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SUBTASK 3
ONLINE SAMPLING AND ANALYSIS

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ONLINE SAMPLING AND ANALYSIS

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1. TERMS AND DEFINITIONS

AMP	2-Amino-2-methyl-1-propanol
AMS	Automated measurement system
ATD	Automated thermal desorption
CEM	Continuous emissions monitoring measurements
CCS	Carbon capture and storage
CPT	Chloro-p-toluidine
DEA	Diethanolamine
DEN	Diethylamine
DGA	Diglycolamine
DID	Discharge ionization detector
DMA	Dimethylamine
Dnpz	1,4-Dinitrosopiperazine
EA	Ethylamine
EDA	1,2-Diaminoethane
EMEA	2-(Ethylamino)ethanol
FID	Flame ionization detector
FPD	Flame photometric detector
FTIR	Fourier transform infrared
GC	Gas chromatograph
HID	Helim ionization detector
IMS	Ion mobility spectrometer
IR	Infrared
I-TEQ	International Toxic Equivalents for dioxins and furans only
LOD	Limit of detection
MAPA	N-Methyl-1,3-diaminopropane
MDA	Methylene dianiline
MDEA	N-Methyldiethanolamine
MEA	Monoethanolamine
MMA	Methylamine
MS	Mass spectrometer
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NIR	Near-infrared
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
PAH	Polycyclic aromatic hydrocarbons
PCDD/F	Polychlorinated dibenzodioxins and furans
PEEK	Poly ether ether ketone
PID	Photoionization detector
PPD	p-phenylene diamine
PTFE	Poly tetra fluoro ethylene
PTR-MS	Proton transfer reaction mass spectrometry
QMS	Quadrupole mass spectrometer
TCD	Thermal conductivity detector
TDA	Toluene diamine
TEA	Triethylamine
TD	Thermal desorption
TMA	Trimethylamine
TOF-MS	Time-of-flight mass spectrometer
UV	Ultraviolet
UVH	Ultra-high vacuum
VOC	Volatile organic compounds

2. SUMMARY

Some promising techniques for the on-line analysis of amines were found during the survey. There is no over the top solution to be recommend for the analysis of separate amine compounds. For the selective methods there is some experience using FTIR (Gasmet, Midac) and process MS –analysers (Airsense) for the amine analysis. Both of the methods suffer from some interferences. The application for the FTIR needs to include all compounds having absorption. Also IR-absorption spectrums between the different amines and ammonia are quite similar so the calibration of analyser is important to be performed. Mass spectrometers without pre-separation (like GC) may also suffer from interferences between different compounds with the same mass. For this reason both of the methods should be validated, if accurate results are needed.

IR-, diode laser- and UV methods are more like summary methods for the ammonia and amines because of lower selectivity. Interferences with other compounds, like water, are also possible. Some of these analysers may be installed in-stack, which makes sampling system simpler. These analysers are available by many vendors.

Colorimetric method (Sensi-Tape) gives a different approach for the summary analysis of ammonia and amines or aromatic amines. Especially it may be good method on daily monitoring of amines, due to its relatively easy analysis principle. Colorimetric method is semi on-line, since it gathers sample before analysis.

If the lowest concentration needs to be measured, it may be possible to transform continuous dioxine/furan sampling system for the sampling of amine, nitrosoamine and other organic compounds. Because the sample needs to be analysed at the laboratory, it is not actually on-line system. However it may be the only solution, if a very low levels needs to be analysed. Sampling time may vary from hours to days, even weeks. If long sampling times are needed, decomposition of the sample should be evaluated. The detection limit is limited by the method used in laboratory. This system is not tested for the amine analysis and some development and validation needs to be done. The system is not on-line.

A faster but still very sensitive and selective system may be possible to apply by using on-line thermal desorption combined to GC-FID or MS systems. The disadvantage of the system is quite complicated and sensitive instrumentation at industrial environment, especially while using MS-detector and relatively low response time, about 10-60 minutes depending on the application.

Ion mobility cell based system (eg. Environics) may be sensitive and selective analyser for the amines. However testing and validation with real matrix needs to be performed. Manufacturer proposed R&D project for the testing of amines. This system may be very sensitive for the matrix.

It is important to decide the level of performance (selectivity, sensitivity, response time, cost and maintenance) needed for the on-line system. Very selective and sensitive system is possible to be acquired for example by using on-line-TD-GC-HRMS system. However, it is very expensive to buy and complicated to run. A realistic balance between the performance and usability looks to be on FTIR and MS-systems. For the FTIR systems Gasmet and Midac Corporation already have experience with amines. Also MS-systems such as Airsense are experienced and ready for the task.

It is recommended to have another analyser for the measurement of summary parameter such as TOC or combined amines and ammonia. It is recommended that summary analyser use different technique. This makes possible to observe unknown compounds or systematic errors compared to e.g. FTIR or MS system. TOC measurements by FID will give important information about the overall TOC-concentrations. Because FID is widely used as EN reference method as well as fixed measurements in waste incineration plants, it is most probable that some environmental limits of CCS-plant emissions will be stated as TOC.

To validate the methods, it is recommended to perform a comparison test for the most promising techniques on some suitable test facility. If test could be arranged at relatively small pilot-scale plant, it may be possible to manipulate the real flue gas by injecting the most important target compounds or distractive elements to the flue gas before sampling point. Based on our experience this works fine at least with gas phase compounds despite the droplets. Manual sampling should also be performed to obtain at least one fixed concentration level.

The effect of filtration and heating during the sampling should be evaluated. It may have a very significant effect for the concentration of some compounds. It looks that filtration and heating are necessary while using sophisticated instrumentation such as FTIR or MS. If the sample handling will reduce concentration of some compounds significantly, the point of using very effective analyser later on the sampling line disappears.

3. PRINCIPLES OF DESIGN

3.1 Delivered information

At the time the report was established detailed information about the CCS-plant was not available. The Common dimensions delivered by the Company are as below:

Table 1 delivered Common values for the starting point of the design

	Unit	Large scale plant	Pilot plant
Gas flow gas rate	million Sm³/h	700 000 - 2 300 000	250-1200
Temperature	°C	25-50	25-50
Moisture		saturated probably with droplets	saturated probably with droplets
Pressure		± outside pressure	± outside pressure
Main body velocity	m/s	2-3	2-3
Gas velocity at pipe exit	m/s	About 20	2-3
Composition			
- oxygen, O_2	mol-%	15	15
- nitrogen, N_2	mol-%	81.5	81.5
- carbon dioxide CO_2	mol-%	0.5	0.5
- water, H_2O	mol-%	3	3
- amines	ppm	< 5	< 5
- ammonia, NH_3	ppm	< 50	< 50
- NO_x	ppm	n/a	n/a
- NO_2	ppm	n/a	n/a
- SO_2	ppm	n/a	n/a

The final item before the duct and AMS measurement site is a demister.

4. BASIC DIFFERENCIES OF ON-LINE ANALYSIS

Continuous stack emission measurement systems could be either in-situ or extractive based on the analysis principle.

4.1 In-situ

In-situ methods are almost always in-stack applications where the measurements are performed as direct measurement of the flue gas inside the duct, albeit some applications are performed from the side flow separated from the main flow. Typical method is cross-stack measurement where a measurand is detected directly from the flue gas due to its distinctive physical or chemical properties. These kinds of measurements are for example flow rate, dust concentration, opacity, and some IR-based methods. The benefits of in-situ measurements are short response time, lack of deposition in sampling lines and, in some cases, more representative sampling than one point measurement. All measurands cannot be measured in-situ because sample treatment is not possible. Often (but not always) transmitter and receiver are installed to the opposite sides of the stack which may cause difficulties in some installations (large ducts or temperature variations may cause misalignment, poor access to the installation places, problems with ATEX-zones). Some measurements like O_2 measurement by zirconium cell, temperature and pressure are often successfully measured at one point in the stack with no significant difference between representativeness compared to extractive sampling done by multipoint measurement.

If compounds of interest are soluble in water and measuring system is sensitive only for the compounds in gas phase, significant error may cause while sampling wet flue gas. The compounds dissolved in water droplet may not be “visible” for the sampling system while the concentration in droplets may be significant. This may be the case with some e.g. IR-based systems.

Pros and cons of in-situ measurements are presented below:

\+ Direct measurement from the raw flue gas, no deposition or degradation in sampling lines
\+ Fast or immediate response time
\+ Representative sample on cross-stack measurements
\+ Sample is measured at real flue gas conditions, no decomposition on sampling system

\- Some system tests may be difficult to perform (e.g. calibration, linearity test)
\- Fouling of the instrument parts by the flue gas contaminants e.g. dust and salts
\- Alignment errors (some devices are with automatic re-alignment systems)
\- Limited selection of measurands are available
\- Systematic errors are possible if drops or droplets are present in flue gas
\- ATEX-related limitations on hazardous areas (ATEX-qualified systems are available)
\- Sample gas cannot be pre-treated (e.g. drying, evaporating, filtering, diluting)
\- Cross-interference between some measurands (water-dust)

4.2 Extractive

On extractive analysis methods sample is analysed outside the stack. A sample gas is taken from the flue gas flow on a sampling probe and conducted by sampling lines to the analysis equipment. On extractive sampling systems analysing equipments could be installed further off the measurement site.

A wide range of analysers are available and even some laboratory systems could be transformed into flue gas sampling.

\+ Wide range of analysers and measurable parameters available
\+ Sample gas could be treated before analysis (filtering, drying, dilution etc.)
\+ Analysers could be positioned further from the stack
\+ Calibrations, linearity tests etc. are normally easy to perform
\+ Analyser is easy to replace at the case of malfunction

\- Sampling with long lines may affect the sample composition
\- Representativeness may suffer on heterogeneous gas flows if only one point sampling is performed
\- Leaks and sampling system malfunctions (clogging) may affect the results. Sometimes if the sampling part is not regularly maintained and tested, systematic error can prevail a long time.

4.3 Comparison between the methods

Comparison between in-situ and extractive methods is not unambiguous. Some parameters, such as flow rate and temperature needs to be measured in-situ, but some parameters such as the water content is not that simple. Water is often measured by IR or FTIR techniques as an extractive manner. In that case sampling must be taken by isokinetic sampling if droplets are present. However, in practise many extractive FTIR or IR system takes sample using straight probe vertical to gas flow. On the other hand, in situ moisture analyser based on IR may no measure accurate water content if droplets and dust are present.

4.4 Main challenges on on-line sampling

On-line sampling of amine based CCS-plant flue gas differs significantly compared to exhaust gas of natural gas fuelled gas turbine.

The flue gas after the demister is expected to be humid and at dew point. Also droplets may be present at least in the case of malfunction of the CCS-process. Because impurities are soluble in water, droplets may carry relatively high proportion of impurities. Sampling should include both gas phase and liquid phase without drying or extraction of water before the analyser. The main challenges on sampling are:

- **Automated isokinetic sampling** on extractive on-line systems are not widely used with on-line analysers and commercially ready systems are relatively rare for this purpose.
- **Representativeness** may be reduced if the flue gas is not homogeneous at the sampling plane and the sampling is from one point only. This should be avoided by sampling from the several points by automated moving probe or other construction. Moving probe requires automatic adjustment of the sampling flow, also analyser afterwards the sampling line should be immune to the flow rate changes.
- **Filtering and drying** is necessary for the most of the analysers. To avoid condensation on the filter, it is normally heated which may decompose some of the amines and filter the high boiling point compounds from the sample gas. If the sample gas is dried by condensation, large amount of amines and other compounds may disappear with condensate. The materials used in permeable driers may absorb the compounds or be under attack of corrosion of amines.
- **Materials** should be chosen carefully. Many plastics are not suitable when amines are present. Also some metals and alloys may suffer from corrosive attack by amines.
- While measuring **humid gases** by partly heated sampling systems a challenge may be “drop evaporation peak”. This occurs if sample is acquired by cold probe and drops will accumulate and grow in the sampling line. When drop enters the heated zone (temp > 100 °C), it will evaporate and formed gas will be seen as a peak on the analyser. This is observed for example when using FTIR which measures also water at very humid conditions and cold parts in sampling system. Sampling of humid gas may bring some other problems related.

5. SAMPLING SYSTEMS

Sampling systems are needed for the extractive analysis methods. The typical sampling system can be divided either wet or dry system based on if water is condensed or not before the analysis. Dry systems can be used only for the water un-soluble compounds such as oxygen, CO, CO_2, NO_x etc. On wet systems flue gas needs to be heated or diluted by dry gas (typically air or nitrogen) over the dew point to avoid condensation inside the analyser.

Heated filter unit is normally used (excluding dust measurements) on both methods to avoid contamination of internal parts of the analyser. Isokinetic sampling is not normally used for gaseous compounds. On typical cases isokinetic sampling is performed only with dust analysis, although it is recommended to have isokinetic sample if flue gas is humid and includes droplets and measured compound is water or soluble into it. This may be the case with FTIR analysers.

After the filter unit, gas is normally conducted by heated sampling lines to the analyser. If dilution method or drying is used before, sampling lines are usually cold. PTFE is normally used material.

5.1 Some observations about the sampling of amines, aldehydes and ammonia

Most of the amines and ammonia are well soluble in water and the concentration balance between the gaseous and liquid compounds are unknown. This means that sample from the humid gas is recommended to acquire from the flue gas by isokinetic sampling if droplets are expected to be present.

Isokinetic sampling probes are available commercially by several vendors (e.g. Zambelli S.r.l. TCR Tecora, Paul Gothe Messtechnik). The typical application is intended to manual sampling of dust, HCl etc, although systems may be applied to the fixed on-line sampling.

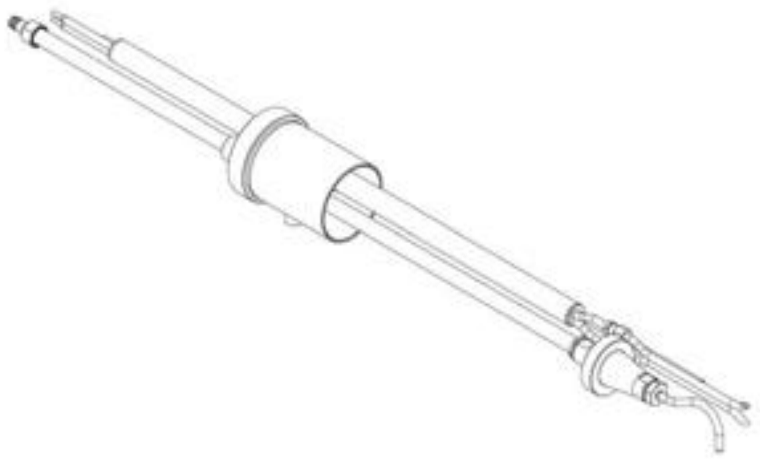


Figure 1 Example of isokinetic combinated sampling probe by Zambelli S.r.l

Adjustment of flow rate on sampling is recommended to be automatic. In practise, some of the cases when flow rate is steady the flow adjustment is preset and checked periodically. Automatic flue rate adjustment units are commercially available, once again intended mainly for the manual sampling purposes, but those are possible to use in fixed systems. Continuous automatic sampling systems for the PCDD/F and HCl are built for the isokinetic sampling (see chapter 6).

On amine sampling heated filter or sampling lines may affect the results significantly. Some of the amines may decompose on the filter while other amines or ammonia may be formed. Also heat stable salts or condensable amines may concentrate on the filter. It is not clear if this is significant if proper temperatures and practises are used. It is estimated to be possible to analyse at least some of the main components at sufficient level based on discussions and experiences of analyser vendors (e.g. Gasmet, Midac, Ionicon, Airsense).

AMS sampling probes on fixed installation are mainly having sample only from one spot. However some installations with pneumatic or electric motor moving sampling probes are constructed, usually as do-it-yourself basis. On these installations sampling rate is usually constant at the different points of the stack even flow rate varies so the sample is not taken as isokinetic sampling. If the sampling rate is adjusted continuously analyser needs to be insensitive to flow rate changes or side flow needs to be used to obtain isokinetic flow. When using side flow adjustment, it is important to ensure that the separation of the flows is homogeneous which in practice means, the sample gas is on totally in gaseous form. This could be done by heating or diluting with by dry gas.

Some of the probe vendors offer different approaches to acquire homogeneous sample.

Three point sampling probe is designed for the gaseous samples. It takes samples from the gas from one of the three points at the time. The inside material and the filter is SS but also PTFE tubes are used at some parts, however the PTFE parts are possible to replace by stainless steel, Figure 2. This system is not designed for isokinetic sampling.

Figure 2 CEM Heated 3 Point Probe (CleenAir Engineering)

Kurz Instruments offers the series 220 sampling rake (Figure 3). It incorporates the Kurz Axial Flow-Low Particle Loss sampling nozzle design, developed especially for the DWPF at Savannah River Site. Rather than use a single "shrouded nozzle" as suggested by ANSI N13.1-1999, it uses low-loss axial flow nozzles to achieve the lower particle loss. Kurz believes its' approach is more realistic, as a single nozzle can "miss" accident conditions n which large particles penetrate the upstream HEPA filters at the seals or any other location.

Figure 3 Kurz Instruments inc. 220 sampling rake

The main difference between the operation of a single-point shrouded nozzle versus the Kurz Series 220 Multi-Point Sample Rakes, is that the shrouded nozzle is normally used with a manually controlled constant sample flow rate (which is questionable at low stack flows) and the Kurz Series 220 Multi-Point Sample Rakes are operated with the sample flow rate proportional to the stack flow rate, either by using the Kurz Automatic Flow Control System or manually controlled. The flow chart of the sampling rake is presented at the Supplements 1.

Dilution probe method is commonly used on emission measurements. The basic idea is to dilute concentration of sample gas by using constant flow critical orifice and dry dilution air to avoid condensation of water and overdrive of response on the analysers. This is good approach when relatively high concentrations (ppm level) are measured with analysers designed to low concentrations such as ambient air monitoring (ppb level). Dilution probe method may give an solution to use very sensitive analysers such as some MS-systems.

Some on-line systems are designed to avoid water and droplets and only gaseous phase is analysed. This may give a significant underestimation of total concentration, because parts of the amines are most probably dissolved into droplets. Validation of sampling and analysis methods between manual and on-line sampling needs to be performed.

6. CONTINUOUS AUTOMATIC SAMPLING SYSTEMS

PCDD/F and PAH compounds are continuously sampled mainly from the flue gas of the waste incineration plants. Because of very low emission limits (total amount 0,1 ng/m³ I-TEQ), PCDD/F- compounds cannot be analysed online at the current state of technology. Even PCDD/PAH compounds differs from amines both waters solubility (poor) and degradation (thermal decomposition occurs at high temperatures) it may be possible to convert automated PCDD/F system to sampling systems for the amines. Actually TCR Tecora advertises that their DECS –system could be upgraded to the sampling for heavy metals, mercury and HCl.

Another vendor for the fixed and continuous sampling system is AMESA a brand of Environnement S.A (formerly Becker Messtechnik).

Fixed continuous PCDD/F sampling systems consists of two parts: the control unit and the sampling unit. The control unit is the interface between the sampling unit and the operator who leads all the system function; it is generally placed in a safe area easily reachable. The control unit controls:

- isokinetic control
- temperatures
- automatic leak tests
- sample volume measurement
- stack velocity measurement
- data logging and communication

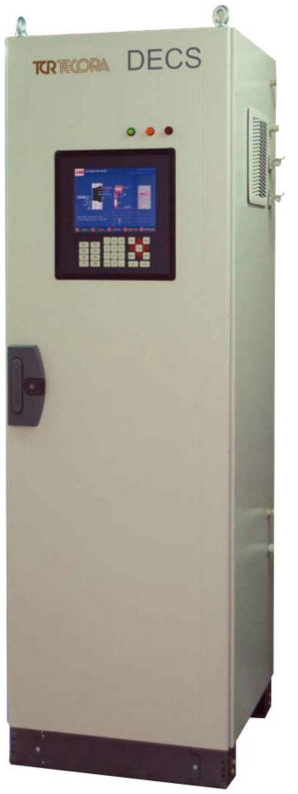


Figure 4 TCR Tecora DECS control unit

The sampling unit is the part installed on the stack sampling point and is responsible for the sample extraction, without altering its composition, and collecting the solid and gas phases on the appropriate device. The sampling unit is composed by:

- Heated Probe with interchangeable nozzle
- Heated box for filter holder
- Condensing system
- Adsorbing trap for XAD-2
- Pitot tube

Figure 5 TCR Tecora DECS system, view inside the condensing unit

TCR Tecora told that DECS was born as a long term dioxin sampling system. Its application is also suitable for other low concentrations micro pollutants in flue gases. It is based on a filter condenser method with a heated probe. For the sampling of amines, system can be used as normal sampling probe without any heating.

The condenser is design following the specifications in the EN 1948-1, filter condenser section. The cooling temperature needs to be, for PCDD/F, below 20°C on the resin and DECS's standard solution is a cooling unit which is responsible only for the condensing coolant.

DECS system is suitable for side stream sampling according to EN 14385 (Heavy metals) and 13211 (Hg) with 250 ml impingers. The side stream flow rate is taken after the thimble, and the flow rate (1 l/min) ensured by a constant flow additional sampler.

It looks very promising to transform the DECS system for the sub-low level amine analysis and manufacturer appears helpful and favourable for the idea.

7. ONLINE ANALYSERS

7.1 Raman

Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light from molecules. The Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations. The mechanism of Raman scattering is different from that of infrared (IR) absorption and Raman and IR spectra provide complementary information. Typical applications are in structure determination, multicomponent qualitative analysis, and quantitative analysis.

Process Instruments Inc. manufactures an optical fiber-based Raman scattering instrument for real-time, on-line analysis of amine processes used to remove acid gases (H_2S and CO_2) from hydrocarbon streams. Raman analysis is well suited to amine monitoring and control for several reasons:

1) Raman scattering requires little if any sample conditioning

2) The high resolution Raman spectra of amine solutions allow the various components (amine, H_2S, and CO_2) to be distinguished and quantified
3) Working in the NIR region allows for fiber-optic coupling of the sample stream probe and the Raman analyzer
4) Working with optical fibers allows for multiplexing many individual Raman probes to one single Raman instrument, reducing instrument calibration and simplifying overall maintenance. Continuous in-situ monitoring of all the critical amine parameters: amine concentration, H_2S, and CO_2 levels can provide almost instantaneous feedback on important changes in the amine process.

Raman has an advantage over infrared (IR) in that there is no interference from water so the probe can be directly inserted into a process stream. Infrared requires a sample conditioner. A single Raman system can be multiplexed up to 18 channels/streams.

The accumulation of Heat Stable Salts (HSS) or other contamination products in amine streams create operational problems such as capacity reduction or corrosion. Many of the degradation products are hard to detect since they often titrate as amines, and so a refiner might think a solution is more active than it really is. Raman analyzers have the ability to detect the onset of formation of these degradation products at trace levels before they start deteriorating the amine performance.

7.2 IR

IR spectroscopy deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals.

7.2.1 Aspectrics

Aspectrics MID Infrared and Near Infrared Analyzers are available for both at-line and On-line applications. As an On-line Analyzer, Aspectrics instruments deliver ultra-fast sampling speed for real-time analysis and LAN based communications for seamless process integration. In addition, the analyzers have good resistance to vibration which ensures accurate and stable results regardless of the operating environment.

There was no information delivered if the analyser could be used in amine analysis.

7.2.2 Gasera

Gasera photoacoustic Multi-Gas Analyzer F10 can reliably and simultaneously monitor of up to 9 different gas components using a gas sample of only few milliliters in volume. The novel multi-component analysis technology ensures effective cross-compensation for interference of other gases. The model based non-linearity compensation provides linear dynamic measurement range of over five orders of magnitude without range adjustment and with just one point span calibration. The vendor ensures that its extremely high stability and lack of consumables ensure low cost of operation. The measurable gases by Multi-Gas Analyzer F10 include for example hydrocarbons, VOCs and corrosive gases. It can be used in many applications. The device is based on photoacoustic IR spectroscopy with cantilever enhanced optical microphone and electrically pulsed IR source (no mechanical chopper). The detection limits are in sub-ppm levels and the response time is configurable from 30 s to several minutes. The operating temperature is informed to be 0 – 45 °C and the analysis can be performed in moisture content of 0 to 90 % non-condensing.

The manufacturer has no experience about the amine analysis. They believe that overall amines could be analysed and were interested to perform performance tests if suitable gas composition is available.

7.3 FTIR

7.3.1 Principle

FTIR stands for Fourier Transform Infrared Spectroscopy. An FTIR gas analyzer detects gaseous compounds by their absorbance of infrared radiation. Because each molecular structure has a unique combination of atoms, each produces a unique infrared spectrum sometimes called as “molecular fingerprint”. From this, identification (Qualitative analysis) and analysis (Quantitative measurement) of the gaseous compounds is possible. An FTIR analyzer simultaneously measures multiple analytes in a complex gas matrix, detecting both organic and inorganic gas-phase species.

However, this technology has also some limitations. Noble or inert gases have no measurable IR-spectrum as well as homonuclear diatomic gases e.g. N_2, O_2, Cl_2, H_2, F_2. Also H_2S is not possible to measure at ordinary levels. Some vendors have circulated this issue by an in-built ZrO_2 cell measurement of O_2.

Quantification on FTIR is based on Beer-Lambert law. Basically it is linear relationship between the absorbancy and concentration of absorbing species generally written as:

$$A=a * b * c$$

Where

A = measured absorbance
a = wave-length dependent absorptivity coefficient
b = (light) path length
c = analyte concentration

Due to the constant absorptivity coefficients of gasses, the calibrations will also remain constant and no recalibration is required if the absorption path length is not changed.

In practice during the normal operation instrument background (means zero) measurement is required daily to compensate for all changes in signal level or in the instrument. Cell temperature and pressure is normally measured and impact is taken into account on quantification so calibration of measured compounds is not necessary during the life time of the equipment if the absorption path length remains same. However, water makes an exception. Spectrum of water is dominant and will strongly affect the quantification of other compounds and should be calibrated periodically. FTIR-instruments are available by several vendors of which some are presented below.

7.3.2 Gasmet

The Gasmet CEMS II FTIR measuring system is designed for continuous emissions monitoring measurements (CEM). Typical application is H_2O, CO_2, CO, N_2O, NO, NO_2, SO_2, HCl, HF, NH_3, CH_4, C_2H_6, C_3H_8, and C_2H_4 monitoring from waste incinerator or large combustion plants. Measured components and calibration ranges can be changed according to application. Simultaneous analysis of up to 50 gas components is possible. The CEMS II is calibrated for standard emission measurements but in case of alternative gases, the calibration can be done to the system (440 or 1010 €/gas compound). The Gasmet CEMS II is market as an ideal tool to use for measuring trace concentrations of pollutants in wet, corrosive gas streams. All parts of the Gasmet CEMS II are be heated up to 180 ºC, however temperature can be decreased if needed. It can be used for undiluted gases and the sample gases do not need drying beforehand. It is possible to run Gasmet at lower temperatures.

The Gasmet CEMS II consists of Gasmet FTIR gas analyzer, Gasmet industrial computer, and Gasmet sampling system. The operation of the system is fully automatic and controlled by the Calcmet software. Additionally all functions of CEMS II can be controlled manually.

The most suitable Gasmet analyzer is Dx-4000 or Cx-4000 FTIR depending if the sampling system is needed to be portable or fixed. The Gasmet FTIR analyzers have been used in multiple CO_2 recovery projects among many other applications in order to measure amine contents. Some specs of the analyser and sampling system are presented below.

- Sampling temperature, 50 – 180 °C (recommendation 120 – 180 °C)
- Scanning time, 10 scans/sec
- The aluminium mirrors are covered with Ni-Rh-Au coating + special protection coating MgF_2 or Si, but alternative coating materials can be used in order to prevent corrosion by amines and other compounds related
- The speed of suction, 4 l/min
- The length of sampling line has usually been 5 – 40 m. The longest continuous line delivered has been 87 m. The length of the line can be altered but it is preferable to keep it as short as possible
- The recommended light path length on emission measurements is 5 m

The recommended sampling method (AMS-installation) depends of the circumstances. Hot sampling system is standardized. The system has a probe with a filter for small particles and the probe inside the channel can be heated. A heated line goes from probe to the measuring system where the sampling unit pumps the sample gas to the FTIR analyzator. The tests have not been performed at varying oxygen and moisture contents but can be done at Gasmet if requested.

The compounds which have been analyzed by Gasmet analyzer are listed at Table 2. Also some analysing parameters are presented. Modification for the measuring parameters can be done if needed.

Table 2 Gasmet compound calibration: list of typical compounds for CO_2 capture (the compounds of interest are marked with orange color).

Compound name	Formula	CAS number	Typical Range	Unit	DL (ppm) 5 m, 180 C, 1 min	Wawe numb cm-1	Notes
Water	H_2O	7732-18-5	25	vol-%	<1000		
Carbon dioxide High	CO_2	124-38-9	100	vol-%	<1000		
Carbon dioxide Low	CO_2	124-38-9	15	vol-%	<1000		
Carbon monoxide	CO	630-08-0	100	ppm	0.493	2177	
Nitrous oxide	N_2O	10024-97-2	100	ppm	0.031	2238	
Nitrogen monoxide (Nitric oxide)	NO	10102-43-9	200	ppm	0.569	1906	
Nitrogen dioxide	NO_2	10102-44-0	200	ppm	0.730	2918	
Sulfur dioxide	SO_2	7446-09-5	100	ppm	0.057	1374	
Ammonia High	NH_3	7664-41-7	4000	ppm	0.261	964	CO_2 and amines disturb
Ammonia Low	NH_3	7664-41-7	20	ppm	0.261	964	
Methane	CH_4	74-82-8	50	ppm	0.105	3018	
Formaldehyde	HCOH	50-00-0	50	ppm	0.172	2802	
Formic acid	HCOOH	64-18-6	50	ppm	0.060	1119	
Acetic acid	CH_3COOH	64-19-7	50	ppm	0.081	1181	
Acetaldehyde	CH_3CHO	75-07-0	50	ppm	0.267	2732	
Methanol	CH_3OH	67-56-1	50	ppm	0.270	1057	
Ethanol	C_2H_5OH	64-17-5	50	ppm	0.406	1049	
1-Propanol	C_3H_7OH	71-23-8	50	ppm	0.161	2972	
Ethylene glycol (1,2-Ethanediol)	$OHCH_2CH_2OH$	107-21-1	50	ppm	0.243	1049	
Methylamine	CH_3NH_2	74-89-5	200	ppm	0.437	2918	
Dimethylamine	$(CH_3)_2NH$	124-40-3	100	ppm	0.188	2810	
Trimethylamine	$(CH_3)_3N$	75-50-3	100	ppm	0.081	2779	

Compound name	Formula	CAS number	Typical Range	Unit	DL (ppm) 5 m, 180 C, 1 min	Wawe numb cm-1	Notes
Triethylamine	C_6H1_5N	121-44-8	100	ppm	0.050	2979	
Ethylamine	$C_2H_5NH_2$	75-04-7	100	ppm	0.287	2964	
Diethylamine	$(C_2H_5)_2NH$	109-89-7	100	ppm	0.120	2979	
N,N-Dimethylethylamine (DMEA)	$(CH_3)_2NC_2H_5$	598-56-1	50	ppm	0.097	2972	
N,N-Diethylmethylamine (N-Methyldiethylamine)	$CH_3N(C_2H_5)_2$	616-39-7	50	ppm	0.087	2979	
Ethanolamine (MEA)	$OHCH_2CH_2NH_2$	141-43-5	200	ppm	0.289	2941	
2-Amino-2-methylpropanol (AMP)	$C_4H_{11}NO$	124-68-5	50	ppm	0.150	2972	
2-Methylaminoethanol (N-Methylethanolamine)	C_3H_9NO	109-83-1	50	ppm	0.173	2949	
Methyl diethanolamine (MDEA)	$CH_3N(C_2H_4OH)_2$	105-59-9	20	ppm	0.1104	2956	
Diglycolamine (DGA)	$NH_2CH_2CH_2OCH_2CH_2OH$	929-06-6	50	ppm	0.068	1134	
2-(Ethylamino)ethanol (EMEA)	$C_2H_5NHCH_2CH_2OH$	110-73-6	20	ppm	0.147	2964	
N-Methyl-1,3-diaminopropane (MAPA)	$CH_3NH(CH_2)_3NH_2$	6291-84-5	20	ppm	0.118	2941	
Diethanolamine (DEA)	$HN(CH_2CH_2OH)_2$	111-42-2	20	ppm	0.116	2941	
2-Dimethylaminoethanol	$(CH_3)_2NCH_2CH_2OH$	108-01-0	20	ppm	0.105	2786	
Piperazine	$C_4H_{10}N_2$	110-85-0	50	ppm	0.074	2949	Solid comp., mp 106 C
N-Nitrosodimethylamin (NDMA)	$(CH_3)_2NNO$	62-75-9		ppm			
N- Nitrosodiethylamin (NDEA)	$(C_2H_5)_2NNO$	55-18-5		ppm			
N-Nitrosomorpholine (NMOR)	$C_4H_8N_2O_2$	59-89-2		ppm			
N-Nitrosopiperidine (NPIP)	$C_5H_{10}N_2O$	100-75-4		ppm			
N-Nirodiethanolamin (NDELA)	$C_4H_{10}N_2O_3$	1116-54-7		ppm			
N-Nitrospiperazine		5632-47-3		ppm			Chemical not available
1,4-Di-Nitrospiperazine		140-79-4		ppm			Chemical not available
Ethylenediamine (EDA)	$NH_2CH_2CH_2NH_2$	107-15-3		ppm			
Formamide	$HCONH_2$	75-12-7		ppm			
Acetamide	CH_3CONH_2	60-35-5		ppm			Solid comp., mp 78-80 C

The is no available chemicals or spectra for N-nitrospiperazine (5632-47-3) or 1,4-dinitrospiperazine (140-79-4) by Gasmet (or NIST). However, Gasmet might be able to provide spectra if the chemicals with material safety data sheets would be delivered. N-nitrosodimethylamine might not be available either but the spectrum by NIST exists. Some of the compounds tested are solid, such piperazine and acetamide, but since piperazine has been tested also earlier a spectrum will be available.

Majority of the compounds have been tested at 180 °C. Even though the heat stability of MEA at the sampling system has been discussed in many applications, Gasmet expects the heat degradation to be too slow for it to occur during the time the sample is at the system. The degradation is expected to appear only above 180 °C. Degradation at lower temperatures, however, might be catalyzed by dissolved oxygen or metals (oxidative degradation). Thus, if the temperature of the sample system is preferred to be lowered, 120 °C could be suitable. Effect of different temperatures can be tested by Gasmet. In that case, calibration would be done at certain temperature and the possible difference could be compensated by the program. Since the absorbance of amines is at the same range, they might disturb each other in analysis. Thus, optimization of a proper analysis library is highly important.

7.3.3 MIDAC Corporation

MIDAC Corporation is specialized in custom made FTIR solutions for gas monitoring. The company has conducted a pioneering feasibility study which gave a positive response in the field of amine analysis. The study led to a number of installations dealing with carbon sequestration projects. MIDAC uses the EPA method 320 ("Measurement of Vapour Phase Organic and Inorganic Emissions by Extractive FTIR Spectroscopy") when analyzing amines with a FTIR type analyzer. According to MIDAC detection limits at ppb levels are generally achievable with percent levels at the high end of analysis. Response time is usually in the order of 30 seconds. MIDAC use a high resolution FTIR analyzer suitable to measure up to 25 compounds simultaneously. This includes all compounds in the treated gas from the amine absorption tower except the O_2 concentration. The O_2 concentration can be measured with an additional instrument.

The FTIR analyzer can be configured for offline measurements. Analysis of compounds suspended in aerosol particles is possible by heating the sample sufficiently to drive all stream components into the gas phase. This is routinely achieved with MIDAC systems and MIDAC routinely supplies such systems as part of application. MIDAC feels that they are competent to supply a sampling system capable of withdrawing representative samples of the treated gas from the amine absorption tower. Possible physical impediments in this application include degradation of the target amine(s) in the sample by reaction with other products or via thermal degradation. This type of application is well established in MIDAC´s set of applications.

MIDAC performed a feasibility study for amine sampling and analysis. The subjects of the study were:

- LOD (approximately 30 ppb)
- Degradation temperature for the proprietary amine (~ 200°C)
- Degradation products of amines and other compounds in the treated gas at various temperatures (90-240°C)
- Moisture content effect (higher moisture content protected the amine from degradation)
- Sampling line material effects (Teflon Perfluoroalkyoxy (PFA), Teflon Polytetrafluoroethylene (PTFE) and Stainless steel (SS)) where SS proved to be the most appropriate material for the sampling lines
- Effects of mixture of amines
- Standard deviation of analysis (~0.001 ppm for a measured concentration of 0.1 ppm)

Water will represent the biggest interference. However, with reference spectra for all compounds the effect of water on amine analysis is likely to be determined and compensated. MIDAC has experience in MDEA, MEA and piperaxine analysis. The recommended sampling method/equipment include swirl-clean, blow back capable stainless steel lines heated to 181 °C, heated pumps and heated sampling manifold. A single 10m Sterling cooled MCT instrument should be suitable for the list of compounds informed. InSb detection would drive down detection limits at the cost of omitting some compounds. More detailed information of the system is given below.

- LOD for the amines is expected to be 0.05 – 0.2 ppm
- Response time for the system is approximately 60 s
- Flow rate of sampling 2 – 5 lpm
- Only stainless steel and Teflon materials are needed to be in contact with the sample
- Maximum length of sampling line is 50 m
- Less than 25 compounds are preferred to be analysed simultaneously
- Calibration must be carried out for all suspected components of sample stream(s)
- Some reference gasses / permeation tubes may be very difficult to locate

For the similar application MIDAC has previously suggested the use of 2 FTIR analyzers, a long path (10 m with gold coated mirrors) and a short path (without mirrors). The analysis equipment would comply with the European ATEX regulations regarding installation in areas classified as Zone 1 or 2. Using a long and a short path FTIR speeds up the system, makes it more accurate and enables for measuring concentrations at ppb levels simultaneously with %-levels. The long path FTIR measures low concentrations and the short path FTIR measures high concentrations. The sampling system lines would be heated to the appropriate temperature as per the feasibility study and constructed in SS316 with aerogel liquid insulation and urethane cover. MIDAC has pointed out the importance of maintaining a high temperature in the sampling lines to prevent amines and other components from plugging the system. In case of power failure the sampling pump is shut off and the system is automatically purged with nitrogen gas. With the suggested system up to 40 sampling points can be monitored. If only one sample point is monitored, the response time is few seconds. Measuring 10 sampling points takes 7 minutes with the short sample cell and 35 minutes with the long sample cell. By the manufacturer the system can measure and distinguish different amines.

To ensure the extraction of representative samples without droplets MIDAC suggests of using isokinetic sampling where the sampling pump is adjusted after the gas flow out of the amine absorption tower. They do not recommend using sampling lines longer than 200 feet (~61 m). If too long sample lines are used the degradation effects on the sample gas will increase along with the pressure drop in the sampling lines. The pressure drop is best kept below 3 psi (~0.21 bar). Placing the shelter with analysis equipment on a platform is not a problem since the equipment is rugged and can handle vibrations.

New information from Midac was presented related to issue with analysers contaminated by amine sludge. It was observed that "A polymer deposit and tarry film was coating both windows." The system was cleaned with soap and water, methanol, acetone, Windex© and Fantastic© cleaner removed all traces of polymer.

Midac promised to deliver detailed information about the LOD-levels of amines presented in the table, and it is on the request.

7.4 On-line gas chromatographs

AGC Instruments Ltd. provides gas analysers and chromatographs for different applications. The AGC series 100 Gas Analyzer is a process gas chromatograph available in many configurations, depending on the gas to be analyzed. The possible detectors are for example thermal conductivity detector (TCD) for low ppm to % analysis, flame ionization detector (FID) for low ppb to % analysis and discharge ionization detector (DID) for low ppb analysis.

Baseline® – MOCON®, Inc. markets a full line of gas detection equipment including the piD-TECH® Plug-In Photoionization Sensor, Series 9000 Total Hydrocarbon/VOC Analyzers, and Series 8900 automated online Gas Chromatographs. The company is experienced in providing toxic gas monitoring systems, air quality testing equipment, and top-of-the-line gas detection equipment and analyzing systems that combine selectivity, sensitivity, and accuracy with reliability, operational simplicity, and serviceability.

The Baseline® Series 8900 GC is a multi-purpose device designed to continuously monitor single or multiple gas components in a wide range of applications. The analyzer is microprocessor based and contains powerful embedded firmware. This makes it an online instrument with GC technology that is virtually transparent to the end user, claims manufacturer. There are a variety of state of the art detector, calibration and gas train options offering the flexibility and precision necessary to analyze from sub-parts per billion (sub-ppb) to percent levels. Detector options include photoionization detector (PID), FID and TCD. Operating conditions are humidity 0-95% and temperature 0-40 °C.

Chromatotec is a group of companies specialized in the manufacturing and sales of gas analyzers. Gas analyzers GC866 are for detecting compounds in air and water. For example Airmo VOC C6C12 is for detecting VOCs in the range of C_6-C_{12}. Airmo analyzers are also available for e.g. compounds with higher and lower carbon content and for acetaldehyde and formaldehyde determination.

Any of the vendors above did not answer to the inquiry.

7.4.1 Applied Instrument Technologies

The FXi Series5 system by Applied Instrument Technologies was developed from a heritage of highly reliable and field proven systems. The FXi Series5 system continuously analyzes and reports component concentrations and physical properties of process gas and liquid streams in a variety of applications in the natural gas, refining, petrochemical, chemical and pharmaceutical industries. FXi Series5 system is a highly stable, field proven and easily maintained analyzer oven provides outstanding chromatographic performance with a high level of uptime. Versatile detector and column options can be integrated with the FXi system to provide application flexibility. Detector options include TCD, FID, flame photometric detector (FPD) and helium ionization detector (HID). Column options include capillary, micro-packed, and packed columns.

Information about the experience of amine analysis was not delivered.

7.4.2 PPM systems/Siemens Applied Automation

Siemens Applied Automation process gas chromatograph Maxum^{TM} edition II have been used for analysis of chemical composition of gases and liquids. The Maxum is built for installation in harsh environments either directly online or nearby in at-line process measurement laboratories. Analysis can be performed from feedstock, partially processed streams, final products and process by-products including wastes and environmental hazards. The Maxum can be used to analyze multiple compounds simultaneously. The composition of measured components can range from a few ppb up to 100% depending on the needs of the application. Measurement times can range from a few seconds up to an hour or longer, again depending on the needs of the application. Ambient temperatures up to 50 °C can be used. Siemens provides also many other process gas analyzers, which might be applicable for the intended purpose.

Information about the experience of amine analysis was not delivered.

7.4.3 SRI Instruments

The SRI instruments GCs are characterized by a modular setup which allows a flexible adaptation to different analytical problems. Beside the wide range of pre-configured GC systems for a lot of different standard methods special systems can easily be built to meet customer's needs. Another advantage of SRI GCs is the fact that the instruments are built up using standard parts. This results in easy execution of repairs without long waiting times for special parts. The instruments are utilizing a reliable electronic which operates even under rough conditions. This makes the use of the instrument outside the laboratory possible – even in mobile laboratories. The electronic inside the GC is built using standard parts also. By this replacement parts are easily available. SRI Instruments provides a wide selection of GC devices with up to 16 alternative detectors. Depending of the analytical needs, GC can be equipped with one to six different detectors. In addition, 12 different injectors are available and up to five can be installed to one GC.

SRI stated that for the ammonia and amines detection limit is 100 ppm and more sensitivity is not possible. In practice, analysing of flue gas is not possible due the high detection limit. The price of the system is roughly 15 000 €, excluding work.

7.4.4 Chromatographic instruments company (CIC)

CIC suggests multidimensional GC with nitrogen sensitive (or possibly MS) detector for amine analysis. Ammonia needs to be analyzed with a separate analyzer. CIC has experience in different flue or effluent gas determinations. The estimated GC run time is around 15 min. The sample is expected to be in contact with fused silica lined tubing. All other compounds, except ammonia, should be able to be analyzed simultaneously. The effect of oxygen and humidity can be tested by CIC. LOD estimation for the analysis is 1-20 ppb and max. concentration 10-20 ppm.

7.5 Semi-continuous thermal desorption

Thermal desorption (TD) is a technique that extracts volatiles from a nonvolatile matrix by heating the matrix/sample in a stream of inert gas. The extracted volatiles are subsequently refocused onto a cold trap from which they are transferred in a narrow band to a gas chromatographic column for analysis. Typically the sample is contained in a small capped tube.

The automated thermal desorption (ATD) takes a sample tube, uncaps it and seals it in the carrier stream. A leak test is automatically performed to ensure that the tube has been sealed correctly and to ensure that the rest of the system is leak-tight. The tube is then purged with carrier gas at ambient temperature to remove oxygen and moisture. The sample is subsequently heated with a flow of inert gas to extract the volatiles. The volatiles are concentrated on a low thermal mass, electrically cooled cold trap prior to transfer to the gas chromatographic column through a heated transfer line. Heating the cold trap rapidly ensures that the analytes are transferred to the gas chromatograph quickly. This sample transfer method is fully compatible with high-resolution capillary chromatography. The ATD is a system that can handle up to 50 samples. The automation system can be programmed to run a series of tubes according to preset methods.

Semi-continuous TD is a sampling mode in which a sample is drawn through the ATD/TD and sampled at regular intervals. During semi-continuous monitoring, the sample is drawn in through an empty sample tube and onto the cold trap. Coldtrap material can be any suitable material which adsorbs analytes. Typical materials are Tenax TA, GR, Carbopack, Spherocarb, Carbosieve etc. The advantage of thermal desorption is direct concentration without any chemicals and direct connection to the capillary GC-MS systems.

Typical instrumentation after the thermal desorption sampler is GC-FID, dual FID or GC-MSD but even laboratory scale HRMS or TOF can be used. However, fixed and long-term sampling with MSD or HRMS may require lot of maintenance and highly experienced technicians.

By sampling side stream of flue gas, it may be possible to install thermal desorption system for amine analysis.

7.5.1 PerkinElmer TD

PerkinElmer is a manufacturer of laboratory gas chromatographs, mass detectors and other analysers. The cheapest suitable thermal desorption system is Turbo Matrix TD with online sampling unit.

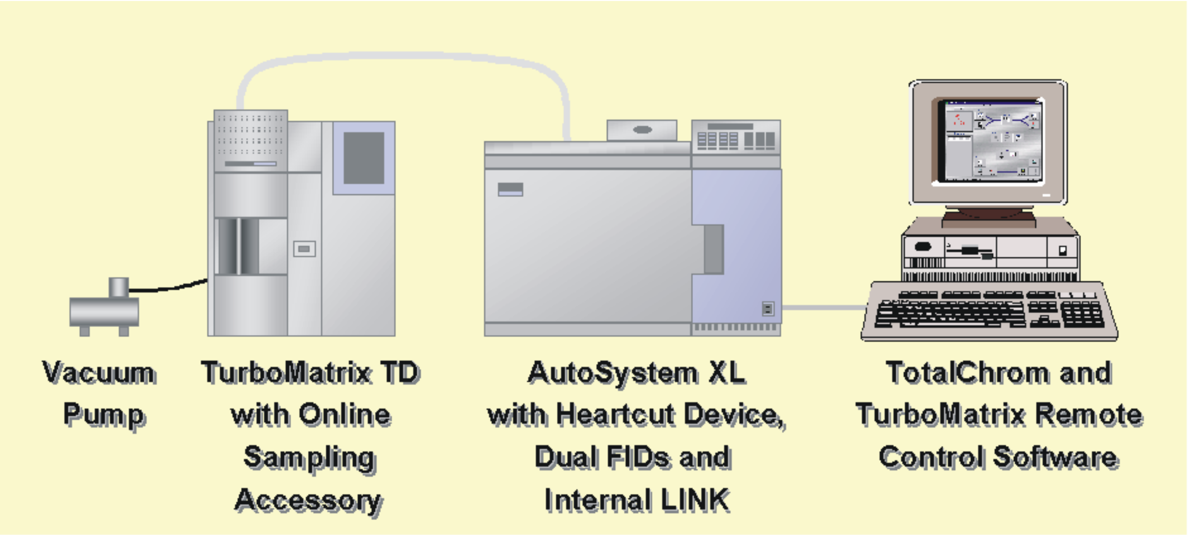


Figure 6 PerkinElmer Thermal desorption system with GC-FID-FID

Semi-continuous, online air sampling and GC analysis is a technique with applications ranging from urban air quality testing to occupational hygiene. In online air sampling a volume of air is pumped directly into the cold trap using a mass flow controller. Air is usually sampled for the greatest possible percentage of the cycle time.

Example: Urban air monitoring methods demand a minimum of 40 minute of sampling per hourly cycle. After sample collection, the trap heats rapidly, transfers the sample to the GC column and begins a GC run. As soon as the trap cools, the system is ready to collect the next sample. The chromatographic analysis of the previous sample continues while the next sample is collected. The air sampler accessory uses a small pump to draw samples of air or calibration gas through the cold trap of the TD. The combination of valves in the system enable you to perform runs that sample air for set periods and to perform calibrations at regular intervals.

Detection limits of the TD-GC-MSD system are quite easily 0.1 $\mu g/m^3$/compound from urban air. Running time may vary between 10-120 min/run.

Even if some amines may degrade at heat, in our experience an application for thermal desorption of amines is still possible and quantitative to perform.

The price for the semi-online TD-GC-MSD system is about 150 000 €.

7.6 Colorimetric analysers

C.I. Analytics provides analytical solutions for laboratories and manufacturing processes**.** The majority of the analyzers utilize dry-colorimetric methods of analysis in order to achieve the exceptionally low-level impurity detection ranges. For aliphatic and aromatic amine and ammonia detection C.I. Analytics suggests a dry-colorimetric method: Ammonia Sensi-Tape and Aromatic Amines Sensi-Tape. Detection limits for the method are at low ppb levels (10 ppb). Sensi-tape offers interesting and different approach of measuring summary of amine or ammonia related compounds.

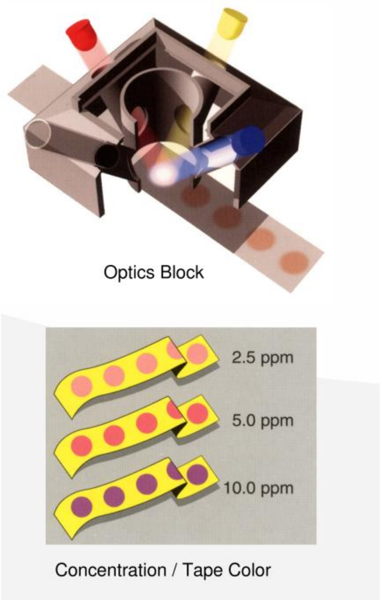


Figure 7 Principle of colorimetric tape system

The Aromatic Amines Sensi-Tape is formulated for sensitivity and specificity to aromatic amines, especially :
- p-Phenylene diamine (PPD)
- Toluene diamine (TDA)
- Methylene dianiline (MDA)

The Aromatic Amines Sensi-Tape will also respond to:
- Chloro-p-toluidine (CPT)
- Methylamine
- Dimethylamine
- Ethylamine

- n-Butyl amine

The Aromatic Amines Sensi-Tape Sensi-Tape WILL NOT respond to:
- Acids
- Alcohols
- Aliphatic Amines
- Amines
- Ammonia
- Benzene
- Carbon Disulfide
- Chlorine
- N,N'-dimethylbenzylamine
- Dimethyl Sulfate
- Freons
- Hydrazines
- Hydrides
- Hydrocarbons
- Hydrogen
- Hydrogen Cyanide
- Hydrogen Sulfide
- Imides
- Isocyanates
- Isocyanurates
- Nitrogen
- Nitrogen Oxides
- Ozone
- Phosgene
- Solvents
- Sulfur Dioxide

The Ammonia Sensi-Tape is formulated for sensitivity to ammonia and to primary and secondary aliphatic amines such as:
- Methylamine
- Dimethylamine
- Ethylamine
- n-Butyl amine
- Diethylamine

Aromatic Amines and Hydrazines also react positively on this Sensi-Tape (note: hydrogen cyanide and nitrogen dioxide give very light stains on this Sensi-Tape). Other compounds that exhibit positive but weaker response include Tertiary aliphatic amines like:
- Triethylamine C
- Trimethylamine C

The Ammonia Sensi-Tape WILL NOT respond to:
- Acids
- Alcohols
- Carbon Disulfide
- Dimethyl Sulfate
- Freons
- Hydrides
- Hydrocarbons
- Hydrogen
- Hydrogen Peroxide
- Hydrogen Sulfide
- Isocyanates
- Nitrogen
- Nitrogen Oxides

- Nitrous Oxide
- Ozone
- Phosgene
- Solvents

7.7 Diode laser technology

Bühler Diode Laser In-situ Gas Analyzer BA 8000 has been used in NH_3 analysis (among O_2, HCl, HF, H_2O, CO and CO_2) when sampling reactive or highly corrosive gases.

Also FUJI Electric Systems in-situ Cross Stack Laser gas analyzer can be used for NH_3 analysis at high speed response (among HCl, H_2O, O_2, CO, CO_2 and CH_4).

Information about the experience of amine analysis was not delivered by the manufacturers.

7.8 UV

7.8.1 ETG risorse (www.etgrisorse.com)

ETG risorse provides UV gas analysers and Laser gas analysers for NH_3 detection. Both systems monitor NH_3 in heated configuration. In both case the measurement temperature is at 180°C and the whole sampling system can be kept at the same temperature to avoid condensation of water vapour and ammonia.

Some specifications:

- UV technique: 0.2 ppm t90 60 seconds (the line is better to be kept as short as possible since NH_3 is a very sticky compound)
- Laser technique: 0.8 ppm t90 60 seconds
- In UV technique the number of compounds could be increased.
- Laser technique is a single component gas analyzer for only NH_3 and H_2O detection

No experience about the amine analysis.

7.9 Mass spectrometers

Analytical technique called mass spectrometry (MS) measures the mass-to-charge ratio of charged particles. It is used for determining masses of particles, for the determination of the elemental composition of a sample or molecule and for specifying the chemical structures of molecules. The MS principle consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measurement of their mass-to-charge ratios. MS instruments consist of three modules: an *ion source*, which can convert gas phase sample molecules into ions; a *mass analyzer*, which sorts the ions by their masses by applying electromagnetic fields; and a *detector*, which measures the value of an indicator quantity and thus provides data for calculating the abundances of each ion present. The technique has both qualitative and quantitative uses.

7.9.1 Resonance Enhanced Multi Photon Ionization

OPOTEK Inc. jet-REMPI portable instrument is for the detection of trace aromatic vapors. The instrument is highly-sensitive, real-time device for the detection of a variety of species with high chemical sensitivity. The detection limit is 100 ppt for a wide variety of vapors, including most common aromatic solvents. It is unclear if the system is capable to analyse amine compounds from the flue gas.

7.9.2 Magnetic sector MS

7.9.2.1 Thermo Scientific

The Prima dB by Thermo Scientific is the latest process mass spectrometers in the Prima series. Prima analytical instruments have been used by petrochemical, pharmaceutical and steel companies. Other possibly suitable devices are Sentinel δB Spectrometer and Prima PRO Process Mass Spectrometer. As an example the LOD of Sentinel δB is 10 ppb and mass range 1 – 150 amu (1000 V ion energy) or 1 – 300 amu (500 V ion energy).

Figure 8 Mass spectrometer by Thermo Scientific

Table 3 Thermo Scientific Prima δB

	Thermo Scientific Prima δB
Measurement Method	Scanning Magnetic Sector Mass Spectrometer
mass range (amu)	1 – 200 atomic mass units
Lower Detection Faraday 20 ppm — typical, may vary with gas matrix	20 ppm — typical, may vary with gas matrix
Lower Detection Single SEM 0.1 ppm — typical, may vary with gas matrix	0.1 ppm — typical, may vary with gas matrix
Lower Detection Double SEM	10 ppb — typical, may vary with gas matrix
Precision (typical)	Better than 0.1% relative over 24 hrs
Stability (typical)	Better than 1% relative over 1 month
Analysis Time (typical)	0.3 – 1.0 seconds per gas component
Maximum Number of Components	Not limited by software
Maximum Number of Peaks per Component	Not limited by software
Maximum Number of Sample Streams	250
Area Classification Options	General Purpose; Z-purged division 2 (optional); X-purged division 1 (optional); CENELEC / ATEX Zone 1, IIC T3 (optional)

Information about the experience of amine analysis was not delivered by the manufacturer, however it looks promising.

7.9.3 Quadropole mass spectrometer

The quadrupole mass analyser consists of 4 circular rods, set highly parallel to each other. In a quadrupole mass spectrometer (QMS) the quadrupole is the component of the instrument responsible for filtering sample ions, based on their mass-to-charge ratio. Ions are separated in a quadrupole based on the stability of their trajectories in the oscillating electric fields that are applied to the rods.

7.9.3.1 Lambda photometrics

The UGA Series Universal Gas Analyzers are bench top mass spectrometers that operate from above atmospheric pressure to ultra-high vacuum (UHV). They are ideal for on-line monitoring and analysis of gas mixtures. The instruments can be used in analysis of trace-level contaminants, solvents, corrosive gases etc. The UGA system uses a two-stage pressure reducing inlet to sample gases at atmospheric pressure. After the pressure is reduced to around 10-6 Torr, the gas stream is sent to a QMS (residual gas analyzer - RGA) which measures the concentration of each mass of interest. The UGA system is equipped with individual heaters for the vacuum chamber (including RGA), the turbo pump connector, and the vacuum inlet assembly. During bakeout, the system can be heated to 120 °C. The system contains stainless steel and poly ether ether ketone (PEEK) materials.

Table 4 Lambda photometrics UGA analyzers

	UGA 100, 200, 300 Universal Gas Analyzers
LOD	1 ppm
mass range (amu)	100, 200 or 300
resolution	Better than 0.5 amu at 10 % of peak height
Reaction chamber heating range °C	<120 °C
response time	<0.2 s
note	Operates in highly corrosive environments

7.9.3.2 Hiden Analytical Ltd (www.hidenanalytical.com)

Hiden MS stated that their gas analysis system is not a solution for the intended process analysis since in the application the number of species is extensive, and the spectral overlaps will be too severe for a good analysis.

7.9.3.3 Extrel Analytical Ltd (www.extrel.com)

Extrel claims to be the world's leading manufacturer of Research and Process Mass Spectrometers, Residual Gas Analyzers (RGA's), Quadrupole Mass Spectrometry Systems and Components.

Extrel has been providing quadrupole mass spectrometry solutions to our Research and Industrial customers for over 45 years, however they don't have experience about the analyzing of amines.

Table 5 Extrel Analytical MAX 300-IG analyzer

	MAX 300-IG
LOD	10ppb* (benzene in ambient air), 10 ppm**
Linearity range	8 orders of magnitude (dual faraday) 5 orders of magnitude**
mass range (amu)	2-250 (300 optional)
Stability	±0,005 over 30 days, 1 %argon concentration with no interferences
Analysis duration	400 ms/compound; 10 compunds 4 seconds etc.
Note	Two filaments with automatic switch during malfunction

**electron multiplier*
***Faraday*

The manufacturer stated that if there is just a single amine at a time in the sample, they can measure it. However, they will need to search library of spectra to see whether there is any strong interference from the bulk compounds in the stack. In the worst case, all amines need to be included in the analysis method, and we may have major interferences, which may limit the detection of some compounds.
The manufacturer informed to do a sample evaluation for the entire list and reply later. As far as MEA is concerned, system can detect it at LDL=1 ppm. Manufacturer informed the linearity range to be from ppm level to 100 %. The resolution system resolves single masses in such an extent that the maximum intensity can be obtained, while maintaining an abundance sensitivity at 5000. This means that at 100 % concentration of a compound on an ion n, the penetration of this ion to ions n-1 and n+1 is 5000 times lower, e.g. 200 ppm

Manufacturer reports that the system has no sensitivity to humidity or oxygen concentrations. Some amines may suffer from spectral interference from bulk compounds in the sample. The analysis parts of the system are made of SS 304 and 316. There is no restriction for the sampling line length, flow rate and temperature as far as condensation is avoided. The typical sampling system will pull the sample from the stack through a heated line (to avoid condensation and adsorption). Manufacturer reports that the sampling system should contain dust filter to remove particulates and coalescing filter to remove mist (upset condition, like the heat tracing fails). The mass spectrometer should be located in a shelter and multiple samples provided to the mass spectrometer's multiposition valve.

Price depends on the packaging of our mass spectrometer and several options, like communication means. The MAX300-LG, laboratory bench top mass spec will cost about $80,000 (including PC, software, spare parts, commissioning spare parts and commissioning service)
The MAX300-IG, industrial packaged mass spectrometer Class I Div.2 will be about $120,000
The ATEX certified for Zone 1 MAX300-IGX will be about $150,000.

Figure 9 Max 300-IG, Industrial gas analyser

Figure 10 Max 300-IGX, Atex-industrial gas analyser

Figure 11 Max 300-LG, Laboratory bench top mass spectrometer

7.9.3.4 Ametek Ltd. (www.ametek.com)

Ametek ProLine process MS has a LOD of 1 ppm and mass range 1 -100 amu (optional 1-200 or 1-300 amu).

More information from Ametek is on request.

7.9.3.5 InProcess Instruments GmbH (http://www.in-process.com)

InProcess Instruments GAM QMS analyzers are claimed to be suitable for on-line gas analysis. Different analysers are presented at
Table 6.

Table 6 InProcess Instruments GmbH

	GAM200	GAM300	GAM400*	GAM500 UT
mass range (amu)	1 - 100 or 200	1-300	5 mass ranges 1 - 16/128/340 and 1 - 300/512 amu	1-512
Reaction chamber heating range °C	operating temperature up to 200°C		up to 300ºC	
response time		300 ms – 2 s	<300 ms	500 ms

* minimal sample gas consumption (< 30 µl/min), reactive and corrosive gas components, trace analysis, automatic batch sampling

Other products:
The GAM 600 SI has been specially developed for analyzing complex gas mixtures where other analytical methods fail. In addition there are analysers such as EDS100, GIA522, LGA407/200, IMU200 and GAM300 ATEX (the latest one especially for explosive substances).

No further details about amine analysis were delivered.

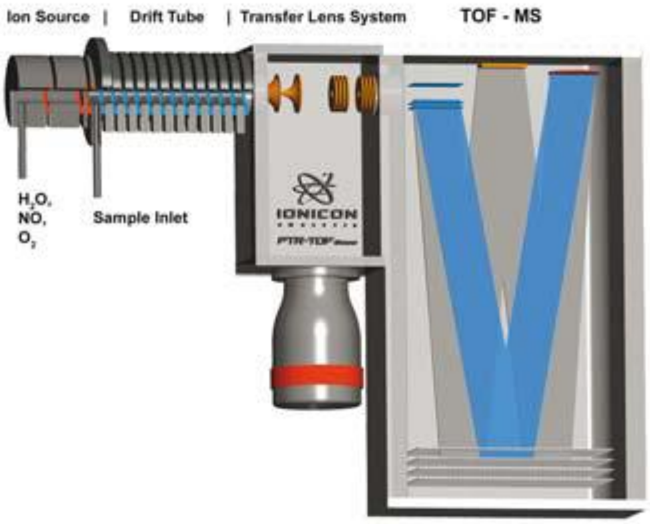
7.9.4 Time-of-flight mass spectrometry and proton transfer reaction mass spectrometry

In time-of-flight mass spectrometry (TOF-MS) ions are accelerated by an electric field of known strength. This results an ion to have the same kinetic energy as any other ion with the same charge. The velocity of the ion depends on the mass-to-charge ratio. The time consumed by the particle to reach a detector at a known distance is measured. This time will depend on the mass-to-charge ratio of the particle (lower speed with heavier particles). From this time and the known experimental parameters the mass-to-charge ratio of the ion can be found.

Proton transfer reaction mass spectrometry (PTR-MS) provides quantitative analysis in real-time. The generation of the precursor reagent ions and the chemical ionization of the volatile organic compounds (VOC) are individually controlled and spatially separated processes. This leads to constant and well defined conditions in the drift tube making the determination of absolute concentrations possible without the use of gas standards. A major advantage of PTR-MS is that the samples do not need to be prepared before the measurement (e.g. pre-concentration or chemical separation procedures), thus whole-air samples can be introduced directly into the drift tube allowing for dynamic headspace sampling or VOC flux measurements.

7.9.4.1 Ionicon Analytik (www.ptrms.com)

PTR-MS (Proton Transfer Reaction - Mass Spectrometry) by Ionicon Analytik are on-line devices for real time gas analysis that have been used for monitoring and absolute quantification of VOCs at very low concentrations. PTR-MS is considered to be an ultra-sensitive chemical ionization MS technology and amine compounds have been detected using PTR-MS instruments. The recommended MS systems by Ionicon Analytik are quardupole and TOF instruments with difference in sensitivity, detection limit, size, weight and budgetary constrains.



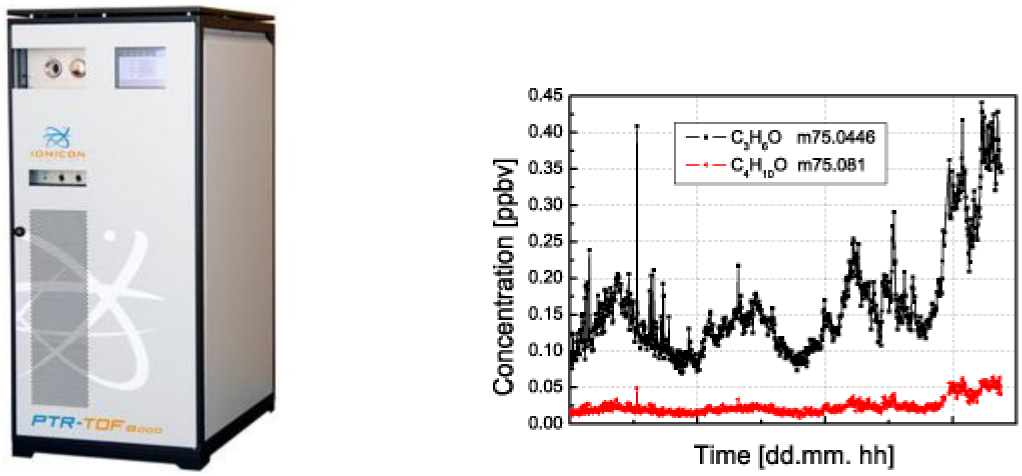


Figure 12 Ionicon PTR-TOF and measured data of two hydrocarbons

Table 7 Ionicon Analytik , on-line PTR-MS analysers and their characteristics

	High sensitivity PTR-MS	**Standard PTR-MS**	**PTR-QMS 300**	**PTR-TOFMS 8000**	**PTR-TOFMS 2000**
LOD	< 1 ppt	< 30 ppt	< 300 ppt	< 10 ppt*	< 5 ppt*
Linearity range	1 ppt - 10 ppm	30 ppt - 10 ppm	300 ppt - 10 ppm	10 ppt-5 ppm	5 ppt - 1 ppm
mass range (amu)	1-512 (up to 2048 on request)	1-512	1-300	1- 50 000	1 - 50 000
resolution	< 1 amu	< 1 amu	< 1 amu	4000-8000	> 1500 m/Δm (FWHM)
Reaction chamber heating range °C	40 - 130°C	40 - 120°C	40 - 130°C	40-130	40 - 130°C
response time	100 ms	2 ms/amu - 60 s/amu	100 ms	100 ms	100 ms

**chlorobentsene*

Some additional specifications are given below:

- Sample flow rate can be adjusted to 50 ml/min – 1 l/min
- Sample would be in contact with following materials: PEEK, polytetrafluoroethylene (PTFE), stainless steel and Viton (O-rings)
- Max. length of sample line depends on the needed response time. Up to c.a. 100 m or even longer (requires additional pump, have to be discussed)
- With PTR-TOFMS all requested compounds can be analyzed simultaneously (see Table 8 comments)
- The method is not sensitive to humidity
- Isokinetic sampling (velocity into the inlet 2 m/s and 20 m/s in our case) should be possible but for the recommendation more information is needed
- Amine handling is tricky since the sticky nature of compounds. However, Ionicon Analytik have experience on handling the kind of molecules and have ides on the setup

Table 8 presents LOD and measuring range of each compound when using Ionicon Analytic devices. It should be noted that the maximum concentration referred (10 ppm) is for the sum of all ionisable compounds, not for a single compound. Total concentration of compounds having higher proton affinity than water should be taken into account since limited number, even though it is quite high, of primary ions are used for sample ionization. For example, because the concentration of NH_3 is expected to be high (up to 50 ppm), a dilution unit is required for performing reliable measurements. The dilution factor will affect on LOD.

Table 8 Ionicon Analytic, list of compounds. All can be analyzed on-line.

Compound	*CAS-number*	*Formula*	*LOD*	*Measuring range, Max (total conc.)*	*Disturbances*
AMP	124-68-5	$C_4H_{11}NO$	10 ppt	10 ppm	
DEA	111-42-2	$C_4H_{11}NO_2$	10 ppt	10 ppm	
EDA	107-15-3	$C_2H_8N_2$	10 ppt	10 ppm	
MDEA	105-59-9	$C_5H_{13}NO_2$	10 ppt	10 ppm	
MEA	141-43-5	C_2H_7NO	10 ppt	10 ppm	
Piperazine	110-85-0	$C_4H_{10}N_2$,	10 ppt	10 ppm	
1,4-dinitroso-piperazine (Dnpz)	140-79-4	$C_4H_8N_4O_2$	10 ppt	10 ppm	
NDELA	1116-54-7	$C_4H_{10}N_2O_3$	10 ppt	10 ppm	
NDEA	55-18-5	$C_4H_{10}N_2O$	10 ppt	10 ppm	
NDMA	62-75-9	$C_2H_6N_2O$	10 ppt	10 ppm	
NMOR	59-89-2	$C_4H_8N_2O_2$	10 ppt	10 ppm	
N-Nitrosopiperazine	5632-47-3	$C_4H_9N_3O$	10 ppt	10 ppm	
NPIP	100-75-4	$C_5H_{10}N_2O$	10 ppt	10 ppm	
Diethylamine (DEN)	109-89-7	$C_4H_{11}N$	10 ppt	10 ppm	
Dimethylamine (DMA)	124-40-3	C_2H_7N	500 ppt	10 ppm	EA, formamide
Ethylamine (EA)	75-04-7	C_2H_7N	500 ppt	10 ppm	DMA, formamide
Methylamine (MMA)	74-89-5	CH_5N	see comment below[a]	10 ppm	O_2, contaminant of PTR source
Triethylamine (TEA)	121-44-8	$C_6H_{15}N$	10 ppt	10 ppm	
Trimethylamine (TMA)	75-50-3	C_3H_9N	10 ppt	10 ppm	acetamide[b]
Acetamide	60-35-5	C_2H_5NO	10 ppt	10 ppm	trimethylamine[b]
Formamide	75-12-7	CH_3NO	500 ppt	10 ppm	DMA, EA
Acetaldehyde	75-07-0	C_2H_4O	10 ppt	10 ppm	CO_2, dependent on H_2O[c]
Formaldehyde	50-00-0	CH_2O	1 ppt	10 ppm	

[a] *MMA can be separeted from O_2 with a TOF-MS, but not with a QMS. Also formamide can be separated from DMA and EA with a TOF-MS, but DMA and EA can not (DMA and EA have the same sum formula).*

[b] *Acetamide and trimethylamine can not be separated with QMS but can with TOF-MS.*

[c] *In case of CO_2 an additional small signal (CO_2H^+) will appear on the same mass on which acetaldehyde would be detected by QMS. However, with TOF-MS the compounds can be separated.*

Measurements of various amines, for example MEA, have been done in climate chambers by Univ of Innsbruck and Univ of Oslo year 2009.

7.9.5 CIRMS (Chemical ionization reaction mass spectrometry)

This technique, recently developed, is an extension to PTR-MS using a greater variety of chemical ionization reagents in the ionization process. Clean sources of the reagents H_3O^+, NH_4^+, NO^+ and O_2^+ have been obtained without any mass pre-selection. The reactions of these reagent ions with a range of test VOCs are found to be rapid, with the chemistry generally paralleling that observed previously with selected ion flow tube measurements, although with some important differences. CIRMS is shown to be a more versatile technique than conventional PTR-MS with the potential for rapid multi-reagent analysis of chemical mixtures. No easily commercial applications are available.

7.10 Ion molecule reaction (IMR)

Ion molecule reaction is a variant of the chemical ionisation.

7.10.1 Airsense

Pro Miljö Sandström AB (PMS AB) offers Airsense analyser. It consists of a highly sensitive mass spectrometer with a soft ionization unit, an automated sample gas inlet and a controller interface. The sensor contains a high vacuum pump system and electronics. All components are mounted in a 19" rack.

Figure 13 Airsense Multi component gas analyser

Primary ionisation source
Ionization of sample gas is performed through soft ionization by charge exchange between a primary ion and the molecule to be analysed (patented method). Primary ions are produced by electron impact in a closed ion source. The Airsense is equipped with 3 source gases. The technology allows interference-free detection of molecules which would not be possible by means of only standard ionization techniques with energetically fast electrons (at least 70 eV) due to fragmentation ionization (mass identity).

Octopole Separator
The primary ions are focused by high frequency fields and guided to the charge exchange chamber. Through mass separation, contamination of the spectrum from source gases is avoided and thus the sensitivity of the system is raised considerably. Long-term stability is achieved by the use of stainless steel and ceramic components. The whole assembly is operated by the computer and optimized by the operating software.

Charge Exchange Chamber
In this component of the system, ions from the primary ion source meet the sample gas which is ionized through charge exchange reactions. Also here the ions are focused by high frequency fields and led to the actual high resolution mass filter. The pressure in the gas exchange chamber is kept constant by the control of the gas inlet system. Through longstanding experience, use of well-chosen material, and advantages of vacuum technique (minimal probe gas flow into the charge exchange chamber, ml/min), this component is kept maintenance-free

Mass Spectrometer

The AIRSENSE uses a highly sensitive quadrupole mass spectrometer. The mass filter consists of four precision rods out of stainless steel with ceramic mountings and ensures linearity and reproducibility to a high degree. A crystal-stabilised high frequency generator generates the power for the mass filter.

Particle Detector
For lowest detection levels of the system the Airsense is equipped with a fast counting

system. Ions at the channeltron (secondary ion multiplier) trigger off pulses that are counted. A high precision discriminator amplifier together with a fast pulse counting unit completes the system.

Vacuum System
Airsense is equipped with a highly efficient high vacuum system which consists of an air-cooled turbo molecular drag pump of high reliability (MTTF 50.000 h) and a four-stage diaphragm pump. This system is oil-free and therefore grants easy service, fast start up, and no hydrocarbon backgrounds signals from oil vapours. Vacuum control is continuously performed by the system via power consumption and speed.

Gas Inlet System
Typical operating pressure of the MS is 10 -5 mbar. The gas inlet system allows pressure reduction from atmospheric pressure to this operating pressure without influencing the composition of the sample gas. Pressure variations are levelled out by absolute pressure measurements coupled to an electronic flow regulator. This inlet system which stood the test of more than 20 years in industrial use is rugged as all parts are of stainless steel and Teflon and it is heated to prevent condensation of the sample gas. The sample gas is brought to the measuring device continuously via a bypass pump.

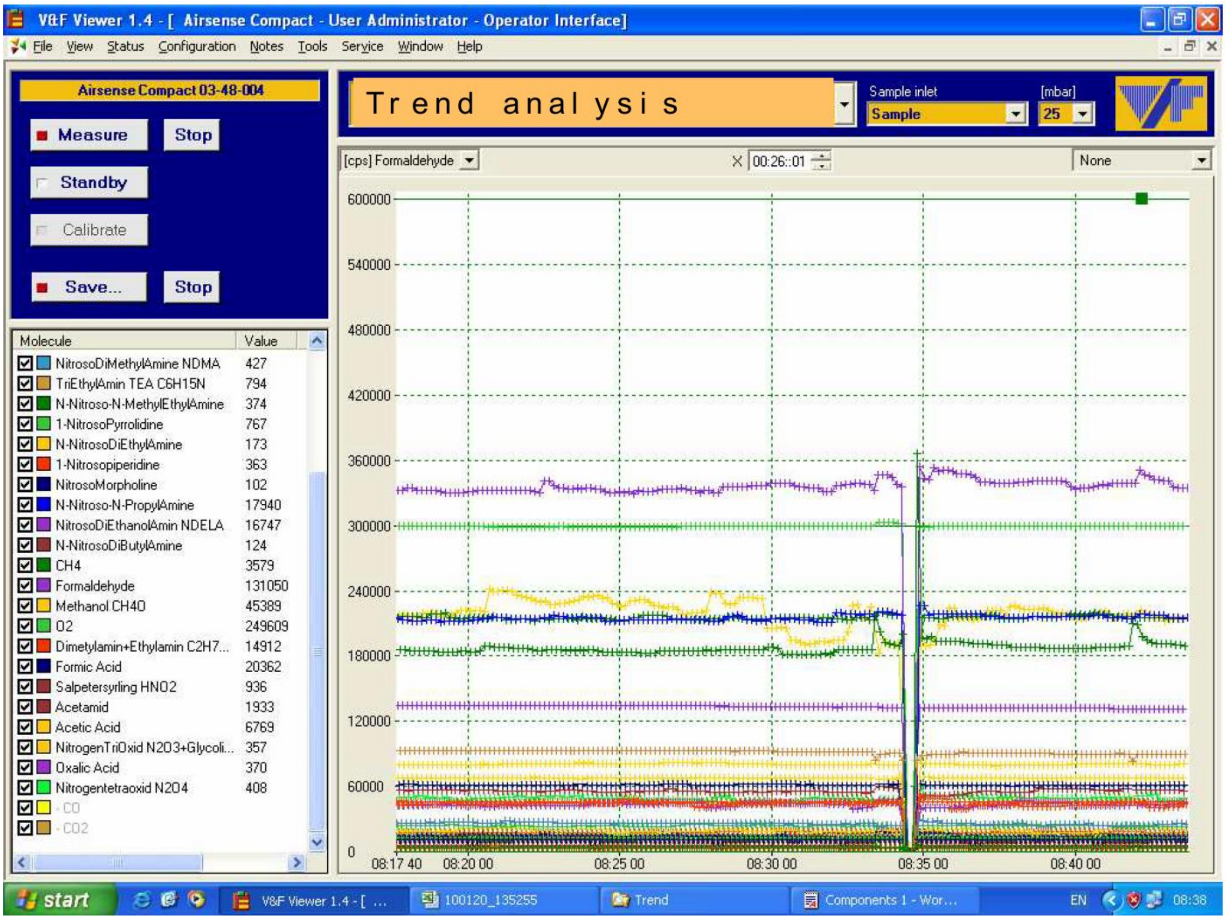
The price for the basic system with software is about 200 000 eur and warranty two years.

The vendor have experience about analysis of amines. Two print-screen captures were send with the information described above (Figure 14 and Figure 15).

Sample inlet: Sample
[mbar]: 25
[cps] Formaldehyde
00:26::01
None

Molecule	Value
☑ 🟩 Ammonia NH3	1168
☑ 🟫 NO	89452
☑ 🟩 Metylamin CH5N	16016
☑ 🟦 Acetaldehyde	9208
☑ 🟩 Ethanol C2H6O	6728
☑ 🟥 NO2	5711
☑ 🟥 TriMethylAmin TMA C3H11N	4004
☑ ⬛ MonoEtanolAmin MEA	851
☑ 🟦 NitrosoDiMethylAmine NDMA	410
☑ 🟫 TriEthylAmin TEA C6H15N	792
☑ 🟩 N-Nitroso-N-MethylEthylAmine	377
☑ 🟩 1-NitrosoPyrrolidine	755
☑ 🟨 N-NitrosoDiEthylAmine	175
☑ 🟥 1-Nitrosopiperidine	334
☑ 🟦 NitrosoMorpholine	122
☑ 🟦 N-Nitroso-N-PropylAmine	18158
☑ 🟪 NitrosoDiEthanolAmin NDELA	17122
☑ 🟫 N-NitrosoDiButylAmine	126
☑ 🟩 CH4	3591
☑ 🟪 Formaldehyde	131130
☑ 🟨 Methanol CH4O	45259
☑ 🟩 O2	249463
☑ 🟥 Dimetylamin+Ethylamin C2H7...	14964
☑ 🟦 Formic Acid	20310
☑ 🟫 Salpetersyrling HNO2	948

Figure 14 Screen capture of the Airsense analyser application for amines, first part of the compounds



Sample inlet: Sample
[mbar]: 25

Molecule	Value
☑ 🟦 NitrosoDiMethylAmine NDMA	427
☑ 🟫 TriEthylAmin TEA C6H15N	794
☑ 🟩 N-Nitroso-N-MethylEthylAmine	374
☑ 🟩 1-NitrosoPyrrolidine	767
☑ 🟨 N-NitrosoDiEthylAmine	173
☑ 🟥 1-Nitrosopiperidine	363
☑ 🟦 NitrosoMorpholine	102
☑ 🟦 N-Nitroso-N-PropylAmine	17940
☑ 🟪 NitrosoDiEthanolAmin NDELA	16747
☑ 🟫 N-NitrosoDiButylAmine	124
☑ 🟩 CH4	3579
☑ 🟪 Formaldehyde	131050
☑ 🟨 Methanol CH4O	45389
☑ 🟩 O2	249609
☑ 🟥 Dimetylamin+Ethylamin C2H7...	14912
☑ 🟦 Formic Acid	20362
☑ 🟫 Salpetersyrling HNO2	936
☑ 🟫 Acetamid	1933
☑ 🟨 Acetic Acid	6769
☑ 🟨 NitrogenTriOxid N2O3+Glycoli...	357
☑ 🟪 Oxalic Acid	370
☑ 🟩 Nitrogentetraoxid N2O4	408
☑ 🟨 - CO	
☑ 🟫 - CO2	

Figure 15 Screen capture of the Airsense analyser application for amines, second part of the compounds

7.11 Ion Mobility Spectrometry (IMS)

Ion mobility spectrometry (IMS) is an analytical technique used to separate and identify ionized molecules in the gas phase depending on their ion mobility in a carrier buffer gas. The technique has many analytical applications. IMS devices come in a wide range of sizes (usually can be tailored for specific application) and are capable of operating under a broad range of conditions. Systems operated at higher pressure are also accompanied by elevated temperature (above 100 °C), while lower pressure systems (1-20 mbar) do not require heating. The major difference between chemical ionisation and IMS is ionisation energy. While CI is very sensitive method, IMS uses very high energy (typically radioactive source) to produce ion-clusters.

Based on our experience the early IMS-systems had a weak point with selectivity if matrix was changed significantly, however systems have evolved during the development.

7.11.1 Environics

Environics GC-IMS devices have been used in some amine and acetaldehyde analysis. The fixed GC-IMS device is recommended for the intended purpose. Some specification for the device is given below:

- Response time is dependent of the measured compound (from few seconds to minutes)
- Temperature of sampling lines and analysis chamber between 50-100 °C
- Speed of suction 0.2 l/min
- Material in contact with sample: PTFE, PEEK, Viton, acid proof steel
- Max. sampling line length 2 m (heated)
- Amount of the compounds that can be analyzed simultaneously need to be evaluated, since it is dependent of GC-columns and other parameters

- Effect of humidity can be compensated. However, the water drops inside the device have to be prevented
- Effect of different O_2 and humidity content can be evaluated
- For the sampling "multiplexer" is recommended

Environics was interested to establish a research and development campaign to develop amine analysis.

The price of the system is about 100 000 €.

7.12 TOC-analysers

The standard method for determining total amount of organic compounds is based on flame ionisation detection. It gives total concentration as mg_{carbon}/m^3 of all organic compounds. Even the method is not selective (some chemical groups gives a shielding to response of some individual compounds so the response is not absolute linear) it gives important information about the overall outflow of organic content. This is important at the cases where organic content is not fully known or the while evaluating the possible "cap" between the selective analysers and TOC concentration.

The method is fully described in standards EN 13526 *Stationary source emissions. Determination of the mass concentration of total gaseous organic carbon in flue gases from solvent using processes. Continuous flame ionisation detector method.*

8. RECOMMENDATIONS

Deciding the level of performance seems to be important (selectivity, sensitivity, response time, cost and maintenance) for selecting the on-line system. Very selective and sensitive system is possible to be acquired for example by using on-line-TD-GC-HRMS system. However, it is very expensive to buy and complicated to run.

A realistic balance between the performance and usability seems to be on FTIR and MS-systems. For the FTIR systems Gasmet and Midac Corporation already have some experience with amines. Also MS-systems such as Airsense looks ready for the task.

It may be good idea to have another analyser for the measurement of summary parameter such as TOC or combined amines and ammonia. Summary analyser is recommended to use different technique to make possible observations of unknown compounds or systematic error compared to e.g. FTIR or MS system. TOC measurements by FID will give important information about overall TOC-concentrations. Because FID is widely used as EN reference method as well as fixed measurements in waste incineration plants, it is most probable that some environmental limits of CCS-plant emissions will be stated as TOC.

If very accurate results are needed, it is recommended to perform a comparison test for the most promising techniques on some suitable test facility. If test could be arranged at relatively small pilot-scale plant, it may be possible to manipulate the real flue gas by injecting the most important target compounds or distractive elements to the flue gas before sampling point. Based on our experience this works fine at least with gas phase compounds despite the droplets. Manual sampling should be also performed to obtain at least one fixed concentration level.

The effect of filtration and heating during the sampling should be evaluated. It may have a very significant effect for the concentration of some compounds. It seems that filtration and heating are necessary while using sophisticated instrumentation such as FTIR or MS. If the sample handling will reduce significantly concentration of some compounds, the point of use very effective analyser later on the sampling line disappears.

9. CONCLUSIONS

Some promising techniques for the on-line analysis of amines were found during the survey. There is no over the top solution to be recommended for the analysis of separate amine compounds. For the selective methods there is some experience using FTIR and process MS – analysers for the amine analysis. Both of the methods suffer from some interferences. The application for the FTIR needs to include all compounds having absorption. Also IR-absorption spectrums between the different amines and ammonia are quite similar so the calibration of analyser is important to be performed. Mass spectrometers without pre-separation (like GC) may also suffer interferences between different compounds with the same mass. For this reason both of the methods should be validated if accurate results are needed.

If the lowest concentration needs to be measured, it may be possible to transform continuous dioxine/furan sampling system for the sampling of amine, nitrosoamine and other organic compounds. Because the sample needs to be analysed at the laboratory it is not actually on-line system, however it may be the only solution, if very low levels needs to be analysed. Sampling time may vary from hours to days, even weeks. If long sampling times are needed, decomposition of the sample should be evaluated. The detection limit is limited by the method used in laboratory. This system is not tested for the amine analysis and some development and validation needs to be done.

Very sensitive and selective system may be possible to be applied by using on-line thermal desorption combined to GC-FID or MS systems. The disadvantage of the system is quite complicated and sensitive instrumentation at industrial environment, especially while using MS-detector and relatively low response time, about 10-60 minutes depending on the application.

IMS-system may be sensitive and selective analyser for the amines, however, testing and validation with real matrix needs to be performed.

Colorimetric method gives a different approach for the summary analysis of ammonia and amines or aromatic amines. Especially it may be good method on daily monitoring of amines, due to its relatively easy analysis principle.

IR-, diode laser- and UV methods are more summary methods for the ammonia and amines because of lower selectivity. Interferences with other compounds, like water, are possible. Some of the analysers may be installed in-stack, which makes sampling system simpler.

Table 9 presents subjective evaluation based on this survey. The rating percent is weighted by the values below:

- **Selectivity** and **sensitivity** are important on amine sampling, especially if decomposition products should be analysed to have accurate information about the environmental emissions and state of process. Selectivity and sensitivity are valued the most important factors for the on-line analyser.
- **Sampling** includes evaluation of representativeness, reliability and response time of sampling system (if included or limiting the operation of the system). Treatments possible affecting the sampling system such as filtering, heating lowers the value
- **Roughness** could be handled at least partly by proper design of sampling environment, however some laboratory equipments are sensitive for the environmental conditions and laborious to maintain. **Maturity** of the system will increase along with the experience while sampling of amines. However it includes risk and possibility that un-mature system will not ever work as planned on CCS-plant.
- **Speed** means response time of the overall system. Very short response time is basic function of in-situ systems and very low on systems when using continuous automated systems.

The evaluation is a suggestive and relative between the analyser type.

Table 9 Subjective evaluation of the different on-line measurement systems based on the survey

1=poor; 5=very good	**Speed**	**Selectivity**	**Roughness**	**Sensitivity**	**Maturity**	**Sampling**	Total
Importance	*10 %*	*30 %*	*10 %*	*30 %*	*10 %*	*10 %*	100 %
Contiuous automated samplers	1	5	5	5	2	4	4,2
IR* in situ	5	2	5	3	4	5	3,4
FTIR	4	4	5	4	4	3	4
On-line-GC	2	3	3	2	3	3	2,6
TD-GC-FID	2	3	2	4	2	2	2,9
TD-GC-MS	2	5	1	5	2	2	3,7
Colorimetric	3	3	4	4	4	3	3,5
Diode-laser, in-situ	5	1	5	2	4	5	2,8
UV	4	2	4	3	4	3	3
MS	4	4	4	4	4	3	3,9
IMS*	4	2	4	3	2	3	2,8
TOC	4	1	4	5	5	3	3,4

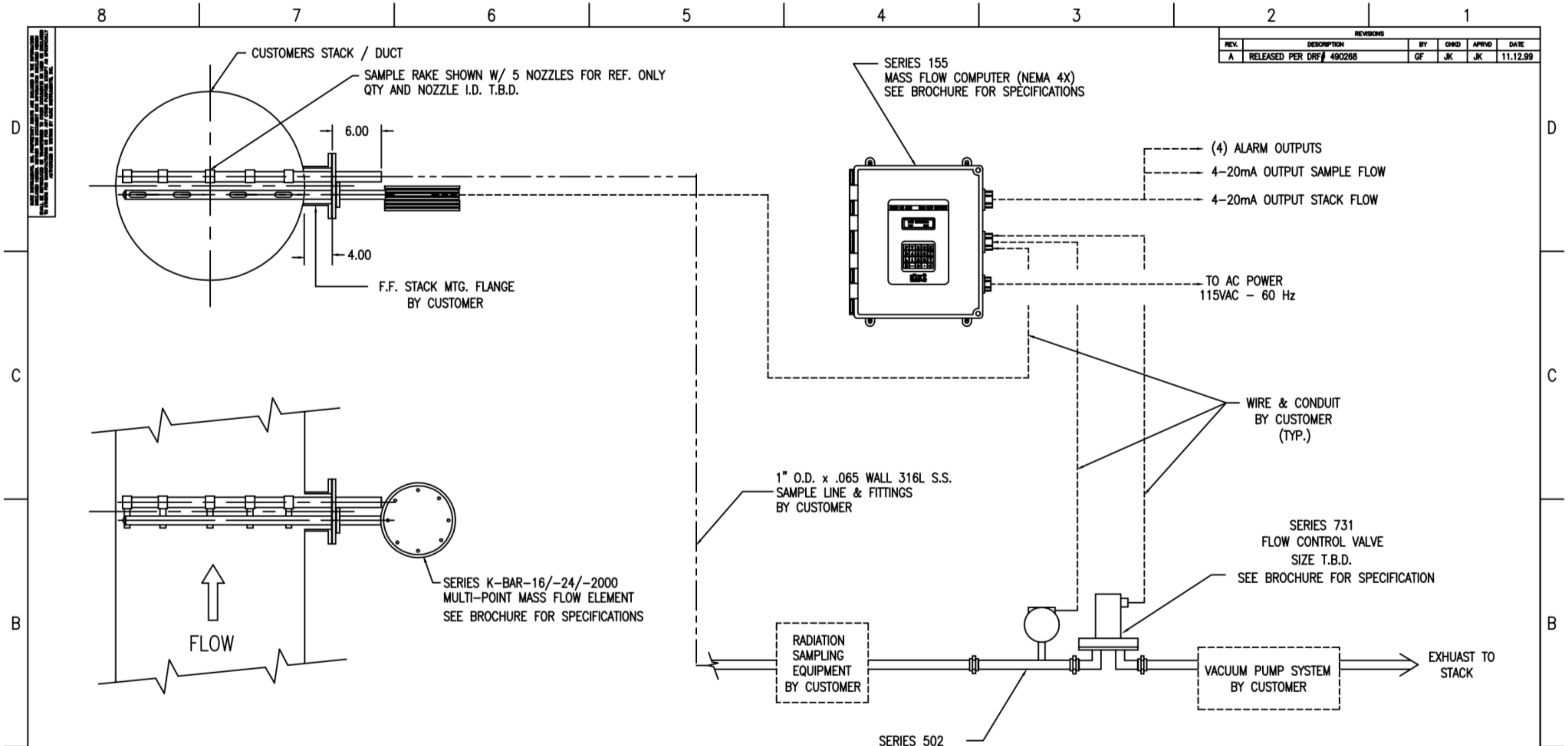
**The selectivity was not informed, and thus it is given according to the previous knowledge*

Speed = response time
Selectivity = specificity between analytes
Roughness = need of maintenance and environmental conditions
Sensitivity = Detection limit
Maturity = How ready the system is for the CCS plant flue gas measurements
Sampling = How the sample is treated (filtering, heating and other lowers the value)

Isokinetic sampling is recommended. However, the significance of it may be low, if droplets or dust are not present or if filtration will affect to the composition of the sample gas.

SUPPLEMENTS 1 FLOW DIAGRAM OF KURZ SAMPLING RAKE

REVISIONS					
REV.	DESCRIPTION	BY	CHKD	APRVD	DATE
A	RELEASED PER DRF# 490268	GF	JK	JK	11.12.99



NOTES:

1) NOZZELS AND AIR VELOCITY SENSORS LOCATED AT THE CENTEROIDS OF EQUAL FLOW AREAS.

2) NOZZLE SIZE FOR ISOKINETIC SAMPLING IS DETERMINED BY USING AN EQUAL VELOCITY INSIDE THE NOZZLE TIP AS IN FREE STEAM. NOZZLE SIZE TO MEET ANSI - 13.1 1999 HAS NOZZLE AREA (3) THREE TIMES ISOKINETIC NOZZLE AREA.

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES	APPROVALS		KURZ INSTRUMENTS, INC.
TOLERANCES ARE	DRAWN BY G.FOSTER	DATE 11.12.99	FLOW PROPORTIONAL AIR SAMPLING SYSTEM OUTLINE
FRACTIONS ± 1/16	CHECKED BY J.KURZ	DATE 11.12.99	
ANGLES ± 1°-0'	APPROVED J.KURZ	DATE 11.12.99	
DECIMALS .X ± 0.1 .XX ± 0.03 .XXX ± 0.003			DWG. SIZE D · DWG. NO. 000220-01 · REV. A
ORIG. RELEASE DATE			SCALE NONE · SHEET 1/1

FINAL
NEXT ASSEMBLY

SUPPLEMENTS 2 THE ANALYZER VENDORS

Questions	Answer	Type, other information
ABB	yes	GC (PGC 2000)
AGC instruments Ltd.	Yes	
'ait@hs.utc.com'	no	
AMESA	no	PCDD/F type of sampling system
Ametek and Land	no	
Aspectrics	no	
Bühler Technologies	no	
C.I. Analytics	yes	Sensi-tape
CIC	yes	Chromatographic Instruments Co
Cleanair	no	
Enviro Technology Services plc	no	OPSIS
Environics	yes	IMS
Environnment S.A.	no	
ETG-risorse	yes	UV and Laser
Gasera	yes	
Gasmet	yes	FTIR
Hiden Analytical	yes	MS
Horiba	yes	FTIR Raman
http://www.agc-instruments.com/	no	
http://www.analyticexpert.com/	no	Rosemount/emerson
http://www.danispa.it/prod.php?lingua=2	no	
http://www.fic-net.jp/eng/	no	Fuji electric systems
http://www.gow-mac.com/	no	http://www.gow-mac.com/
http://www.guided-wave.com/	no	Process analysers
http://www.lab-impex-systems.co.uk/eu/products.asp?type=8	no	
info@alpeslasers.ch	no	
In-process	yes	Vendor of ionicon
Ionicon Analytik Gesellschaft m.b.H.	yes	PTR-MS
Kontram	yes	Only probes
'lasers@lambdaphoto.co.uk'	no	
mcz	no	
Midac corporation	yes	FTIR
MKS	no	
monitor labs Teledyne	no	
Ms-nordic	yes	Vendor of ionicon
Norsk analyse	no	
OPSIS	no	
PerkinElmer	yes	
PLD	no	
PMeasuring	no	
Redwing	no	
sales@kurzinstruments.com	no	
Siemens	yes	Vendor PPM-systems
SRI-instruments	yes	Multigas GC
Tecora	yes	PCDD/F type of sampling system
wasson-ece.com	yes	Unable to do the required analysis
Westech instruments	yes	Probes & sampling
www.extrel.com	yes	MS-systems