubes only measures in single positions.

## 5 ANALYTICAL SYSTEMS

Evaluation of different online analyzers required comprehensive contact to several suppliers. The challenge is to retrieve reliable information with respect to an instruments performance and limitations. The authors choose therefore to contact a limited number of suppliers covering the most suitable analysis principles. Analyzer principles which do not fulfil the given requirements (multi-component analysis and detection limit ~1 ppm) were omitted from the survey.

Limiting the number of suppliers also opens up for more in-depth discussions with technical personnel of the suppliers. Previous experience with similar projects<sup>3</sup> showed that “sales information” is in general not sufficient for an evaluation of applicability of an analysis system. Further, SINTEF has an extensive analysis instrument park, such that some of the information is based on own experience.

Selection of suppliers started from these which were included in a previous Gassnova project<sup>3</sup>; the list of suppliers including some vital information is presented in Table 5-1. The inquiry send to selected suppliers is presented in Appendix 1, together with contact information in Appendix 2.

Table 5-1: Information summary

Company	Sampling System	Analysis Technology	Detection limit for requested compounds	Compounds of interest in addition to request	Comments	Evaluation for application of entire measurement problem
Sick Maihack	Heated extractive sampling system	IR, UV, TDLAS, FTIR /46/	No experience with MEA or other amines for emission monitoring.	HCN, NO <sub>x</sub> (NO, NO <sub>2</sub> , NO <sub>3</sub> ), O <sub>2</sub> , CO <sub>2</sub> , NH <sub>3</sub> SO <sub>x</sub> (SO <sub>2</sub> ,SO <sub>3</sub> ), CO, FID (TOC), ultrasonic flow meters	IR-analyser in MCS100E HW: Acetaldehyde 0.02 ppm; expect severe cross sensitivities to other compounds	<b>Not applicable</b>
OPSIS AB	In-situ cross-stack for dry flue gases or “fast loop” for wet flue gases	DOAS for IR and UV analyser Path length 10 m	Proof-of-Concept: MEA ~1 mg/Nm <sup>3</sup> Acetaldehyde Formaldehyde	HCN, NO <sub>x</sub> (NO, NO <sub>2</sub> , NO <sub>3</sub> ), O <sub>2</sub> , CO <sub>2</sub> , NH <sub>3</sub> SO <sub>x</sub> (SO <sub>2</sub> ,SO <sub>3</sub> ), CO	The analyser is dependent on gaseous state for the samples (>135°C), space requirements because of fast-loop makes installation difficult /3/.	<b>Not applicable</b>
YAGA Gasmel /47/	Extractive sampling system 180°C	Gasmel FTIR	Verified e.g.: 0,15 ppm Ethylamine in dry N <sub>2</sub> with 5 m optical path. Claims that high water concentration or other compounds have limited influence on LOD.	H <sub>2</sub> O, CO, CO <sub>2</sub> , SO <sub>2</sub> , NO <sub>x</sub> , NH <sub>3</sub> , N <sub>2</sub> O, O <sub>2</sub> , TOC other gases dependent on configuration	GASMET FTIR applied by Aker Clean Carbon for process monitoring. Calibrated for MEA, AMP and Piperazine.	System integrator med GASMET  <b>Applicable</b> , need improvement
Q-Interline ABB, Protea, Extrel, Kaiser		FTIR analyzer from ABB and Protea	Verified: 0,1 ppm MEA in dry air with 10 m optical path. Expect interferences between high molecular weight compounds and water.		Suggests low sample line temperature (60°C). “Dry” application: FTIR; ABB MB3000 with > 10m cell “Wet” application MS Claims that 1mg/Nm <sup>3</sup> MEA@16 Vol% H <sub>2</sub> O (130 gr/m <sup>2</sup> ) is possible. High water content makes analysis difficult.	System integrator with ABB, Protea, Extrel.  <b>Applicable</b> for gas phase Research partner



Company	Sampling System	Analysis	Detection limit	Compounds	Comments	Evaluation
<b>Protea</b>	Temperature controlled extractive sampling system.  Suggests to limit sampling temperature to 60°C to avoid thermal decomposition with long sampling lines	<b>FTIR</b> based on ABB –Bomem Interferometer	With given gas matrix: Clean amides and aldehydes possible at > 5 ppm-level; however speciation may be difficult at low levels (<5ppm) Alkylamines possible, given high enough concentrations. No experience with N-Nitroamines and other amines.	H <sub>2</sub> O, CO, CO <sub>2</sub> , SO <sub>2</sub> , NO <sub>x</sub> , NH <sub>3</sub> , N <sub>2</sub> O, O <sub>2</sub> , TOC and NMHC (other gases on request)	Expect challenge to distinguish between species such as N-Nitrosodimethylamine and N-Nitrosodiethylamine.  Bigger molecules give similar "lumps" in certain spectral regions; interference. State that development of a good model will be a challenge because of wide boiling point range and expected thermal degradation.	<b>Applicable</b> for gas phase  Experience of amine, aldehydes and alkylamines analysis from other industries  Research partner for analysis system
<b>MIDAC Corp.</b>	Extractive flue gas sampling system available	<b>FTIR</b>	MEA ~0.1 ppm, tests performed with MDEA and Piperazine Experience with MEA degradation at 140-180°C; condensation of MDEA <180°C	H <sub>2</sub> O, CO, CO <sub>2</sub> , SO <sub>2</sub> , NO <sub>x</sub> , NH <sub>3</sub> , N <sub>2</sub> O, O <sub>2</sub> Other gases depend on configuration	Analysis of several heavy compounds in mixture need careful calibration  Performed proof-of-concept studies for analysis, real flue gas not tested. Tested SS316 and PTFE-tubes Require non-condensable gases	<b>Applicable</b> for gas phase  Research partner for analysis system
<b>Thermo Scientific</b>	Extractive flue gas sampling system available	<b>GC-MS, LC/MS, NDIR and Isotope Ratio MS</b>	Detection in range below 10 ppm is not possible at current time	HCN, NO <sub>x</sub> (NO, NO <sub>2</sub> , NO <sub>3</sub> ), O <sub>2</sub> , CO <sub>2</sub> , NH <sub>3</sub> SO <sub>x</sub> (SO <sub>2</sub> , SO <sub>3</sub> ), CO, FID (TOC), flow meters	Advanced MS Analyzer used for biofuel and biogas application, not applied for amines in wet flue gases	<b>Not applicable</b>  Supplier needs more research
<b>PMS AB</b>	No flue gas sampling system available Direct injection of non-condensing sample gases	<b>PTR-MS</b>		Measures VOC	Claim that extractive sampling system and analyzers handles wet gas	<b>Suitable</b> , proof-of-concept with varying humidity necessary, need for gas pre-treatment system
<b>Iconon</b>	No flue gas sampling system available Direct injection of non-condensing sample gases	<b>PTR-MS PTR-TOF-MS</b>  Inlet temperature < 180°C	LOD ~10 ppt for Amines, Nitrosamines Max. Concentration 500 ppm	Measures VOC	Maximum concentration for the sum of all ionisable compounds app. 10 ppm	<b>Suitable</b> , proof-of-concept with varying humidity necessary, need for gas pre-treatment system

Company	Sampling System	Analysis	Detection limit	Compounds	Comments	Evaluation
Extrel	No flue gas sample system available. Ambient air systems operated at 60-80°C	MS	Direct injection of gas to MS 1 ppm detection possible for higher amine “Lower” amine and aldehydes have ions which interfere with ions from air, 1 ppm not possible			<b>Limited applicable</b> for gas phase  Research partner for analysis system
Enviro-nics & IUT GmbH	No flue gas sampling system available	IMS	Initial test performed with MEA at 25 and 50%RH @ 50°C LOD ~7 ppb /48/. Water above dew point need to be removed	Measures only VOC	Water droplets entering the system are detrimental for instrument survival; system operates at maximum 90% RH.  Supplier informs that analyzer elevated temperatures solve the humidity issue.	<b>Suitable</b> , proof-of-concept with varying humidity necessary, need for gas pre-treatment system
G.A.S.	No flue gas sampling system available	IMS combined with: UV or radioactive Ionization source; Capillary columns for pre-separation	2-Hexenal < 50 pptv; operation temperature 80°C; Only non condensing gases	Measures only VOC	Suggest removal of water to dew point 20°C, rehaeting to 80°C to reduce water content in gas.	<b>Not applicable</b>  Research instrument for detection of trace compounds
NEO	In-situ sensor	TDLAS not applicable for wet gases	Verified Formaldehyde at ppm level. No experience with other compounds	H <sub>2</sub> O, CO, CO <sub>2</sub> , SO <sub>2</sub> , NO <sub>x</sub> , NH <sub>3</sub> , N <sub>2</sub> O, O <sub>2</sub> , CH <sub>4</sub>		<b>Not applicable</b>

**Applicable** (with comment): We refer to comments for gradation

**Not applicable:** Self explaining

**Limited applicable for gas phase** (with comment): Need for considerable improvement

## 6 DISCUSSION

### 6.1 Gas sampling system

#### 6.1.1 Heated sampling lines

There are few sources on studies of the effects of heated sampling lines on the gas matrix of interest, i.e. emitted flue gas from amine absorber towers. The relatively long sampling lines used for online sampling for extractive systems with remote analyzers, represent a potential for thermal degradation and artefact formation in the gas sample prior to analysis. Little or insufficient data have been found on the effects on the gas matrix as a function of temperature, residence time and material selection for the heated sampling lines. More experimental studies needs to be done in order to test the theoretical considerations of this report.

Heating of the sample is a precaution to preserve the instruments, the rule of thumb is 15°C above the highest boiling component to avoid condensation; this is clearly not possible considering compounds presented in Subtask 2: Manual sampling<sup>2</sup>. Further, from a thermo dynamical point of view; it is not necessary to heat a sample containing some milligrams of a high-boiling component to the boiling point of this particular component. However, this needs experimental verification and will be potential detrimental for the analysis and analyser; if fails. The first case is if compounds are not detected, the latter either slugging in sample lines occurs and/or liquid enters the analyser and form deposits.

Possible effects by the use of heated sample lines would be reduced by reducing the length or the residence time of the gas in the sampling line. However, short sample lines would require the analyser to be located at stack level, which could represent a practical problem.

#### 6.1.2 Thermal degradation

The elevated temperatures of heated sampling lines could induce thermal decomposition of compounds present in the gas. The classical heated sample lines in 316 stainless steel or PTFE are heated to temperatures between 120 and 180°C. MIDAC<sup>7</sup> has performed proof-of-concept experiments for their FTIR technology which show that the lowest temperature (121°C) approved by EPA 320<sup>6</sup> is best suited for the analysis of MEA in a gas containing H<sub>2</sub>O and O<sub>2</sub>; no degradation to NH<sub>3</sub>, CO<sub>2</sub>, CO was observed. Extension of this experiment with MDEA and piperazine showed that no MDEA was detected at the analyzer (condensation in the tube), increasing the temperature to 180°C enabled detection of the higher absorbents at a “*slight*” degradation. This simple experiment shows that the sample line temperature has a major influence on the analysis. This result can directly be transferred to the operation temperature of an analyser: is the operation temperature high enough to protect the equipment from condensation, oxygen and water are present, combined with a suitable residence time; this will result in thermal decomposition of the sample. Further, it is unclear which effect nitrous oxides will have with respect to decomposition or side reactions of organic flue gas compounds.

#### 6.1.3 Formation of artefacts

Heated sampling lines also represent a potential risk for artefact formation in the sample. In addition to water, the complex gas mixture of organic compounds also contains oxygen, NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> among others. Heating of this mixture could in theory lead to accelerated artefact formation and induce chemical change of the sample. This should especially be taken into consideration for gas mixtures containing NO<sub>x</sub> and secondary amines or other nitrosamine precursors in order to avoid artefact formation of nitrosamines during sampling. Precursors of

nitrosamines could also be formed as a result of thermal degradation of the sample. More work need to be done in order to investigate potential artefact formation upon heating of the gas sample. The potential for these unwanted effects has to be evaluated for each emitted gas matrix from different solvent systems.

## 6.2 Analyzer types

The collected data are presented in a rather condensed manner in Table 5-1. None of the suppliers have a system which copes completely with the online analytical challenges given by the framework posed by the process (see Chapter 2 and 3) as well with statutory regulations as e.g: IPPC-directives<sup>49</sup>. Classic flue gas analysis will be easily performed by these analysers; however the type and number of organic compounds, their physical properties and their expected low concentration in sub-ppm range generates substantial problems for these analysers. To our knowledge, little research has been performed by the large CEM system suppliers in order to adapting the current CEM systems to flue gas measurement from amine absorber columns.

SINTEFs approach to the selection of gas analyzers for the emitted gas of interest has been to (if possible) find analyzers that can analyze *multiple* compounds simultaneously, and preferably the complete list of compounds of interest. The analyzer should preferably be *generic*, in a way that the analyzer can be used for emissions from different solvent systems, and have the possibility to tackle future extensions to the list of compounds in case of new knowledge regarding other compounds presently not known of in the gas matrix.

### 6.2.1 Soft ionization mass spectrometry (PTR-MS/PTR-TOF-MS)

High resolution gas analysers based on MS (mass spectrometry) are optimized for analyzing ambient air. Dry gases and great care is necessary to avoid condensing humidity and water droplets in the gas stream entering the instrument. To avoid problems with water most gas analysers are built with a heated inlet applying a temperature ranging from 110-180°C. The option for analysis of gas with high water content and droplets is heating to elevated temperatures (e.g. 300°C).

There are mainly two different ionization techniques used, electron impact (EI) and proton transfer/soft ionization (PTR). EI-instruments do not seem to have the necessary sensitivity and there were concerns from the suppliers about the water content of the flue gas. The two suppliers of instruments with PTR/soft ionization, Ionicon and PMS (Airsense) claim to handle the water content well and seem have sufficiently low detection limits. The instruments could be used to characterize a dried gas with respect to unknown compounds at ppt-levels. Application of PTR-MS is predominately for analysis where identification and quantification of trace gases is targeted. The analyzers depend on non-condensing gases at the inlet port; this is achieved by heating of the sampling unit and pressure reduction. There is an upper limit of total volatile organics, exceeding this limits and an inlet dilution unit is necessary. Ionicon expressed concerns about the total concentration of organic compounds in the flue gas.

Instruments with PTR/soft ionization seems to be the most promising mass spectrometry instrument for online analysis, and should also be a good alternative if it is decided to dry the gas prior to analysing. The missing process interface to a flue gas stack requires attention with today's commercially available analysers.

If heated sampling lines are shown to *not* represent a problem for the chemical stability of the sample, SINTEF recommends the use of an isokinetically operated sampling unit and a PTR-

TOF-MS analyser with heating of the gas sample for the online analysis of the gas of interest. This solution to online emission monitoring would involve the development of a gas sampling system suited for this type of analyser. The PTR-MS and the PTR-TOF-MS instruments are both very sensitive instruments. The High sensitivity version of PTR-MS has a ten time lower detection limit compared to the PTR-TOF 8000. The PTR-TOF-MS on the other hand has a much better mass resolution, making it less vulnerable for interferences and better suited for characterization of unidentified compounds.

### 6.2.2 Ion Mobility Spectroscopy (IMS)

IMS based instruments are generally designed for ambient air applications, thus gaseous samples containing droplets or aerosols are not intended to enter the analyser. Some analysers are equipped with hydrophobic membranes in the inlet port to ensure that droplets contained in wet flue gas do not enter the instrument. Adaption of instruments require development of a suitable sample handling system (e.g.: evaporator) to safely transfer the sample into an *all* gas sample; though excessive temperature could give rise to component decomposition. Alternatively, suppliers suggest a gas dryer to remove humidity to about 25% or 50% RH<sup>48</sup>, this in turn will remove some of the water soluble compounds, making the analysis incomplete. Detection limits of the instruments are in order of 1 to 10 ppb, but because of the number of possible component combination verification is needed. For a dry flue gas stream with a relative humidity in the order of 50 % RH the application is possible in an industrial environment. Compared to the PTR-TOF-MS technology, IMS is regarded as inferior, since the analysis does not give molecular weights of the compounds analysed as the PTR-TOF-MS does, thus making it a less generic tool.

As for PTR-MS, an interface for sampling wet flue gases is presently to our knowledge not commercially available, and such a system needs to be developed for the application if IMS is used for gas emission monitoring from amine absorber towers.

### 6.2.3 Fourier Transform Infrared spectroscopy (FTIR)

Infrared spectroscopy or FTIR based instruments are frequently used in emission analysing systems, however the adaption of these instruments to the organics in question requires considerable work. While flue gases (e.g.: NH<sub>3</sub> and SO<sub>x</sub>) have narrow absorption lines in the IR-spectrum, complex organics show broader bands of absorption. The overlapping of these bands is expected since compounds have comparable molecular structure and functional groups, e.g.: the amine group in aliphatic amines will absorb similarly, independent if MEA or DEA are considered. Increasing number of compounds (absorbents and degradation products) will increase the complexity of the analysis.

The lower detection limits given by the instrument suppliers are in general given for a single component in dry N<sub>2</sub>, which is an indication for the performance of the instrument. There is considerable uncertainty regarding the influence of a combination of increased water content (water absorbs a large portion of the IR-frequency range) and several organic compounds in mixture on the lower detection limit. Real data with high water concentration and amines could not be retrieved from the suppliers. Even though it is well known (Protea ProTIR204, 6,4 m cell) that at 30vol% H<sub>2</sub>O, NO can be measured below 0.2 ppm, the supplier is sceptical to guarantee 1 ppm of MEA at the same conditions<sup>50</sup>. From performed initial experiments, a wide absorption band is observed; in combination with the wide spread absorption from water, a distinct change in the spectre as function of concentration change needs careful evaluation. Alternatively, application of a different analyser where a considerable longer optical path (>10 m cell) is suggested in order to obtain detection limits in the low ppbv range. SINTEF expects difficulties

with obtaining detection limits in the low ppbv range by FTIR without lowering the water content of the sample prior to analysis. Comprehensive work is needed to numerically “remove” the water spectre to identify changes in the remaining data which requires instruments with high resolution and accuracy. The masking of water needs be seen in relation to high temperatures to ensure that water is in the vapour phase and degradation tendency of e.g. formamide. A sample temperature of maximum 60°C is suggested<sup>50</sup>; the applicability of this solution needs to be verified experimentally and is in contradiction to experiments of MIDAC considering higher temperatures were condensation effects hindered that higher amines (MDEA) reached the analyser.

Even though FTIR analysers of today’s design are not the optimum analyzer, they are well suited to assist in emission monitoring, considering the above mentioned limitations regarding component speciation, possible thermal decomposition or artefact formation of compounds and masking of low component concentrations by water.

#### **6.2.4 Gas analyzers not considered for further investigation**

The fact that Tuneable Laser Absorption Spectroscopy (TDLAS) uses absorption bands instead of absorption spectra complicates analysis of complex gas matrices.

For similar reasons NDIR analyzers are not suitable for the given application.

The application of a DOAS system requires a long measurement path which is difficult to implement in a stack; further the flue gas needs to be free from droplets and aerosols.

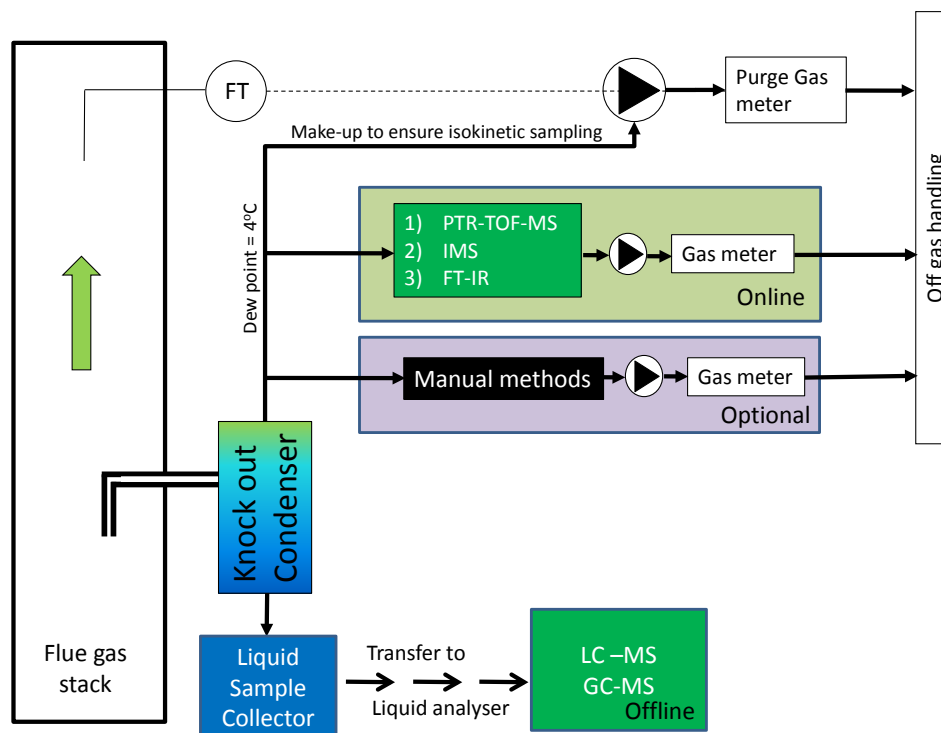
Ultraviolet-visible spectroscopy (UV-vis) is not suited for the analysis of the present complex matrix of different organic compounds.

Analysis of the flue gas by means of gas chromatography (GC) is ruled out because of the complexity of the necessary detectors in parallel to cover the various compounds and due to the insufficient detection limits in the commercially available instrumentation.

### **6.3 Setup for online sampling and analysis suggested by SINTEF**

Based on the assumption that heated sample lines *do* represent a problem for representative analysis of the sample for the temperatures necessary for a complete vaporization of the sample, SINTEF suggests the following setup for online sampling and analysis:

Isokinetic sampling is a prerequisite based on today’s knowledge of the gas matrix, most commercial systems are based on heated probes and sample lines; however, heated sampling systems might generated erroneous data. Alternatively, instead of heating the sampled gas, cooling the gas with a cooled probe combined with a condenser is suggested. The dry gas downstream the condenser can then be representatively split and subjected to different methods in parallel.. The dried gas exiting the condenser is analysed by a multi-component gas analyser operating at relatively low temperature. Candidates for this dry gas analysis are PTR-TOF-MS, IMS, FTIR (in that preferred order). Figure 6-1 visualises the suggested principle. Heating the dried gas phase to 60°C prior to analysis would ensure a temperature well below temperatures where decomposition has been observed. Sample gas temperature exiting the condenser should be less than 4°C this corresponds to a water content of app. 0.5 wt%. Analysis of such a dry gas would enable very low detection limits.



**Figure 6-1: SINTEF's suggested setup for online sampling and analysis.**

The condensed liquid is transferred manually to an LC-MS or GC-MS liquid analyser for further analysis. The sample preparation for the LC-MS/GC-MS analysis of condensate is straight forward and the water sample can be directly injected into the analyser. The accumulation of the liquid sample can be performed over a certain amount of time, from this liquid volume a sample is taken and manually analysed. This scheme can be easily operated on a schedule were e.g.: every 6 hours a sample is taken for analysis, thus making the analysis of condensate a semi-continuous process. The sum of gas and liquid analysis data represents the concentration of a component in the sample. For additional investigations, liquid or solid absorbents can be placed in parallel to the online analyzer for verification of calibration and accuracy of the online analyser.

SINTEF is currently in the process of patenting a concept for online liquid analysis which has been demonstrated in an in-house research project in 2010. This application can be used in order to fully automate the suggested condensate analysis in Figure 6-1.

Advantages of the proposed setup:

- Representative gas sampling and analysis of the gas without thermal degradation or accelerated artefact formation in the sample.
- Efficient solution to the challenge of a high water content of the flue gas. A dry sample gas stream is generated, thus enabling fast and high resolution analysis and trace component detection in the gas analyser.
- Access to high resolution analysis of the liquid phase by means of LC-MS/GC-MS.

#### **6.4 Evaluation summary**

Given the received information (literature and supplier discussions) it does not seem likely to find a complete online analyser system currently available commercially. Some emerging technologies like PTR-MS/PTR-TOF-MS and IMS have a great potential, but suited gas sampling systems needs to be developed for such analysers.

The main challenge for online sampling is assessed to be the use of long heated sampling lines. Due to the high water content of the sampled gas, the temperature in such sampling lines needs to be relatively high in order to ensure complete evaporation of the sample. This creates a potential for induced degradation and artefact formation in the gas sample upon sampling.

In order to avoid the use of heated sampling lines, SINTEF recommends a setup for online sampling which involves cooling of the gas prior to the analyser. This methodology requires analysis of the liquid condensate formed in order to make the analysis complete.

Based on the information given by suppliers summarised in Table 5-1 together with our knowledge of the different detection principles described in Chapter 4 and the discussion regarding analyser selection in Chapter 6, SINTEF gives a suggested suitability ranking of the instruments in Table 6-1.



**Table 6-1: Summary of the expected suitability for online monitoring of absorber gas emissions**

		Applicable	Verification needed						Not applicable	
Online Methodology		Chemical component for analysis							Comments	
		Combustion products	Amines	Ammonia	Aldehydes	Amides	Alkylamines	Nitrosamines		
<b>One analyser for entire analysis</b>	FTIR	OK, 3	1,2,3	OK, 3	1,2,3	1,2,3	1,2,3	1,2,3	Need for verification at low concentrations	
	NDIR	OK,2,3	1,2,3	OK, 3	1,2,3	1,2,3	1,2,3	1,2,3		
	TDLAS	OK,2,3	2,3	OK	2,3	2,3	2,3	2,3		
	UV-vis	2,3	0	2,3	0	0	0	0	Limited absorbance	
	GC	OK	1,2,3	OK, 3	1,2,3	1,2,3	1,2,3	1,2,3	Would require multiple detectors depending on compound of interest (current ranking includes GC-MS).	
	IMS	3	3	3	3	3	3	3	Need for verification, no proper process interface	
	PTR-MS/ PTR-TOF-MS	3	3	3	3	3	3	3	Need for verification, no proper process interface	
<b>Combination of separate analyzer for gas phase and for liquid phase</b>	PTR-MS/PTR-TOF-MS (gas) & LC-MS/GC-MS (liquid)	OK	OK	OK	OK	OK	OK	OK	More complex analyzer structure, compounds with higher boiling point (condensable / water soluble) will be analyzed in liquid phase.	
	IMS (gas) & LC-MS/GC-MS (liquid)	OK	OK	OK	OK	OK	OK	OK		
	FTIR (gas) & LC-MS/GC-MS (liquid)	OK	OK	OK	1?	1?	1?	1?		

0) Not applicable

1) Insufficient detection limits (depending on drying of the gas prior to analysis)

2) Potential interference problems due to the complexity of the gas matrix

3) Heated sample lines might cause thermal decomposition and artefact formation.

## 7 CONCLUSION

The response from most of the suppliers of traditional emission monitoring systems has been limited with respect to the requested compounds. This is primarily due to, for the time being, a non-existent market.

New technologies have been considered, these are in general available for laboratory style applications or tailor-made for single or few compounds of a subset of the compounds. Most progress has been made for dedicated ambient air analysis and monitoring, this development is driven by safety considerations. However, the design of the equipment is to date only suitable for non-condensing gases. These instruments will need considerable improvements until continuous operation 24/7 with wet flue gases is possible.

During this project work, an overview of available technologies has been established, and the application of the different methodologies has been evaluated for the given task. Only one commercial application is identified where an analyser operates continuously to monitor MEA, consisting of a heated sample line and FTIR system (MIDAC, US). Further, Aker Clean Carbon operates a FTIR from GASMET FTIR at their Mobile Test Unit and a similar analyser is installed in the pilot plant at the Esbjerg power station.

Three possible methodologies have been identified as potential candidates for the current task, capable of monitoring multiple compounds simultaneously; 1) Mass spectrometric instruments using PTR/soft ionization, 2) IMS and 3) FTIR in that preferred order. Mass spectrometric instruments using PTR/soft ionization are considered favourable due to their low detection limits and generic approach to the identification of compounds. Ion Mobility Spectroscopy (IMS) does not have the advantage of identification of compounds by molecular weight. Application of PTR-MS or IMS with today's commercial analysers requires the development of an appropriate gas sampling system. In contrast to PTR-MS and IMS, FTIR is the only instrumentation of the three above candidates that has commercial available complete systems for online sampling and analysis suited for the current task. However, FTIR detection limits and potential problems due to interference are of concern.

All the considered analysers described above require a non-condensing gas for proper function. A main challenge for online sampling is assumed to be the use of long heated sampling lines for online sampling to these analysers. Due to the high water content of the sampled gas, the temperature in such sampling lines needs to be relatively high in order to ensure complete evaporation of the sample. This creates a potential for induced degradation and artefact formation in the gas sample upon sampling. SINTEF recommends that the chemical stability of the gas sample in relation to the effect of heated sampling lines should be investigated in experimental studies.

In order to avoid heating of the gas sample, SINTEF suggests application of an isokinetic sampling unit, cooled probe and a condenser. The dried flue gas can be heated gently and transferred to PTR-TOF-MS, IMS or FTIR for high resolution gas analysis. The collected condensed liquid phase can be periodically transferred to an LC-MS/GC-MS for speciation and quantification. Limited research and development is necessary to implement such a solution.

## 8 RECOMMENDATION AND FUTURE WORK

The effects of heated sampling lines should be investigated, in order to determine possibilities and limitations for heating of the gas sample prior to analysis. These potential unwanted effects of heating should be evaluated for every new solvent system. Depending of the outcome of these investigations, SINTEF recommends two possible approaches for online gas analysis of the gas of interest:

- 1) If heated sampling lines do *not* represent a problem for the stability or artefact formation of the sample, SINTEF recommends the use of an isokinetically operated sampling unit and a PTR-TOF-MS analyser with heating of the gas sample for the online analysis of the gas of interest.
- 2) If heated sampling lines *do* represent a problem for the stability or artefact formation of the sample, SINTEF recommends the application of an *isokinetically* operated sampling unit, *cooled probe* and *condenser* which generate a dry flue gas that can be analysed by PTR-TOF-MS or IMS with gentle heating of the gas (60°C). The collected liquid phase condensate can be periodically transferred to an LC-MS/GC-MS for speciation and quantification. In order to apply FTIR-analysis of this dry gas downstream the condenser, it is expected that a special gas cell with long optical path length (> 10 m) is required in order to obtain detection limits in the low ppbv range. SINTEF expects difficulties with obtaining detection limits in the low ppbv range by FTIR without lowering the water content of the sample prior to analysis.

The stability of the gas sample should be investigated regarding the effects of heated sampling lines in relation to sample line temperature, length and residence time of the sampling line together with sampling lines material selected and flue gas composition. Reference methodology for analysis should be used to analyse a defined realistic gas matrix before and after sampling at different conditions by varying the above mentioned parameters for the sampling line. From these experiments, it should be possible to determine whether the gas matrix undergoes chemical change due to the sampling procedure. A research project investigating a defined number of solvent systems could be completed within 6 months.

If the findings of this study show that heated sampling lines represent a problem regarding degradation and/or artefact formation of the sample, SINTEF proposes a proof-of-concept study of the two-analyser scheme with a knock-out-condenser with analysis of liquid condensate and a subsequent dry-gas analysis downstream the condenser as described above in order to solve the problem. Such a proof-of-concept study could be completed within a 6 months research project.

## APPENDIX 1

### Request send to selected Analysis Equipment Suppliers

To whom it may concern,

SINTEF Materials and Chemistry is assisting a client in the work to evaluate emission monitoring. As part of this work we are evaluating the possibility to monitor online the following component **groups**: N-Nitrosamines, Alkylamines, Amines, Amides and Aldehydes. The specific components are:

- N-Nitrosamines
  - N-Nitrosodimethylamin (NDMA) 62-75-9
  - N- Nitrosodiethylamin (NDEA) 55-18-5
  - N-Nitrosomorpholine (NMOR) 59-89-2
  - N-Nitrosopiperidien (NPIP) 100-75-4
  - N-Nirodiethanolamin (NDELA) 1116-54-7
  - N-Nitrospierazine 5632-47-3
  - 1,4-Di-Nitrospierazine 140-79-4
- Alkylamines
  - Methylamine 74-89-5
  - Ethylamine 75-04-7
  - Dimethylamine 124-40-3
  - Diethylamine 109-89-7
- Amines
  - Mono-ethanol-amine (MEA) 141-43-5
  - Di-ethanol-amine (DEA) 111-42-2
  - Piperazine 110-85-0
  - 1,2-Di-amino-ethane (EDA) 107-15-3
  - 2-Amino-2-methyl-1-propanol (AMP) 124-68-5
  - N-Methyl-di-ethanol-amine (MDEA) 105-59-9
- Amides
  - Formamide 75-12-7
  - Acetamide 60-35-5
- Aldehydes
  - Formaldehyde 50-00-0
  - Acetaldehyde 75-07-0

The gas conditions are as follows: 15wt% oxygen, 80wt% nitrogen, 4wt% H<sub>2</sub>O and <1wt% CO<sub>2</sub> at a temperature between 25 to 50C and atmospheric pressure. The expected concentration of amine is lower than 5 ppmv. Concentration of the other components is for the time being not known but expected to be considerable lower (ppb to < 0.1 ppm).

We would like to ask for information which of the components above can be measured online in the given gas matrix. Please state lower detection limits and which gas pretreatment ahead of the analyzer is necessary.

Please, don't hesitate to ask for more information; also we are aware of that this application is no standard application, thus an open discussion on how to solve this problem is appreciated.

Best regards,  
-Bernd

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Sem Sælands Ved 2A  
7465 Trondheim  
Norway

## Appendix 2

### Table 8-1: Supplier Information and Contact

Company	Address	Contact	Comments
SICK MAIHAK AB	SICK MAIHAK AB Botkyrvägen 4 SE 143 35 Vårby Sweden	Steen Jensen sales@sick-maihak.se  <a href="http://www.sick-maihak.se">www.sick-maihak.se</a>	Strong supplier of CEMS systems with considerable experience for sampling and analysis. Own development department and laboratory facilities.
OPSIS AB	OPSIS AB Box 244 Skytteskogsvägen 16 S 244-02 Furulund Sweden	Peter Frieberg <a href="mailto:info@opsis.se">info@opsis.se</a>  www.opsis.se	Limited experience with components in question. Ability to calibrate and perform laboratory experiments
Norsk Analyse	Wirgenes Veg 10 N 3101 Tønsberg	Morten Myhre Andresen Morten.Mhyre.Andresen@norskanalyse.no <a href="http://www.norskanalyse.no">www.norskanalyse.no</a>	Supplier responds to request but didn't supply information.
ABB Norge	Lambrechts Instrument Services AS Leirvikflaten 23 5179 Godvik Norway	<a href="mailto:roger@instrumentservices.no">roger@instrumentservices.no</a>  <a href="http://www.instrumentservices.no">www.instrumentservices.no</a>	Supplier respond to request but didn't supply information  Strong supplier of CEMS systems with considerable experience for sampling and analysis.
ABB	ABB AB Lunnagårdsgatan 4 431 90 Mölndal Göteborgs/Bohus Län	<a href="http://www.abb.com/">http://www.abb.com/</a>	Own development department and laboratory facilities.
YAGA	Yaga Ltd. Solbakkveien 18 1405 Langhus Norway	Hans Jørgen Mastad <a href="mailto:hjm@yaga.no">hjm@yaga.no</a>	Sales organization which combines sensors from different suppliers. No laboratory facilities, dependent on suppliers for research and calibration.
Gasmet	Gasmet Technologies Oy Pulttitie 8 A FI-00880 Helsinki Finland	<a href="http://www.gamet.fi">www.gamet.fi</a>	Strong supplier of CEMS systems with considerable experience for sampling and analysis. Own development department and laboratory facilities.
Q-Interline	Q-Interline A/S Stengårdsvej 7 DK-4340 Tølløse Danmark	<a href="http://www.q-interline.com">http://www.q-interline.com</a>  <a href="mailto:al@q-interline.com">al@q-interline.com</a>	Specialized company for combination of chemometrics and spectroscopic analytical solutions with own research. Comprehensive experience in demanding flue gas analysis with analyzers from Protea and ABB.
Protea	Protea Limited First Avenue Crewe Cheshire CW1 6BG Great Britain	Andrew Toy <a href="mailto:Andrew.toy@protea.ltd.uk">Andrew.toy@protea.ltd.uk</a>  <a href="http://www.protea-monitoring-services.co.uk">http://www.protea-monitoring-services.co.uk</a>	Specialist for application of IR and MS-technology for challenging process and environmental monitoring. Perform analyser development, training, maintenance as well as emission monitoring, Develop in-house calibration models for analyzers.  Own reserach and test facilities
MIDAC Corp	Midac Corporation 130 McCormick Avenue #111 Costa mesa, California, 92626 USA	Peter Zemek <a href="mailto:pzemek@midac.com">pzemek@midac.com</a>  <a href="http://www.midac.com/">http://www.midac.com/</a>	FTIR-analyser in operation at a CCS-plant in US. Proprietary information, therefore limited information given.  Specialized in custom made FTIR analyzers.

			Own research and test laboratory
EXTREL	Extrel CMS, LLC 575 Epsilon Drive Pittsburgh, PA 15238 United States	Zbigniew Krieger <a href="mailto:zbigniew.krieger@gmail.com">zbigniew.krieger@gmail.com</a>  <a href="http://www.extrel.com/">http://www.extrel.com/</a>	Specialized supplier of online mass spectrometer for industrial applications.
Environics	Environics Oy Graanintie 5 P.O. Box 349 FI-50101 Mikkeli Finland	Simon Bockisch <a href="mailto:s.bockisch@iut-berlin.com">s.bockisch@iut-berlin.com</a>  <a href="http://www.environics.fi">http://www.environics.fi</a>	Company specialized in supply of ambient air analysis systems for chemical, biological radiological and nuclear protection. Continuous aspirated Ion
IUT	IUT Institut für Umwelttechnologien GmbH Volmerstraße 7 B Charlottenburg 12489 Berlin Germany	Simon Bockisch <a href="mailto:s.bockisch@iut-berlin.com">s.bockisch@iut-berlin.com</a>  <a href="http://www.iut-berlin.com">www.iut-berlin.com</a>	Mobility sensors for ambient air surveillance developed for detection of e.g.: toxic chemicals, biological agents and radioactive materials in buildings.
G.A.S.	G.A.S. Gesellschaft für analytische Sensordysteme mbH Bio Medizin Zentrum Dortmund Otto-Hahn-Str. 15 44227 Dortmund Germany	Thomas Wortelmann <a href="mailto:Wortelman@gas-dortmund.de">Wortelman@gas-dortmund.de</a>  <a href="http://www.GAS-Dortmund.de">www.GAS-Dortmund.de</a>	Specialized for ambient air measurements, food and medical application.  Detection of organic trace components in various applications ion range of ppt to ppb.
NEO	Norsk Elektro Optic Solheimsveien 62 1471 Lørenskog Norway	Peter Kaspersen <a href="mailto:peter@neo.no">peter@neo.no</a>  <a href="http://www.neo.no">www.neo.no</a>	Develop, market and manufacture in-house technology.  Heavier components don't have absorption lines but bands, measurement principle based on single line spectroscopy is not suitable.
Thermo Scientific	27 Forge Parkway Franklin, MA 02038 US	<a href="http://www.thermoscientific.com">http://www.thermoscientific.com</a>	Strong supplier of CEMS systems with considerable experience for sampling and analysis. Own development department and laboratory facilities. No system available for given request, development possible
Svanholm	Nordic Pharma and Analyser Center Svanholm 4760 Vordingborg Denmark	Bent Svanholm <a href="mailto:Bent@svanholm.com">Bent@svanholm.com</a>  <a href="http://www.svanholm.com/">http://www.svanholm.com/</a>	System Integrator with Thermo Scientific
PMS AB Pro Miljö Sandström AB	PMS AB Västra Esplanaden 2 90326 Umeå Sverige	Göran Sandström <a href="mailto:goran@pmsab.se">goran@pmsab.se</a> <a href="http://www.pmsab.se">http://www.pmsab.se</a>	Specialized in monitoring off gases and detection of trace components (VOC) in engine technology and gas processing.
Ionicon Analytik	Ionicon Analytik Ges.m.b.H. Eduard-Bodem-Gasse 3 6020 Innsbruck Austria	Stefan Jaksch <a href="mailto:Stefan.Jaksch@ionicon.com">Stefan.Jaksch@ionicon.com</a>  <a href="http://www.ptrms.com/">http://www.ptrms.com/</a>	Specialized in detection of trace volatile organic gases < 1ppt

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