



Project no.: **508283**

Project acronym: **S-SCIL**

Project title: **Development and Testing of new Standards for Sorption Measurement and Characterisation of Ionic Liquids**

Instrument: **Co-operative Research Project**

## **Final Activity Report**

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Duration: **27 month**

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## Final activity report

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# The S-SCIL Project

## Development and Testing of new Standards for Sorption Measurement and Characterisation of Ionic Liquids

### A CRAFT Project in the RP6

**Project Acronym:** S-SCIL

**Contract Number:** CT-2004-508283

**Web site:** [www.s-scil.eu](http://www.s-scil.eu)

**ABSTRACT:** The results of S-SCIL are new standards to measure the selective sorption of multi component gas mixtures in porous solids and Ionic Liquids. This technology brings huge advantages for various kinds of chemical, pharmaceutical, environmental, food and energy processing. The new standards can be used to characterise the substances which are used to perform the process (porous solids, (nano-)particles, polymers, liquids) concerning their selective behaviour in gas-mixtures as well as to investigate the process itself in terms of temperature, pressure and composition. In addition, the main single gas sorption measuring standards, including the new multi gas ones developed by this project, have been adapted for the characterisation and investigation of pure and multi gas processing based on Ionic Liquids. The selective sorption of multi component gas mixtures in Ionic Liquids has been measured. New instruments for sorption measuring in solid and liquid fixed beds have been developed and are commercially available now.

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# 1 S-SCIL Consortium

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## 2 S-SCIL Execution Summary

Global warming, ending resources, increasing of earth population are only three matters which characterize a situation where the global society needs a tremendous effort to at least reduce the problems and dangers being related to this developments.

The main contribution which is expected from science and technique to solve this big future challenges are closed sustainable loops for nearly all fields of our modern life, as there are for example energy and food production, industrial and consumer goods and for waste treatment.

Sorption technique can deliver a substantial contribution for the development of sustainable technologies. Those are new or improved technologies for flue gas cleaning, biogas and hydrogen production and treatment and storage, material production, waste recycling and others more.

As new materials with tailored micro- and nanostructures are developed and synthesized in an increasing number of laboratories around the world, it is to be expected that adsorption as a separation technology for gaseous (and liquid) mixtures will be of growing importance and impact to chemical, biochemical and environmental technology as well as to other fields of sciences (medicine, pharmacy) and engineering.

This will result in an increasing demand for sorption data which includes the equilibrium properties as well as kinetic data for both fundamental research and process application.

Multi gas sorption measurements and the investigation of Ionic Liquids for its use in a tremendous number of chemical and energy processes are thereby two big future tasks for the sorption measuring technique. As a result a steadily increasing demand for new measuring standards and instrumental investigations will appear in this new application field. This fact is reflected in the vast diversity of potential customers for instruments which can help to find these solutions.

All commercially available measuring instruments can only determine the sorption of a pure gas. Nevertheless real sorption processes take place in mixtures and not in pure fluids. This applies especially to many kinds of separation, purification, exhaust gas cleaning, particle design, hydrogen and natural gas storage, carbon dioxide reduction and other processes where adsorption technology is used. Another very interesting field with high need for studies are processes using supercritical fluids like carbon dioxide or water. These high pressure methods are currently being developed for various applications like: polymerisation, solvent extraction, dyeing of fibres, conditioning of polymers, Particle design and production etc.

During the last five years, a new type of fluids, the Ionic Liquids, have become more and more focussed by scientists all over the world. These new liquids are salts with a melting point near ambient temperature. Meanwhile Ionic Liquids are recognised as novel solvents for the so called "green industrial chemistry" whose aim is to reduce ecologically harmful waste to a minimum. These fluids can be designed to offer a tremendously high amount of different abilities according to the required specifications of the aimed process.

As a result of this the same amount of characterisation and process studies will be necessary. And similar to supercritical fluid applications, measuring instruments are, in the best case, only available to determine single gas absorption. Therefore, one more wide future

application field requires the possibility of carrying out selective sorption measurements for Ionic Liquids applications.

## 2.1 Introduction

The S-SCIL project is dealing with the development and testing of new standards to measure the selective sorption for multi gas applications. This technology, brings huge advantages for various kinds of chemical, pharmaceutical, environmental, food and energy processing. The new standards will be used to characterise the substances which are used to perform the process (porous solids, (nano-)particles, polymers, liquids) concerning their selective behaviour in gas-mixtures as well as to investigate the process itself in terms of temperature, pressure and composition. In addition, the main single gas sorption measuring standards, including the multi gas ones developed by this project, have been investigated and adapted for the characterisation and investigation of pure and multi gas processing based on Ionic Liquids.

The goals of the S-SCIL project have been achieved by 8 work packages which's interrelation is shown in the figure below.

In WP4 existing mono gas sorption measuring methods were upgraded for a broader temperature and pressure range and for multi fluid mixture dosing and pressure regulation. To enhance the measuring apparatus of WP4 for multi fluid sorption measuring WP3 was used. It delivered the sorptiv gas analysis methods for the new standards for multi gas sorption analysis of WP5. In WP6 the existing mono gas and the new multi gas standards have been adapted and applied for Ionic liquid application. WP7 was used to generate new commercial sorption analyzers based on the results of WP5 and WP6.

The main results gained by the S-SCIL project are:

- A new standard for multi gas sorption measuring in quasi static atmospheres
- New apparatus for multi gas sorption measuring in solid and fixed beds
- Mono and multi gas measuring methods for Ionic Liquids
- New methods for high pressure gas analysis

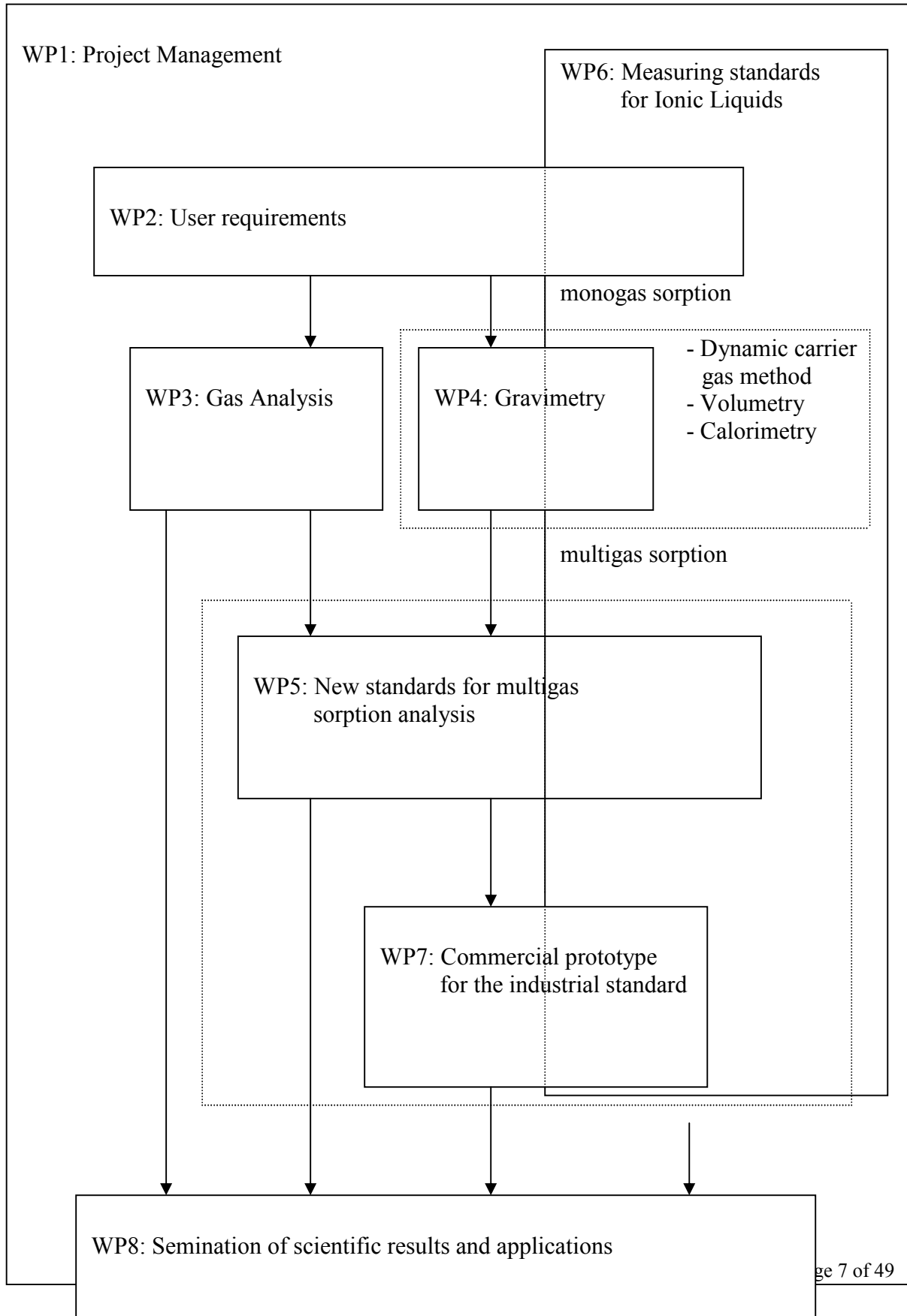


Fig. 1: S-SCIL Workpackage interrelation

## 2.2 Sorption Measuring Methods

The expression *sorption* is used to characterise the feature of gas- and liquid molecules to settle on a solid surface (*adsorption*) and of gas molecules to penetrate in a solid or liquid and to be dissolved there (*absorption*). These two physical phenomena are applied in many areas of process and environmental technology. Sorption measuring technique is used to investigate and characterise the process itself and all substances which belong to it. In the case of adsorption the solid body is called *adsorbent* and the gas or liquid phase is called *adsorptive* (compare figure 2). The adsorptive can be a pure fluid or a mixture. The molecules which settle on the surface are called *adsorbate* which can also be a pure substance or mixture.

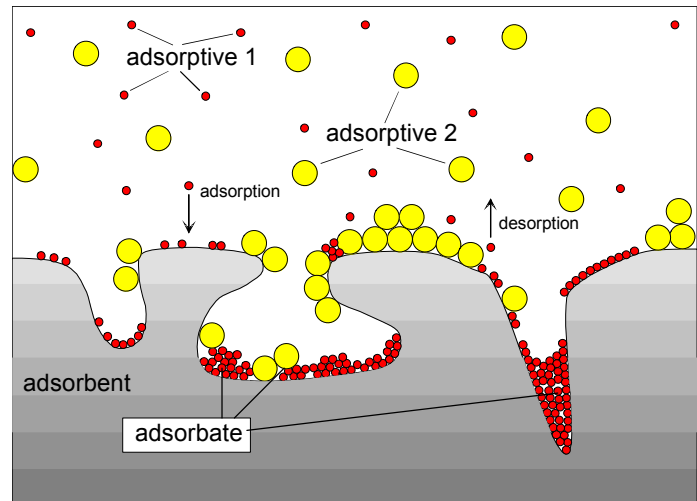


Fig. 2: Terminology of adsorption.

The three most well recognised sorption measuring methods are:

### *Volumetry or manometry:*

The sorption is measured by monitoring a pressure change in a closed measuring cell. A well known amount of pure gas is introduced from a dosing volume in a measuring cell containing the sample. The pressure drop which is achieved with the sample is compared to that one without sample in the same free volume. A schematic setup of a volumetric instrument for sorption measurements is shown in the figure beside.

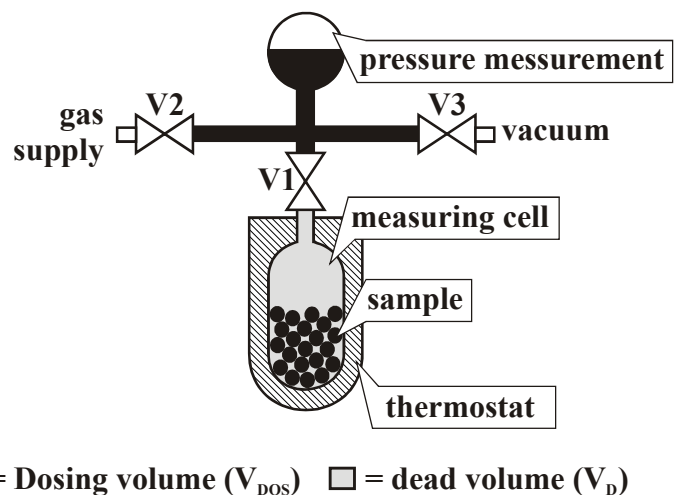


Fig. 3: Schematic setup of a volumetric instrument



*Dynamic analytical carrier gas method:*

Sorption is determined by measuring a concentration change of the adsorptive in a not-adsorbed inert gas flow (carrier gas). A schematic setup and a picture of a dynamic analytical carrier gas instrument is shown in the figures below.

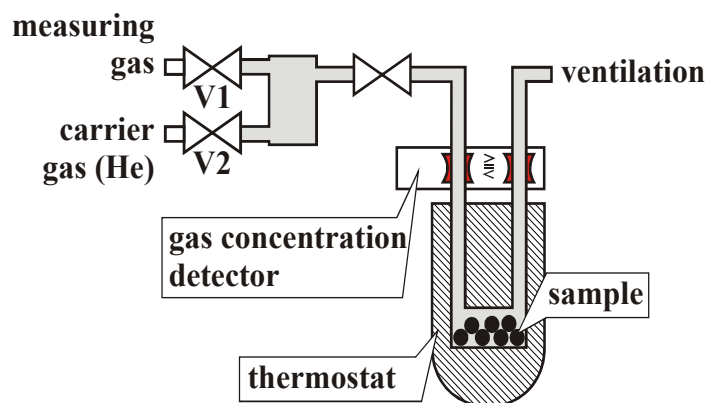


Fig. 4: Schematic setup of a instrument using the dynamic analytic carrier gas method



Fig. 5: Sorptometer Kelvin Dynamic analytical carrier gas instrument from Costech

The sample is prepared in the holder, fluxing carrier gas at high temperature to be sure of complete degassing of substances from the sample. During the flux, there is a time when the adsorbing gas concentration decreases, because the gas remains adsorbed on the sample until equilibrium is reached. Afterwards, returning to the starting conditions with a flow of carrier gas and, raising the temperature, the adsorbed gas is released. The Sorptometer from Costech provides the opportunity to investigate six samples simultaneously, with high accuracy and reliability. It calculates the difference between the starting and the equilibrium condition and is typically used to determine the specific area of materials, using helium as carrier gas, nitrogen as adsorbed gas and liquid nitrogen as coolant. The same principle can be used with other kind of gases, at different temperatures and for other types of determination.

*Gravimetry:*

Sorption is determined by measuring the weight change of the ad- or absorbing material (sample) by means of a highly accurate balance. This balance is located inside the measuring chamber. A schematic setup of a gravimetric instrument is shown in the figure below.

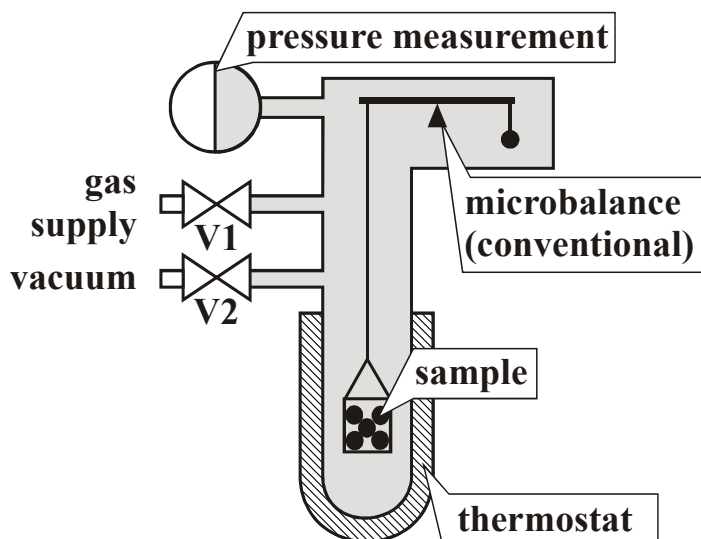


Figure 6: Schematic setup of a gravimetric instrument (not equipped with magnetic suspension balance).

Data to be measured are in all cases the so called *sorption equilibria* (how many molecules are ad- or absorbed) and *sorption kinetics* (how fast the sorption takes place) depending on temperature and pressure.

The volumetric, gravimetric and dynamic analytical carrier gas measuring methods are very well established to measure single gas ad- and absorption. Determination of nitrogen adsorption at sub-ambient pressure and liquid nitrogen temperature ( $-196^{\circ}\text{C}$ ) is used to characterise all kinds of porous solids and particles in terms of specific surface and porosity. *Specific surface* means the whole active surface which is available for molecules to be adsorbed (up to  $3000\text{m}^2/\text{g}$  in the case of activated carbon). *Porosity* means the pore size distribution (how many pores with varying diameter). This can be done fully automated and quite easily by all three methods mentioned above. Because of its lower price and some advantages at very low pressures, volumetric and carrier gas methods are normally used for this standard procedure. To investigate sorption process in a wider temperature and pressure range and to measure the kinetics of adsorption gravimetric instruments are used which offers many advantages. The main disadvantage of gravimetry, the installation of a highly sensitive balance inside a measuring cell is solved by the commercial availability of magnetic suspension balances where the sample weight changes are transmitted out of the measuring cell to a microbalance located outside under ambient conditions. In the figure below a conventional gravimetric instrument (left) is compared with a magnetic suspension balance (right):

The unique magnetic suspension balance technique of Rubotherm opens a wide application field to gravimetry. Using magnetic suspension balances gravimetric measurements can be performed under nearly all measuring conditions (high temperature, high pressure and aggressive atmospheres).

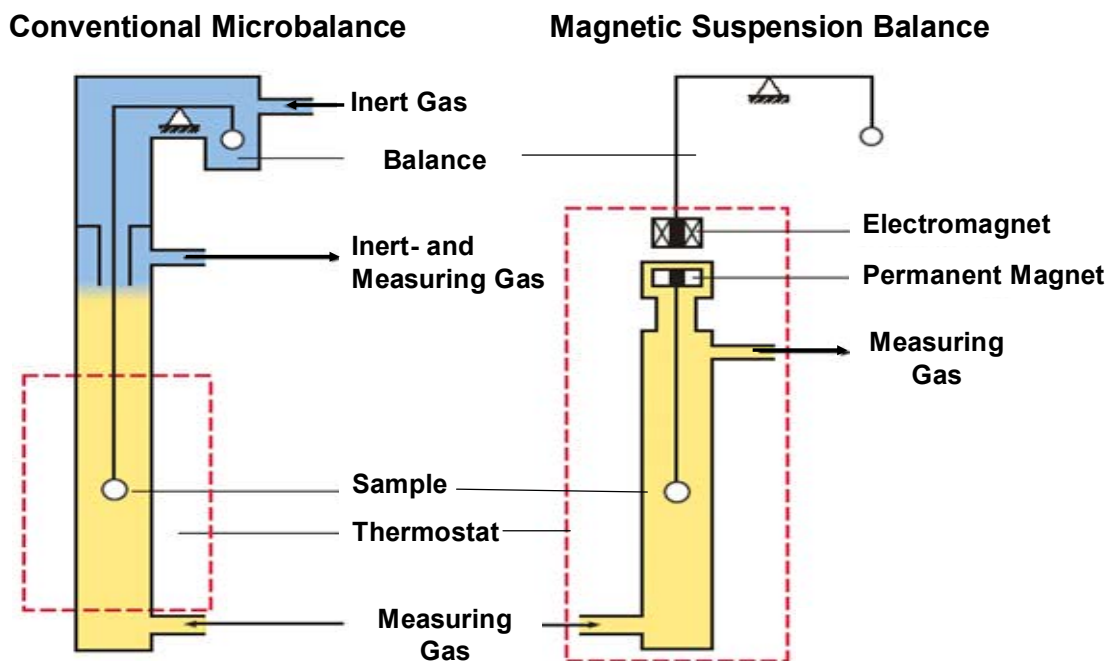


Fig. 7: Comparison of a conventional gravimetric instrument (left) and a magnetic suspension balance

## 2.3 New Standard for Multi Gas Sorption Measuring

### **A new Standard for Multi Gas Sorption Measuring in Circulating Quasi Steady Atmospheres.**

In order to apply the gravimetric measuring method for sorption measuring in multi component mixtures in a wider range of temperature and pressure the apparatus representing the current state of the art was improved and enhanced by instrumentation for sorptiv gas analysis.

Figure below shows the mixing and circulation loop of the multi gas sorption measuring standard. The procedure is explained for the generation and sorption measuring of a binary mixture. The calibrated dosing volumes  $V_{D1}$  and  $V_{D2}$  are filled with pure fluids. By measuring temperature and pressure in a high accuracy and using an equation of state of low uncertainty the masses of the pure gases introduced can be determined with an uncertainty of less then 0.1%.

By circulation, a homogenous mixture is generated in the dosing circle. In a second step the valves connecting the dosing part of the apparatus with the magnetic suspension balance (MSB) and the sample are opened and the mixture is now circulated through the measuring cell. After equilibrium is reached according to the sorption process the composition of the mixture has changed. This change can be determined in case of binary mixtures using the simultaneous sorptive gas density measuring. For multi component mixtures a high pressure sampling is used to separate and extract a representative sample of both, the feed and the resulted mixture.

The entire gas dosing system consists of four calibrated storage volumes ( $VD1 - VD4$ ). They are connected with automatic valves in such a way that they can be on the one side evacuated by using a rotary and turbo-molecular vacuum pump and on the other side filled with gases and vapours. The accuracy of the volumetric measurement is limited by the pressure measurement. In this installation a cascade of three pressure sensors with different full scales is used. This cascade provides a pressure measurement with high accuracy and reproducibility for every pressure in the storage volume and / or the measuring cell volume. The gas dosing system is arranged in a thermostatic air bath, which allows to operate the plant in a wide temperature and pressure range.

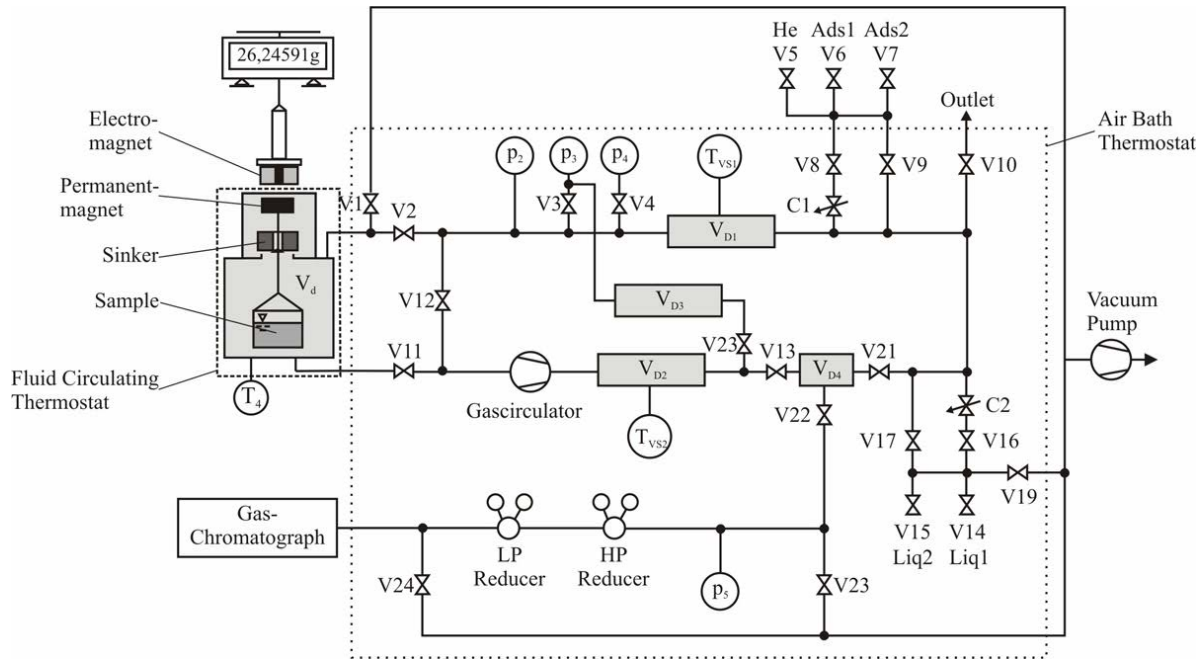


Fig. 8: Functioning principle of the apparatus for multi gas sorption measuring standard in circulating quasi steady atmospheres.

The magnetic suspension balance for the gravimetric measurement of the sorbents mass change is connected to the volumetric gas dosing system by two electrically heated tube lines and valves. By utilizing the free magnetic force transmission, the magnetic suspension coupling allows the balance to be placed outside the measuring cell. Together with the sample a sinker (titanium or silicon) can be weighed. This additional feature allows a highly accurate determination of the sorptive gas density surrounding the sample.

Several pure gases and liquids can be introduced in this four calibrated dosing volumes. The generation of mixtures consisting of more than four components is achieved by evacuation the mixture partially and feeding additional pure gases. The dosing volumes  $V_{D1}$  and  $V_{D4}$  are used for this purpose. Each of such a procedure dilutes the mixture generated before and remaining in  $V_{D2}$  and  $V_{D3}$ , by two more components. The homogenization of the mixture is realised by circulating through all dosing volumes in different procedures.

After mixture preparation,  $V_{D4}$  is used to extract a well defined amount of the mixture and to transfer it to the low pressure gas analyzer. First these proceedings guarantee the separation of a representative sample. This sample is now transferred to low pressure using a decomposition free pressure reduction in two steps always keeping the dosing temperature constant up to 200°C.  $V_{D4}$  can be extracted and analysed in several steps to proof the reproducibility of transfer and analysis. After the sorption equilibrium is reached, again  $V_{D4}$  is used to extract and analyse the final sorptive gas composition.  $V_{D3}$  can be used to store a part of the feed mixture and to use it after the sorptive gas analysis as a reference to proof the overall homogeneity.

To realize the low pressure instrumental analysis module a gas chromatographic technique is used. The task of this module is to determine the concentration changes in the sorptive gas

atmosphere before and after the sorption process. Because of the discontinues nature of this batch HP sampling, which is in case of the scientific standard necessary to achieve a representative sample, the abilities of a gas chromatographic separation can be ideally applied. The monitoring of the continuous change of the sorptiv gas mixture and thereby the kinetics of the sorption process is carried out in total using the measured integral mass change or selectively, using the measuring of sorptiv gas density and other properties.

Figure 1 shows also the MSB which allows to determine the total amount adsorbed and the sorption gas density change with utmost precision. In addition the temperature and pressure measuring, the circulation pump and other parts are shown. The density measuring feature is also used as analysis module as explained in deliverable. The main specifications of the new installed sorption plant with the accuracy details are listed in table 1.

**Table 1:** Technical specifications of the new multigas sorption measuring standard:

max. adsorbent weight:	<b>40g</b> accuracy: $\Delta m = \pm 0,03$ mg
max. dosing-temperature:	<b>200°C</b> (volumetric and gravimetric) accuracy: $\Delta T = \pm 0,03$ K
max. sample temperature:	<b>500°C</b>
max. pressure:	<b>200 bar</b> (with three pressure sensors) P1: 200,00 bar – 10,35 bar, <b>0,04%</b> full scale P2: 10,34 bar – 0,35 bar, <b>0,04%</b> full scale P3: 0,34 bar – 0,00 bar, <b>0,07%</b> full scale
density measurement for two component analysis and GC concentration verification:	accuracy: $\Delta \rho / \rho = \pm 2\% / \rho$
GC-measurement for more then two component mixtures	accuracy: $\Delta x = \pm 0,2\%$

Generally the gas chromatographic analysis module together with the density measurement and a new high performance mixture EOS (GERG 2000) allows to determine the change of the sorptive gas concentration with an uncertainty of  $\pm 0.2\%$ .

A picture of the entire apparatus is shown in below. It consists of a circulating fluid thermostat (left), the magnetic suspension balance, the automatic dosing system and the gas chromatograph (right)



Fig. 9: Picture of the apparatus for multi gas sorption measuring in circulating quasi steady atmospheres

## 2.4 New Apparatus for Multi Gas Sorption Measuring in Solid and Liquid Fixed Beds

By means of the S-SCIL project a ‘family’ of marketable, standardised mono and multi gas sorption measuring instruments was developed and designed. This new type of instrument consists of five different modules; a high pressure reaction vessel including a magnetic suspension balance, a gas dosing and pressure regulating module, a vapour dosing module and a module for the analysis of the measuring atmosphere, and integrated analytical software.

The principle set up of the modules is shown in the figure below. The minimum configuration and thereby also the lowest price solution will be the analyzer for mono gas sorption measuring in static atmospheres. Upgrades are for vapour dosing, mono gas flowing atmospheres, flowing vapour, binary gas/vapour mixtures and multi component gas/vapour mixtures which contains all modules in the highest configurations.

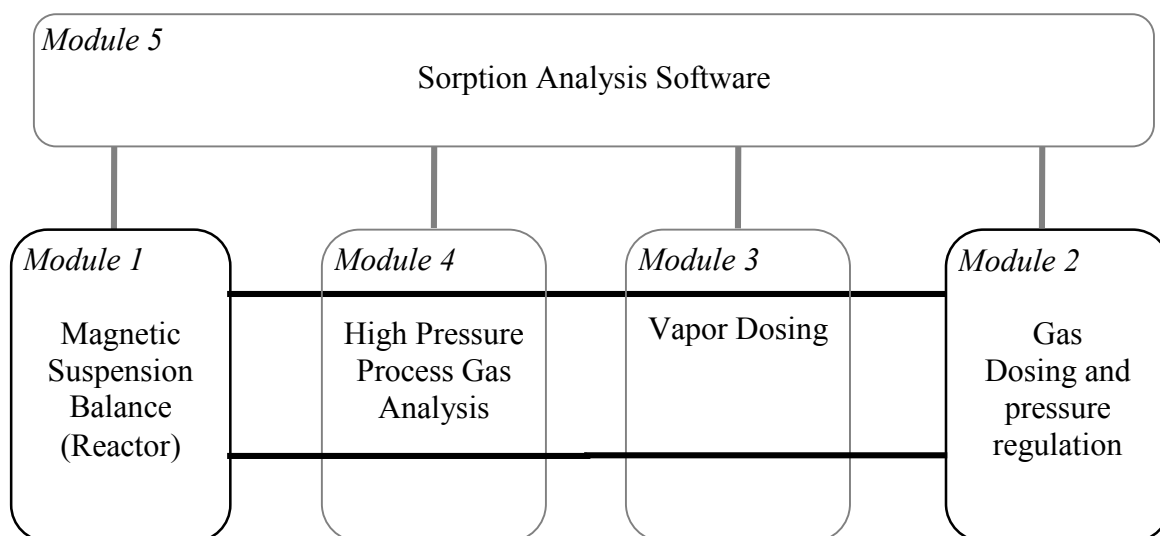


Fig. 10: The different modules for the new gravimetric analyzer for mono and multi gas sorption measuring in a forced flow through and steady atmospheres

The standardized platform will provide a modular up and down grade and allow experiments with simple systems with only one gas, as well as complex systems with gas and vapour mixtures. The different instruments will be:

- Easily upgradeable
- Easy and safe to handle
- Easy to maintain
- Allow a remote diagnosis via the internet
- Equipped with self-explanatory analytical software



## 2.4.1 ISOSORP Mono vapor HP-static

Sorption analyzer for measuring the kinetics and equilibrium of the ad- or absorption of vapours on solid or liquid samples. The sorption is determined gravimetrically by weighing the sample using the patented magnetic suspension balance.

The pressure in the gaseous atmosphere surrounding the sample is controlled by means of a vapour dosing and pressure controlling system. This system can be used to control pressure changes in the reactor by feeding vapour from the supply into the reactor (pressure increase) or by allowing gas flowing out of the reactor into ventilation or vacuum (pressure decrease).

The vapour dosing is generated by a vapour pressure cell thermostated in a liquid bath from -40°C to +150°C. All transfer tubes like the reactor itself can be heated up to 200°C.

The complete setup is manufactured using corrosion resistant materials and the magnetic suspension balance prevents the balance from being corroded. As a result of that, experiments using corrosive gases can be carried out. The application of a magnetic suspension balance enables experiments to be carried out in a large temperature and pressure range (cp. technical data). An excellent long term stability and accuracy is typical for magnetic suspension balance instruments. This is achieved by the fully automatic, regularly checking of a reference measuring point which eliminates any drift of the baseline of the instrument. Additionally the sensitivity of the balance is checked and calibrated during the experiments automatically.

The density of the gaseous atmosphere in the reactor is determined highly accurate by applying Archimedes' principle. A sinker is weighed by the balance, so determining the buoyancy effect acting on it. The measured data sample mass, pressure, temperature and density of the vapour phase in the reactor are continuously recorded by the software and displayed on-line.

A schematic flow diagram of the ISOSORP<sup>®</sup> Mono vapour HP-Static is given in the figure below:

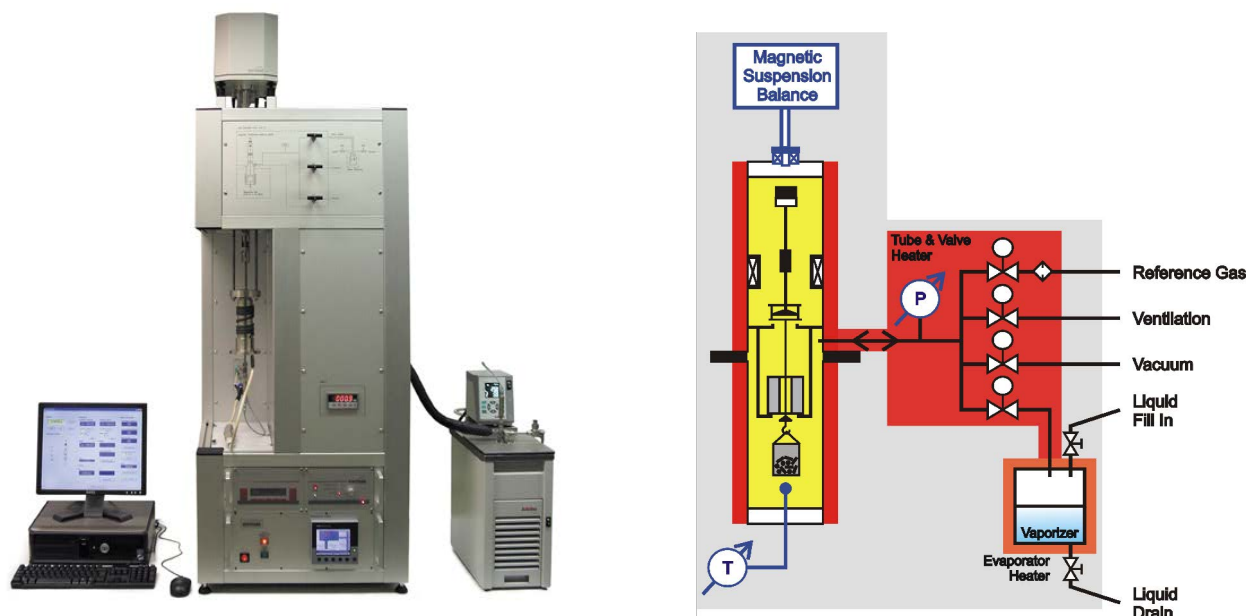


Fig.11: Picture and flow chart of the ISOSORP Mono vapour HP-static

**Technical Data:****Magnetic Suspension Balance:**

sample mass:	up to 10 g
dynamical weighing range:	up to 25 g
resolution:	0.01 mg
reproducibility:	± 0.02 mg (standard deviation)
relative error:	< 0.002 % M.V.
materials with gas contact:	1.4439 (= ASTM 317LN), Gold

**Density Measurement:**

measuring range:	0-2000 kg/m <sup>3</sup>
resolution:	0.0025 kg/m <sup>3</sup>
reproducibility:	± 0.0075 kg/m <sup>3</sup> (standard deviation)

**Pressure Control:**

pressure range:	Vacuum...50 MPa at t < 50°C <i>(up to 40 MPa at t &lt; 150°C and up to 35 MPa at t &lt; 250°C)</i>
controlling range:	Vacuum...50 MPa
materials with gas contact:	1.4439 (= ASTM 317LN), Kalretz <sup>®</sup> , Teflon <sup>®</sup>

**Pressure Sensor:**

measuring range:	Vacuum...50 MPa
resolution:	0.01 MPa
reproducibility:	± 0.08% F.S.
typical stability:	0.1% F.S. per year

**Temperature Sensor:**

measuring range:	-40°C...500°C
resolution:	0.1°C (display), 0.01°C (software)
accuracy:	½ DIN IEC 751, class B (= 0,1°C at 0°C)

**Temperature Control (using liquid circulator as thermostat):**

controlling range:	20°C...150°C or -30°C...150°C (optional) or +30°C...200°C (optional)
controlling accuracy:	± 0.01°C (thermostat)

**Electrical Sample Heater:**

temperature range:	up to 450°C
controlling accuracy:	± 0.5°C (heater)

**Vapor pressure cell incl. pressure, additional heated transfer lines and circulating fluid thermostat:**

temperature range:	-40°C – 150°C
controlling accuracy:	t <sub>s</sub> = ± 0.01°C

## 2.4.2 ISOSORP Mono Gas HP-flow

Fully automatic sorption analyzer for measuring the kinetics and equilibrium of the adsorption of gases on solid or liquid samples. The sorption is determined gravimetrically by weighing the sample using the patented magnetic suspension balance.

The gaseous atmosphere surrounding the sample is flowing continuously through the measuring cell. Up to two gases can be mixed and the pressure of the gas flow along the sample is controlled by means of a fully automatic gas dosing system. This system can control gas flows and pressure changes in the reactor by feeding continuously gas from the gas supply into the reactor by means of two mass flow controllers and by allowing gas flowing out of the reactor into ventilation or vacuum by means of a cascade of two pressure controlling valves. The complete setup is manufactured using corrosion resistant materials and the magnetic suspension balance prevents the balance from being corroded. As a result of that, experiments using corrosive gases can be carried out. The application of a magnetic suspension balance enables experiments to be carried out in a large temperature and pressure range (cp. technical data). An excellent long term stability and accuracy is typical for magnetic suspension balance instruments. This is achieved by the fully automatic, regularly checking of a reference measuring point which eliminates any drift of the baseline of the instrument. Additionally the sensitivity of the balance is checked and calibrated during the experiments automatically.

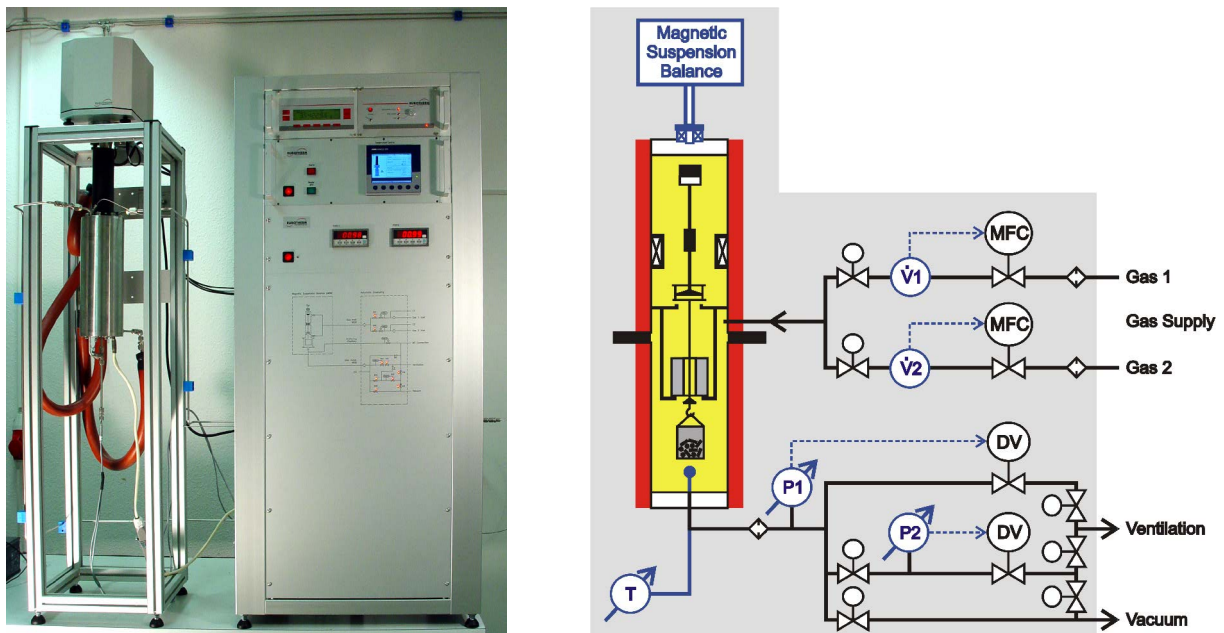


Fig. 12: Picture and flow chart of the new ISOSORP Mono Gas HP-flow

The density of the gaseous atmosphere in the reactor is determined highly accurate by applying Archimedes' principle. A sinker is weighed by the balance, so determining the buoyancy effect acting on it.

The measured data sample mass, gas flow(s), pressure, temperature and density of the gas phase in the reactor are continuously recorded by the software and displayed on-line.

A Picture schematic flow diagram of the ISOSORP Mono Gas HP-flow is given in the figure 12.

### **Technical Data:**

#### **Magnetic Suspension Balance:**

sample mass:	up to 10 g
dynamical weighing range:	up to 25 g
resolution:	0.01 mg
reproducibility:	± 0.02 mg (standard deviation)
relative error:	< 0.002 % M.V.
materials with gas contact:	1.4439 (= ASTM 317LN), Gold

#### **Density Measurement:**

measuring range:	0-2000 kg/m <sup>3</sup>
resolution:	0.0025 kg/m <sup>3</sup>
reproducibility:	± 0.0075 kg/m <sup>3</sup> (standard deviation)

#### **Gas Flow Control:**

pressure range:	Vacuum...35 MPa
controlling range:	2 x 10 ml <sub>STP</sub> /min...400 ml <sub>STP</sub> /min (calibrated for N <sub>2</sub> )
typical accuracy:	± 1%
materials with gas contact:	1.4439 (= ASTM 317LN), Viton, Teflon <sup>®</sup>

#### **Pressure Control:**

pressure range:	Vacuum...35 MPa
controlling range:	0.05 MPa...35 MPa
typ. controlling accuracy:	± 0.01 MPa
materials with gas contact:	1.4439 (= ASTM 317LN), Kalretz <sup>®</sup> , Teflon <sup>®</sup>

#### **Pressure Sensor:**

measuring range:	Vacuum...40 MPa (P1), Vacuum...4 MPa (P2)
resolution:	0.01 MPa, 0.001 MPa
reproducibility:	± 0.08% F.S.
typical stability:	0.1% F.S. per year
materials with gas contact:	ASTM 316L & Hastelloy

**Temperature Sensor:**

measuring range: -200°C...500°C  
resolution: 0.1°C (display), 0.01°C (software)  
accuracy: 1/3 DIN IEC 751, class B (= 0.1°C at 0°C)

**Temperature Control RT Range** (using external [Julabo F-25MB](#) liquid circulator):

controlling range: 20°C...150°C  
controlling accuracy: ± 0.01°C (thermostat)

**Temperature Control LT Range** (*OPTIONAL*, using dewar vessel for cooling):

controlling range: approximately -196°C (LN2 temperature)

**Temperature Control HT Range** (*OPTIONAL*, using electrical heater):

temperature range: up to 500°C  
controlling accuracy: ± 0.1°C (heater)

**Sample temperature control**

LN2-cooling (77 K)

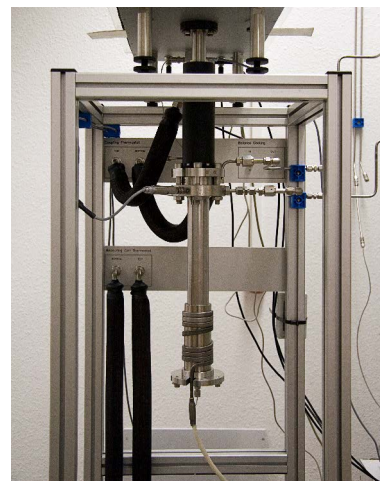
heating / cooling by  
liquid circulator  
(240 K – 420 K)electrical heating  
320 K – 780 K

Fig. 13: Different Measuring cells and thermostating devices for the new ISOSORP Mono Gas HP-flow



### 2.4.3 ISOSORP Multi Gas and Vapor HP Flow



Fig. 14: Pictures of the new ISOSORP Multi Gas and Vapor HP-Flow

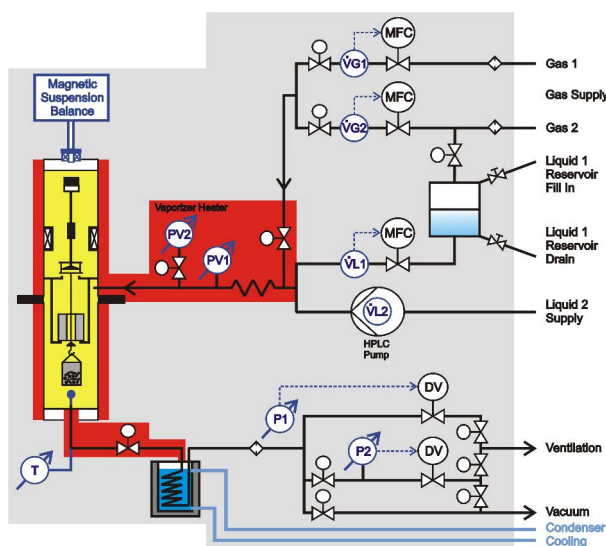


Fig. 15: Flow chart of the new ISOSORP Multi Gas and Vapor HP-Flow

Fully automatic sorption analyzer for measuring the kinetics and equilibrium of the ad- or absorption of gas and vapour mixtures on solid or liquid samples. The sorption is determined gravimetrically by weighing the sample using the patented magnetic suspension balance.

The gaseous atmosphere surrounding the sample is flowing continuously through the measuring cell. Two or more gases can be mixed with two liquids. After mixing, gases and liquids are heated up and feed into the reactor. The pressure of the flow along the sample is controlled by means of a fully automatic dosing system. This system can control mixture flows and pressure changes in the reactor by feeding continuously gas from the gas and liquid supply into the reactor by means of two or more mass flow controllers for gases and one for liquids. A second liquid is dosed using a HPLC pump. After the reactor all vapours are extracted by cooling down the mixture flow in a condenser to ambient temperature. The measuring pressure is controlled in the cold area by allowing gas flowing out of the reactor into ventilation or vacuum by means of a cascade of two pressure controlling valves. The flow chart of this apparatus in the minimum configuration is shown beside. The complete setup is manufactured using corrosion resistant materials and the magnetic suspension balance prevents the balance from being corroded. As a result of that, experiments using corrosive gases can be carried out. The application of a magnetic suspension balance enables experiments to be carried out in a large temperature and pressure range (cp. technical data). An excellent long term stability and accuracy is typical for magnetic suspension balance instruments. This is achieved by the fully automatic, regularly checking of a reference measuring point which eliminates any drift of the baseline of the instrument.

Additionally the sensitivity of the balance is checked and calibrated during the experiments automatically.

The density of the gaseous atmosphere in the reactor is determined highly accurate by applying Archimedes' principle. A sinker is weighed by the balance, so determining the buoyancy effect acting on it.

For measuring selective sorption in more component mixtures, on line gas analysis modules are installed. Gas analysis modules are available for continuous analysis by mass spectrometer or for discontinuous analysis by gas chromatography. In both cases representative sample is extracted by a high pressure sampling device and fed in the low pressure analyzer. Together with the density measuring device a software module based on the Gerg 2004 mixture EOS can be used to control the concentration measurement by calculation the density with uncertainty below 0.1%. The concentration of a binary mixture can be determined directly using this tool. Additionally a concentration measuring module based on a non-disperse IR-technology is available. This module allows to determine concentration changes directly in the high pressure feed and outgoing flow. Optional a capillary can be used to sample the mixture in the reactor itself directly near the sorbens (see Fig. below).

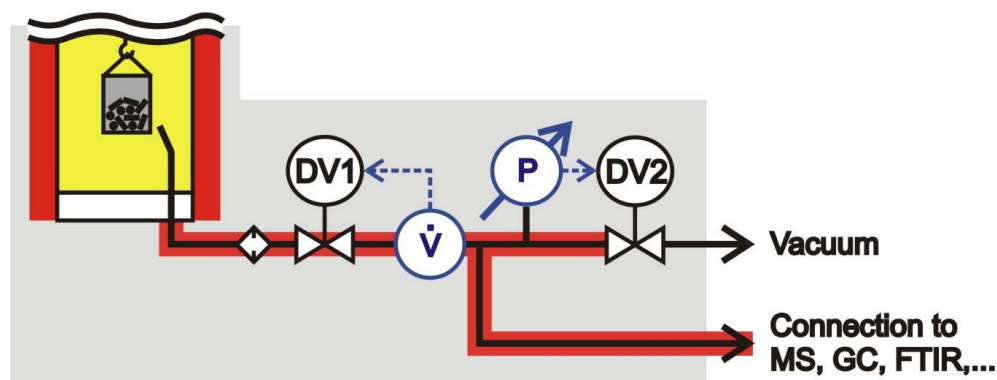


Fig.16: Direct capillary sampling device for qualitative analysis

The measured data sample mass, gas flow(s), pressure, temperature and density of the gas phase in the reactor are continuously recorded by the software and displayed on-line. All experimental data are saved in an ASCII-data file. The equilibrium data are automatically extracted from the experimental data and are saved in a separate data file.

**Technical Data:**

For this high end sorption measuring standard customized solutions will be offered according to the certain application. The technical data mentioned before for the three mono gas versions are also valid for the ISOSORP Multi Gas and Vapor HP-Flow. Beside this generally available specification will be:

Weight measurement:      • Samples up to 20g with 1 microgram resolution  
                                      • Samples up to 200g with 10 microgram resolution  
                                      • Temperature in the range between -196°C and 500 °C

Density measuring:         • uncertainty less than 0.001 kg/ m + 0.02%

Concentration measuring: • low 1 ppm < C < 1g/m<sup>3</sup> :  $\Delta C \leq \pm 1$  ppm + 1%  
                                      • 0 < C < 1:  $\Delta C \leq \pm 0.1\%$

Gas dosing:                 • 2 – n gases,  $\dot{m} \hat{=} 10 - 1000$  ml<sub>STP</sub>/min

Liquid dosing:             • 1-n liquids,  $\dot{m} \hat{=} 10 - 2000$  ml<sub>STP</sub>/min

Pressure control:         • Pressure range:         vacuum - 500 bar

                                     • Stability:                 0.1 bar         20 – 500 bar  
    0.005 bar         1 – 20 bar  
    0.001 bar         0 – 1 bar

                                     • Dynamic and static atmosphere



## 2.5 Mono and Multi Gas Measuring Methods for Ionic Liquids

During the last five years the focus of many research groups was put on a new type of fluids, the Ionic Liquids. These new liquids are salts with a melting point near ambient temperature. Meanwhile Ionic Liquids are recognised as novel solvents for the so called "green chemistry" whose aim is to reduce ecologically harmful waste to a minimum. These fluids can be designed to offer a tremendously high amount of different abilities according to the required specifications of the aimed process.

The great interest in room temperature Ionic Liquids (RTILs) has recently rendered them one of the most attractive materials. Since RTILs are comprised entirely of ions, physical and chemical properties, as generally characterized by nonvolatility, nonflammability, chemical and thermal stability, and high ionic-conductivity, can be easily tuned simply by changing the structure of the component ions. For practical use in different applications above all, their chemical properties, such as solubility of gases must be known. For some reactions, quantitative and systematic solubility measurements, in particular, of carbon dioxide in Ionic Liquids are of basic interest.

Furthermore, comprehensive understanding of the general aspects of properties and their correlation with the structures of the RTILs requires a systematic investigation of a wide variety of Ionic Liquids with different cationic and anionic structures.

During the S-SCIL project the main sorption measuring methods including the newly developed instruments have been adapted and evaluated for their applicability to characterise Ionic Liquids and the processes based on this new kind of fluids.

Well established mono gas sorption measuring methods have been applied to investigate the sorption behaviour of different gases in Ionic Liquids. Multi gas sorption measuring on Ionic Liquids were carried out using the new standard for multi gas sorption measuring in circulating quasi steady atmospheres. These measurements have also been published and presented at several international conferences.

## 2.5.1 Mono Gas Sorption Measuring Results on Ionic Liquids

Several mono gas measuring methods have been adapted and applied to investigate the absorption of different gases in Ionic Liquids. For low pressure measuring mainly a modified Sorptometer 1042 of Costech was used in order to obtain an instrument able to measure single gas absorption in Ionic Liquids in the presence of different gases (like CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>). Additionally also volumetry has been applied. The flow chart and a picture of the Sorptometer 1042 is shown below

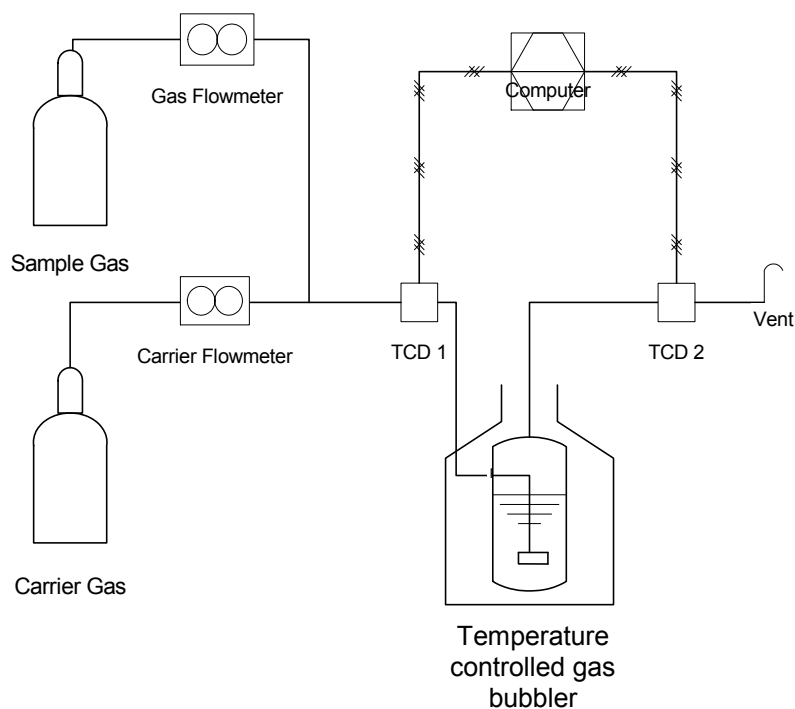


Fig. 17: Sorptometer 1042 – General Scheme.

The sample is prepared in the holder, fluxing carrier gas at high temperature to be sure of complete degassing of substances from sample. During the flux, there is a time when the adsorbing gas concentration decreases, because the gas remains adsorbed on the sample until equilibrium is reached. Afterwards, returning to the starting conditions with a flow of carrier gas and, raising the temperature, the adsorbed gas is released.

These events are detected by instrument sensors, generating an electrical signal on a graphic plot presenting two peaks: a first positive and a second negative peak, which represent respectively the adsorption and the desorption of the gas. To construct isotherm curves, the measures are repeated at different adsorbing gas concentrations.

This method calculates the difference between the starting and the equilibrium condition. It is typically used to determine the specific area of materials, using helium as carrier gas, nitrogen as adsorbed gas and liquid nitrogen as coolant. The same principle can be used with other kind of gases, at different temperatures and for other types of determination. Devices based on this method are economic, fast, easy to use, easy to construct and do not need high vacuum to work.

With this dynamic measuring method, the ionic liquid is prepared in a sample holder and the carrier gas is flown through it at room temperature. During the carrier flow, the absorbed gas

concentration decreases because part of it is absorbed by the ionic liquid, until the system reaches the equilibrium.

The absorbed gas is released when the system temperature rises.

All is detected by instrument sensors that generate a graphic representation of two peaks, the first one positive and the second one negative, showing absorption and desorption of CO<sub>2</sub>. A TCD measures the thermal conductivity variation of a gas stream and records a continuous signal during absorption and desorption. Isothermal curves were measured changing CO<sub>2</sub> concentrations.

The experimental results show that CO<sub>2</sub> is absorbed in every ionic liquid at room pressure and temperature, and the absorption is proportional to CO<sub>2</sub> concentration with a different behaviour for each ionic liquid. Further results obtained on CH<sub>4</sub> and N<sub>2</sub> show that there is no or very low absorption of these gases under these conditions, regardless of the concentration and the ionic liquid.

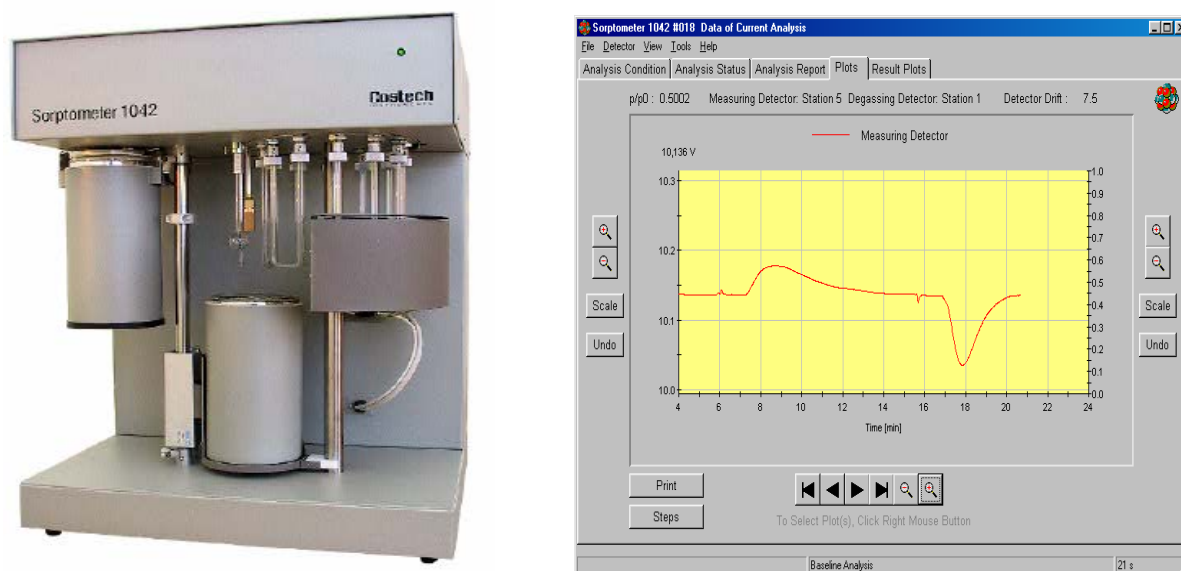


Figure 18: Picture of Sorptometer Kelvin 1042 and example of absorption and desorption peaks

In order to host Ionic Liquids in the instrument, some new sample holders with different form and geometry were developed.

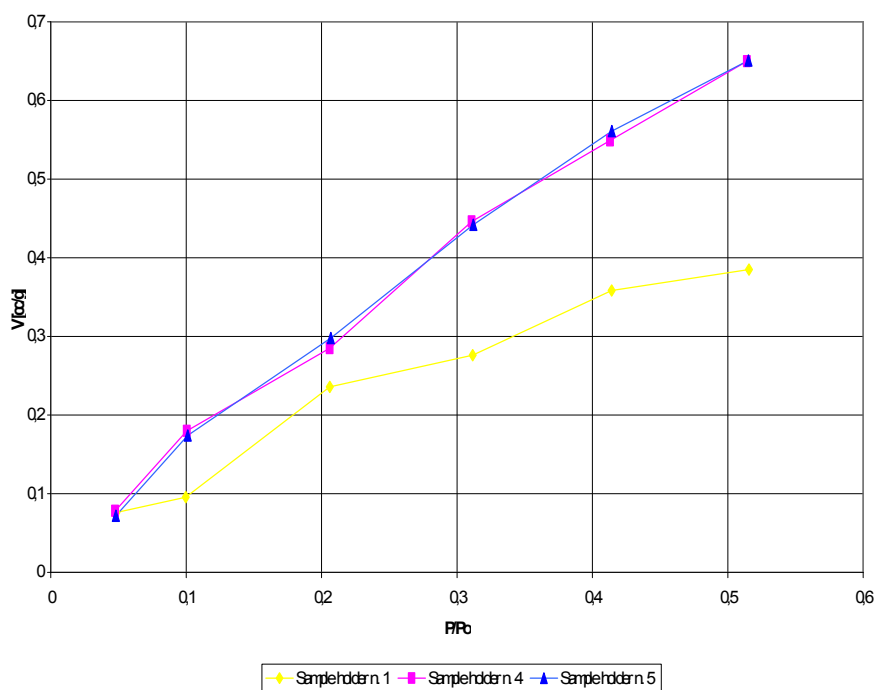
The first three sample bubblers have been designed and realized *ad hoc* to perform the contact between Ionic Liquids and gases. These new holders have substituted the original ones used in Sorptometer 1042 by Costech. According to the gained sample experiences new holders (Type 4 and 5) were designed. They are shown below attached at the sorptometer.



Fig.19: Sample holder type 4 and 5

The measuring results achieved with the final sample holders compared to the first ones are shown below.

#### CO<sub>2</sub> absorption in 1-butyl-3-methylimidazolium[BF<sub>4</sub>] using different sample holders

Fig. 20: Effect of the different kind of sample holder for 1-butyl-3-methylimidazolium[BF<sub>4</sub>].

For 1-butyl-3-methylimidazolium [BF<sub>4</sub>] the differences between sample holders number 4 and 5 are very small, as shown by the two absorption isotherms. In this case the patterns are basically the same point by point, except for very little variations.

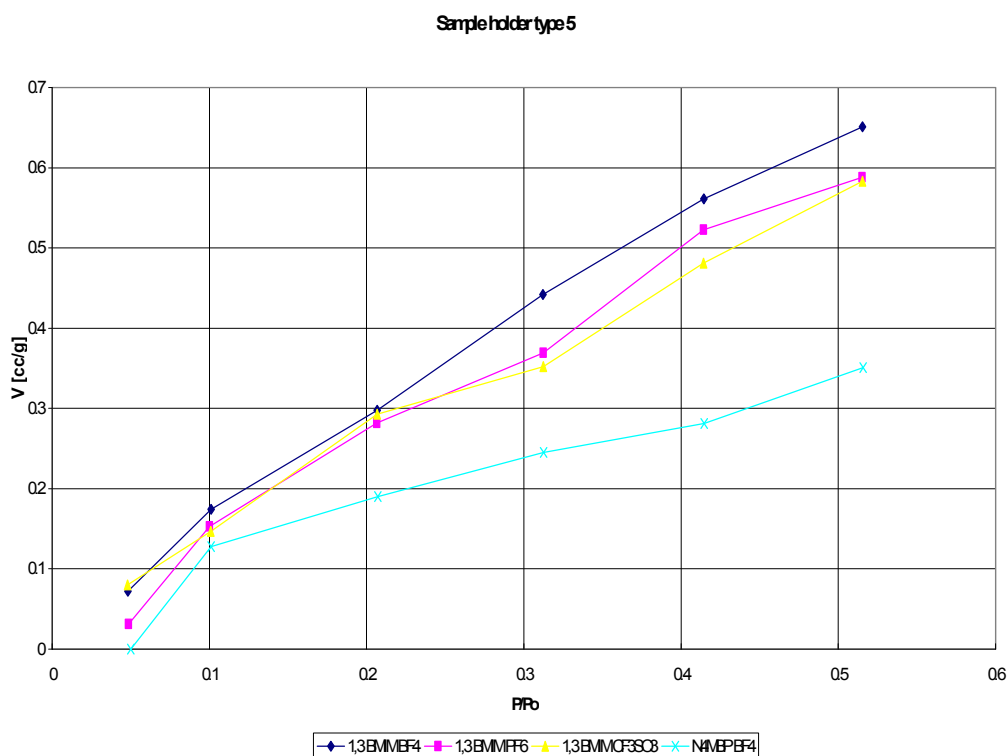


Fig. 21: CO<sub>2</sub> sorption isotherms obtained in different ILs using the sample holder no. 5.

These are CO<sub>2</sub> adsorption isotherms for sample holder no. 5. Trends are basically the same but, with a narrower capillary size, the bubbling effect groups the isotherms closer to each other.

Diagram of CO<sub>2</sub> absorption into 1-butyl-3-methylimidazolium[BF<sub>4</sub>] shows a regular trend, while the other isotherms are more regular with the exception of n-butyl-4-methyl-piri-dinium.

For high pressure mono gas sorption the Rubotherm ISOSORP Mono Gas HP-flow has been used.

Below two diagrams show the temperature dependency of the sorption of CO<sub>2</sub> and CH<sub>4</sub> in [EMIM][EtSO<sub>4</sub>]. Sorption decreases for both gases like expected when the temperature rises from 25 to 50°C. For Methane the temperature effect is higher than for Carbon Dioxide: the mass uptake at 50°C is round about a third of the value at 25°C

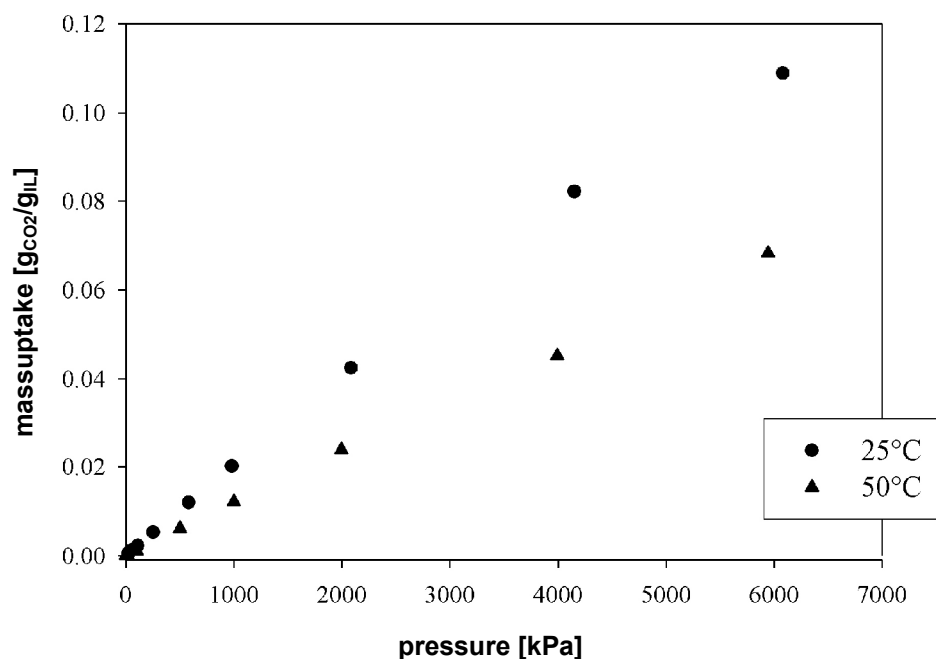


Fig. 22: Sorption of CO<sub>2</sub> in [EMIM][EtSO<sub>4</sub>] at temperatures of 25 and 50°C

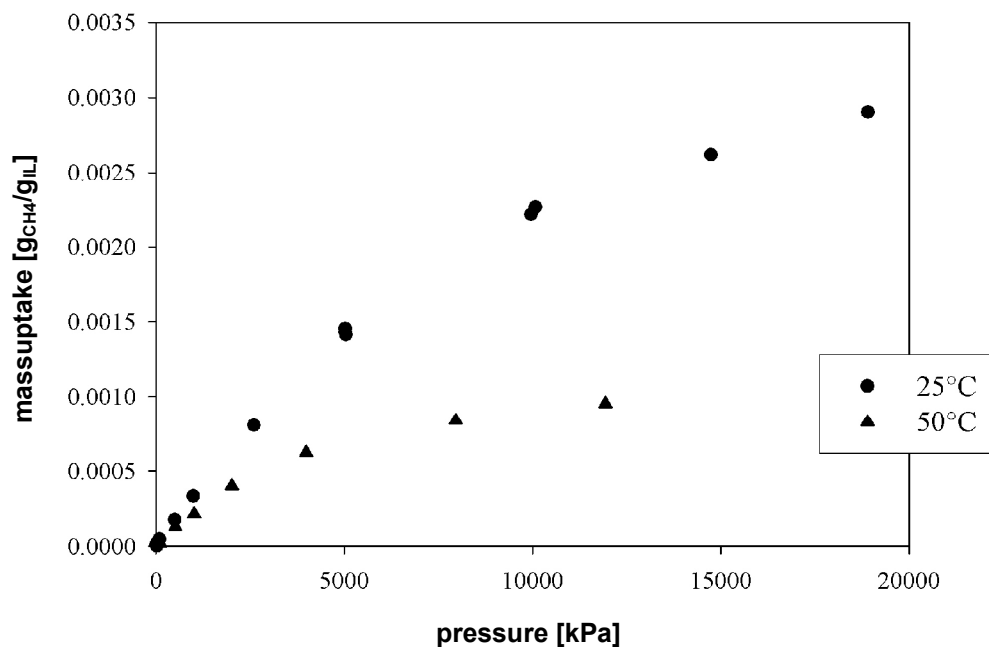


Fig. 23: Sorption of CH<sub>4</sub> in [EMIM][EtSO<sub>4</sub>] at temperatures of 25 and 50°C

## 2.5.2 Low pressure Multi Gas Sorption Measuring on Ionic Liquids using the Dynamic Analytical Method

For this type of measurements we have used the modified ECS 4010 by Costech. With this system, combining an oven, GC column and TCD, it was possible to evaluate the selective amount of gas adsorbed by the ionic liquid in a mixture.

Dynamic tests using mixture of two gases can be carried out in the following system at different temperatures and low pressure:

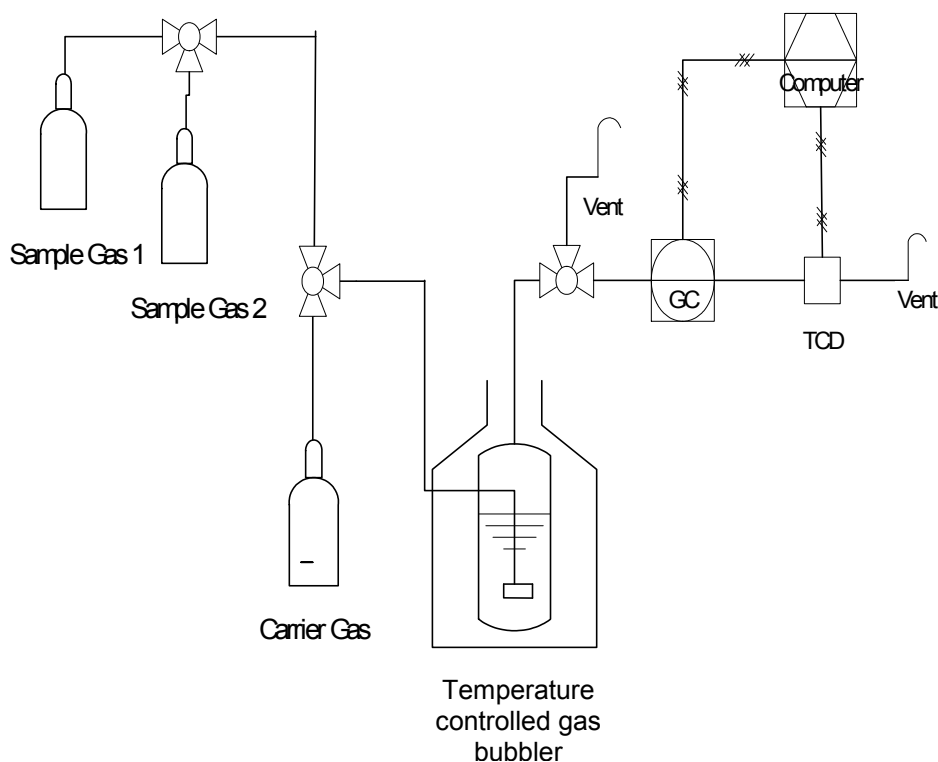


Fig. 24: Multigas Measuring System based on the ECS 4010 by Costech

For the ECS 4010 measurements, a gas mixer was realized to obtain good gas homogeneity. Some articles in the scientific literature show that gas mixtures are often inhomogeneous, due to differences in density, viscosity and chemical nature of the gases. To avoid this problem, it is necessary to build an apparatus which assures a homogeneous gas mixture before the gas absorption analysis. The apparatus is formed by 2 mass flow controllers and by a gas mixing chamber filled with a granular inert substance to perform the intimate mixing between the two gases. Below pictures of the apparatus are shown.



Fig. 25: ECS 4010 - Global View and Mass Flow Controllers for Mixture Preparation.

The diagram below shows the result of a binary mixture experiment with the ECS 4010.

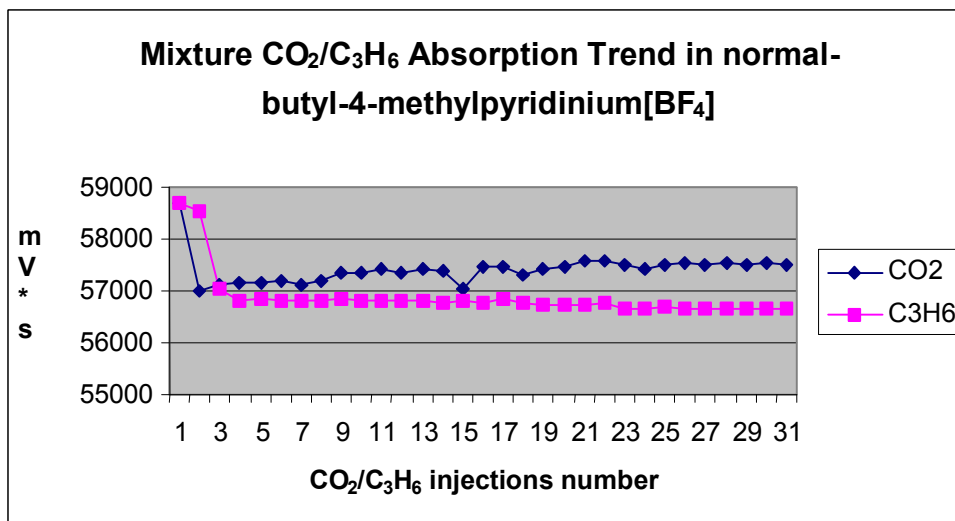


Fig. 26: Absorption trend in nB4MP[BF<sub>4</sub>]; 25°C; 10cc injections; mixture ratio in volume: CO<sub>2</sub> = 50% - C<sub>3</sub>H<sub>6</sub> = 50%.



### 2.5.3 High Pressure Multi Gas Sorption Measuring on Ionic Liquids using the New Standard for Multi Gas Sorption Measuring

The New Standard for Multi Gas Sorption Measuring (see 2.3) was applied for measurements of multigas sorption in Ionic Liquids. A imidazolium based [EMIM][EtSO<sub>4</sub>] ionic liquid was used. This ionic liquid with a melting point of -65°C has a purity of 99.7% and was delivered by Solvent Innovation. Methane and carbon dioxide were delivered by Linde Gas with a purity of 99.995%. Ethane was delivered by Messer Group and has a purity of 99.95%. In first test series of measurements, the sorption behaviour of the pure gases methane, ethane and carbon dioxide in an ionic liquid were measured. Below the sorption isotherms of the three pure gases are illustrated for pressures up to 60 bar.

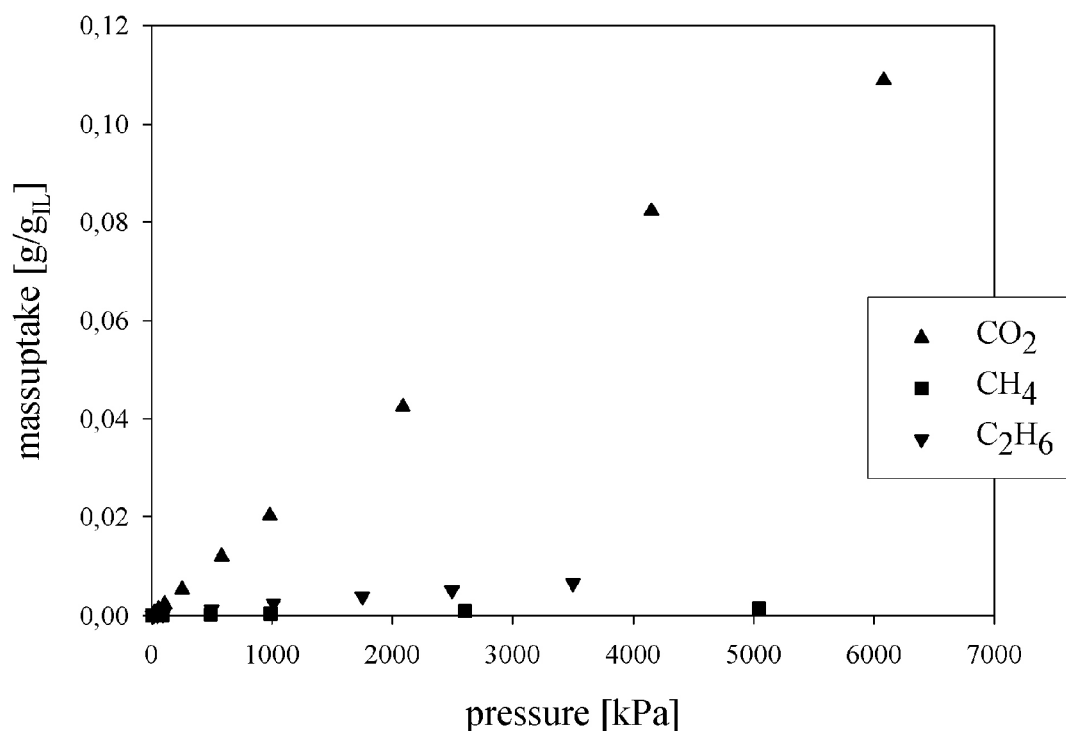


Fig. 27: Mono gas sorption [EMIM][EtSO<sub>4</sub>] (25°C)

The mass uptake of carbon dioxide reaches a maximum of about 0.131 g per gram ionic liquid (6100 kPa). The uptake of methane and ethane are much lower with about 0.0065 g/g (3500 kPa) for ethane and about 0.0029 g/g (1900 kPa) for methane. The selectivity for the uptake of carbon dioxide is increased with the pressure.

Additional to the mono-gas sorption, measurements with binary gas mixtures were performed. The results for the binary mixture of 92 wt.% CH<sub>4</sub> and 8 wt.% CO<sub>2</sub> and for the binary mixture 50 wt.% CO<sub>2</sub> and 50 wt.% C<sub>2</sub>H<sub>6</sub> are presented below. Both diagrams show the selective sorption for each component of the binary mixtures. Additionally the pure gas equilibriums are shown related to the partial pressure of the component in the mixture. This allows a comparison between the selective sorption of the ideal mixture and the actual one which was measured in the real fluid mixture.

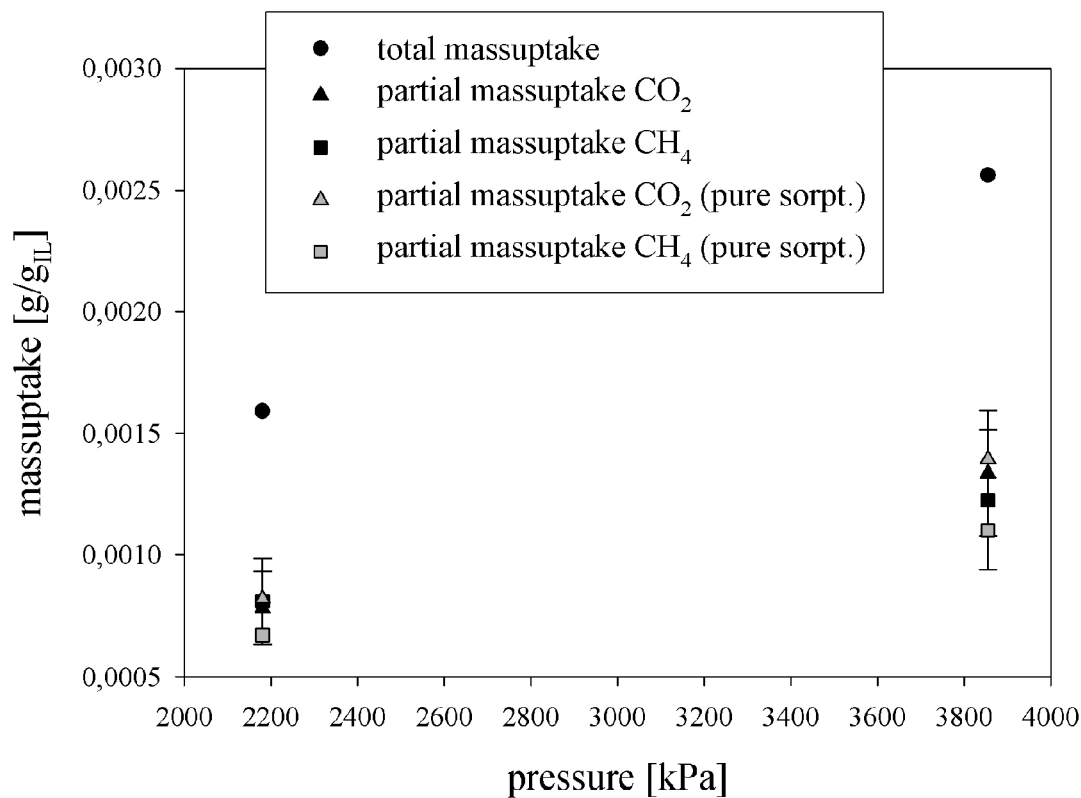


Fig. 28: Binary gas sorption [EMIM][EtSO<sub>4</sub>]-CH<sub>4</sub>-CO<sub>2</sub> (92-8 wt.-%, 25°C)

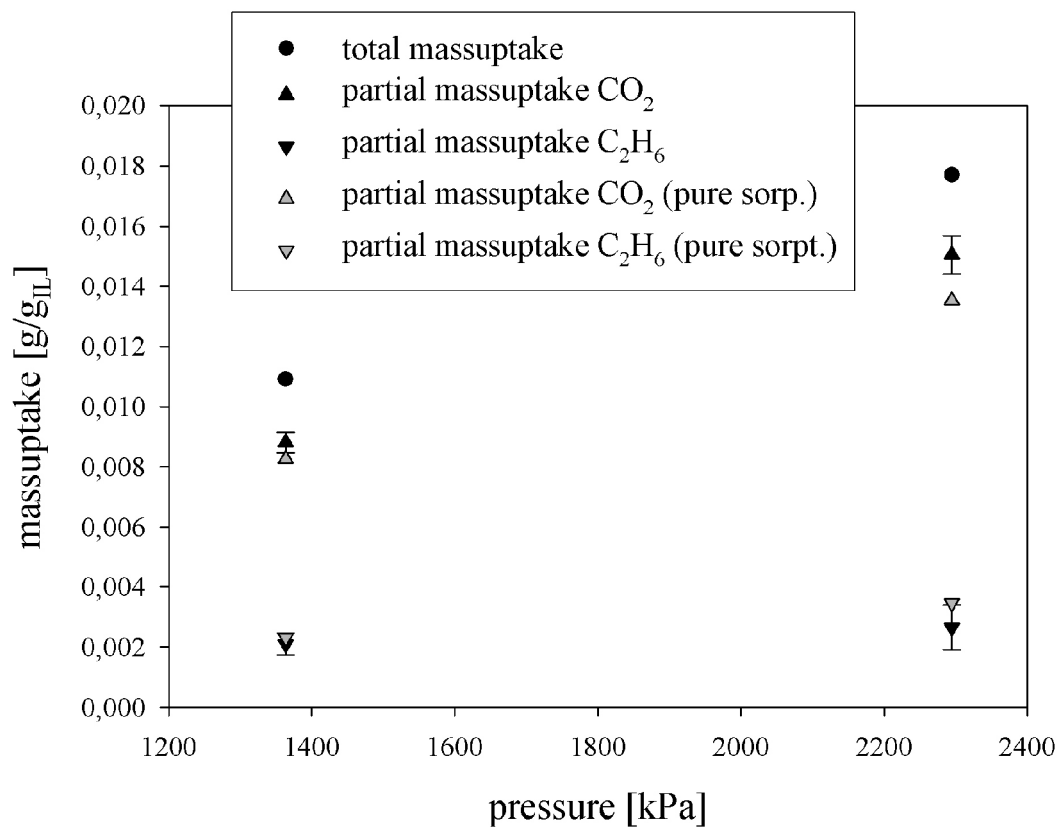


Fig. 29: Binary gas sorption [EMIM][EtSO<sub>4</sub>]-C<sub>2</sub>H<sub>6</sub>-CO<sub>2</sub> (50-50 wt.-%, 25°C)

The mass uptake of ethane fits very well, with the accuracy, with the pure sorption of ethane. In contrary to that the mass uptake for methane and carbon dioxide differ from data of the pure sorption measurements. This effect becomes more significant with increasing pressure. The maximum uptake of carbon dioxide is reduced, compared to the mono-gas sorption, while the uptake of methane is improved.

To get an impression how the three components methane, ethane and carbon dioxide affect the sorption behaviour, the ternary mixture  $\text{CH}_4\text{-C}_2\text{H}_6\text{-CO}_2$  (84-8-8 wt.-%) was investigated at 25°C. The diagram below shows the sorption behaviour of this three component mixture for 2221 kPa and 3936 kPa. Again the pure gas equilibriums are shown related to their partial pressure in the mixture.

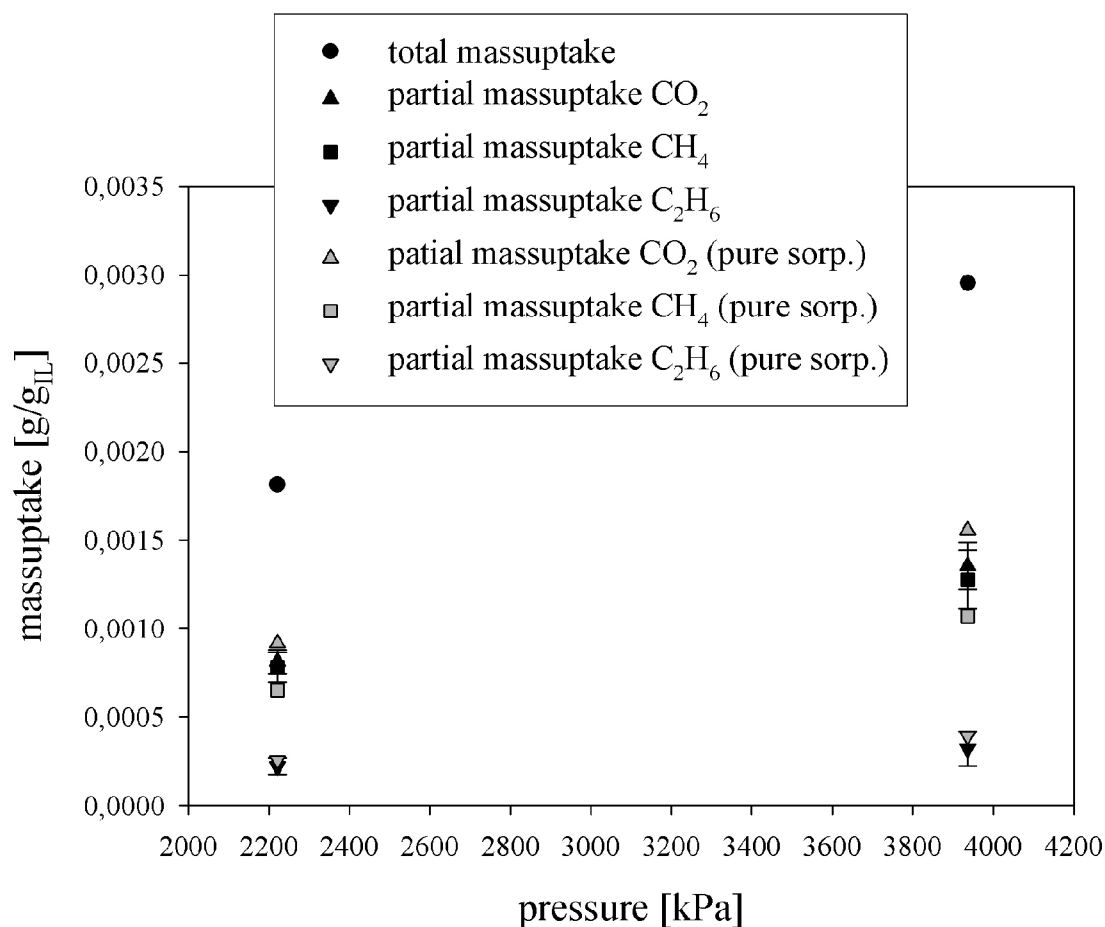


Fig.30: Ternary gas sorption [EMIM][EtSO<sub>4</sub>]- $\text{CH}_4\text{-C}_2\text{H}_6\text{-CO}_2$  (84-8-8 wt.-%, 25°C)

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### 3 S-SCIL Dissemination and use

Planned /actual Dates	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
May 2005	<i>Conference</i> COPS in Salzburg, Austria Characterisation of process solids	<i>Research +Industry</i>	International	400	<i>rubo cosi ubo</i>
November 2005 + 2006	<i>Conference</i> AICHE (USA)	<i>Research +Industry</i>	International	2000	<i>rubo inc ubo</i>
August 2006	<i>Conference</i> 60 Encontro Brasileiro sobre Adsorcao (Brasiel)	<i>Research +Industry</i>	International	300	<i>ubo inc</i>
November 2006	3rd Chinese National Chemical and Biochemical Engineering Annual Meeting Nanning, (People's Republic of China)	<i>Research +Industry</i>	International		<i>rubo ubo</i>
May 2007	Conf. Fundamentals of Adsorption (Italy)	<i>Research +Industry</i>	International	300	<i>rubo ubo</i>
May 2007	<i>Exhibition</i> Achema	<i>Industry + Research</i>	International		<i>rubo cosi stec apo</i>
2007	<i>Publications</i> Journal of super critical Fluids	<i>Industry + Research</i>	International		<i>rubo ubo</i>

Planned /actual Dates	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
2007	<i>Project web-site</i> www.S-SCIL.eu	<i>Industry + Research</i>	International		<i>all</i>
<i>November 2007</i>	<i>Conference</i> AICHE	<i>Industry + Research</i>	International	2000	<i>rubo inc</i>

#### **4 Final plan for using and disseminating the knowledge**

All pre-existing know how of the partners remains in their ownership if it is not already shared with other partners in any way.

All kind of knowledge either pre-existing or new is clearly owned by the respective partner if this knowledge is directly and only dedicated to his own products and technology field. These fields are:

- High pressure gravimetry and high pressure volumetry for Rubotherm.
- Low pressure characterisation by sorption analysis especially using the dynamic analytical carrier gas method for Costech (I and EST).
- Low pressure gas analysis concerning to elemental analysis in particular to combustion, catalysis, gas-chromatography and TCD -or MS- detection for Costech (I and EST)
- High pressure process technology using supercritical fluids for JVS engineering.
- High pressure gas analysis concerning IR and other spectroscopy, in situ thermo physical properties, impedance spectroscopy and continuous and discontinuous high pressure sampling for low pressure instrumental analysis for Rubotherm

Results and knowledge which are generated during the project and to which the part before does not clearly apply will be owned jointly by all SME partners. They can use this knowledge to improve and increase their technique, methods, products, applications, sales, pricing and consulting. A partner who distributes products and methods of another partner can use the jointly owned knowledge to improve his sales work belonging to these products in his distribution area.

The SME partners are not allowed to use any know how pre-existing or new belonging to the S-SCIL consortium to produce products of other partners by their own if this is not directly licensed by the concerning partner. The same applies to the distribution areas of the partners, they have strictly to be respected.

During the project new knowledge and partially also patentable ideas have been generated as the discontinuous high pressure analysis module to measure sorptiv gas concentration in static or quasi static atmospheres, the continuous high pressure analysis module for dynamic flow, the high pressure TCD, the forced flow through technique for liquid samples to be weighed,

and methods for multi gas characterisation of solid sorbents and ionic liquids. Evaluation of patentable ideas has started and probable patent claims will be owned by the main four SME partners together shared according to the individual contribution made by each one. The ownership of those results belonging to the main objectives of S-SCIL will be divided as follows:

**Overview table**

<b>Exploitable Knowledge (description)</b>	<b>Exploitable product(s) or measure(s)</b>	<b>Sector(s) of application</b>	<b>Timetable for commercial use</b>	<b>Patents or other IPR protection</b>	<b>Owner &amp; Other Partner(s) involved</b>
Improved vol./grav. sorption measuring method D.4.1.	Improved Rubotherm standard for vol./grav. measurements in steady atmospheres	sales worldwide by all S-SCIL partners and other distributors	2007	./.	rubo
Improved grav. sorpt. in forced flow through D.4.2.	improved Rubotherm standard for gravimetric measurements in a forced low through		2007	./.	rubo
high pressure sampling (WP3) for low pressure instrumental analysis	high pressure sampler for GC and MS	commercial use as accessory/supplement for high pressure gas analysis sales worldwide by all S-SCIL partners and other distributors	2007	./.	rubo
new thermal conductivity measuring method (WP3)	high pressure TCD	commercial use as a stand alone unit sales worldwide by all S-SCIL partners and other distributors	2008	2008	cosi/cose/ rubo
high pressured IR-analysis	high pressures optical techniques e.g. hp-cell, hp-optical fibres with sealed lead throughs and adjustable optical path length.	commercial use as accessory/supplement for high pressure gas analysis sales worldwide by all S-SCIL partners and other distributors	2008	2008	rubo
high pressure gas analysis by impedance spectroscopy	capacitive and inductive high pressure gas analysis and sorbate analysis	commercial use as accessory/supplement for high pressure gas analysis sales worldwide by all S-SCIL partners and other distributors	2008	2008	rubo/inc
HP concentration measurement using physical properties D 3.2; D 3.3	high pressure gas analysis modules	commercial use as stand alone unit sales worldwide by all S-SCIL partners and other distributors	2009	2008	rubo
Improved dynamic analytical method for ionic liquids (WP6)	Improved sorptometer for mono gas measuring, elemental analyzer for multi gas measuring	sales worldwide by all S-SCIL partners and other distributors	2008	2008	cosi/cose
scientific multigas sorption meas. standard for steady atmosphere D.5.1.	new volumetric/gravimetric sorption meas. standard	<ul style="list-style-type: none"> <li>- scientific use for varius kind of research</li> <li>- implementation as reference standard</li> <li>- sales worldwide</li> <li>- advertising instrument</li> </ul>	2007	./.	rubo
prototypes for mono and multi gas sorption measuring in forced flow throughs and steady atmospheres D.7.2.	Several new Instruments for mono and multi gas measuring in forced flow throughs and steady atmospheres	<ul style="list-style-type: none"> <li>- sales worldwide</li> <li>- use for scientific and industrial process studies</li> </ul>	2007	./.	rubo
new measuring methods for ionic liquids and processes with ionic liquids WP6	new methods for IL processing	<ul style="list-style-type: none"> <li>- new application for instruments</li> <li>- sales worldwide</li> <li>- scientific and industrial research</li> </ul>	2007	2008	rubo cosi/JVS



One of the resulting methods and instruments of this project will become a new international standard for multigas sorption measurement. This standard allows the selective sorption equilibria of solid and liquid sorbents to be determined and substances concerning their selective behaviour in multi gas mixtures to be characterised.

Several experimental mono and multi gas sorption studies which are carried out to verify the success of the project will lead to measuring results which own an extremely high value for scientific and industrial research in sorption processes. These results have been presented to the public during the project at international meetings (WP8) and will be published in scientific and industrial journals. A publication dealing with the new international standard for multi gas sorption measurement and the results gained for ionic liquids I mixtures have been accepted for publication in 2007 in the journal of super critical fluids. For all instrumentation developed by this project Rubotherm, Costech (I) and Costech (EST) will act as a manufacturer and seller. JVS and partially Costech (I) will act as a user of new measuring techniques for process developments and optimisation and in addition as a seller for adapted measuring technology. Apollo and STEC will improve position and sales success in their countries. The manufacturing of instruments will be divided between Rubotherm (D), Costech (I) and Costech (EST).

All pre existing know how and all new results and knowledge are, if not else wise decided by the SMEs, confidential and restricted strictly to members of the consortium. To present the non confidential results to the scientific and industrial public a comprehensive semination program is carried out. ct. Beside this several application seminars are planned to inform more nationally industrial or university researchers. A S-SCIL homepage has been installed dealing with every public results gained by the project. These have also been and will in future additionally be spread by measures like press releases, mailings, seminars, distributors meetings, exhibitions (eg. Achema 2006) and others.