

Gas reaction studies and catalysis research



Customer Contributions:

Catalytic combustion of methane

S. Colussi & A. Trovarelli :: Università di Udine

Regeneration mechanism of Lean NO_x Trap (LNT) catalyst

S. Chansai :: Queen's University Belfast

Glucose production from hydrolysis of cellulose over a novel silica catalyst

H. Wang, C. Zhang, H. He & L. Wang :: Chinese Academy of Sciences

Catalytic CH₄ reforming with CO₂ over activated carbon based catalysts

M. Fan :: University of Wyoming

Using Mass Spectrometry to Understand the Effect of Hydrogen Impurities on the Performance of a PEM Fuel Cell

K. Kortsdottir :: KTH-Royal Institute of Technology

Related Products:

HPR-20 QIC R&D

- for Advanced Research

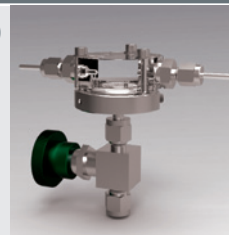
QGA - for Real time Gas & Vapour Analysis

HPR-40 DSA - for Analysis of Gases, Vapours & VOCs in Liquids

In the press:

HIDEN HPR-40

Membrane Inlet Dissolved Gas Monitor



A very big thank you to all who have contributed:



Catalytic combustion of methane: the influence of ceria and other rare earths on PdO stability

The catalytic combustion of methane is a key technology for the production of clean energy and for after-exhaust treatment. Its application in gas turbines (high temperature catalytic combustion – HTCC) leads to ultra-low emissions of CO, NO_x and unburned hydrocarbons, while the use of a catalytic converter in natural gas fuelled vehicles (low temperature catalytic combustion – LTCC) is necessary for the abatement of unburned methane, recognized as a strong greenhouse gas.

Among the different materials that have been tested for the catalytic combustion of methane, supported palladium oxide is known to be the most active. However it suffers from strong deactivation at high temperature due to the decomposition of PdO to metallic Pd. Moreover, Pd re-oxidation takes place at significantly lower temperature thus leading to a wide window of stability of less active Pd metal. This issue is of paramount interest when dealing with HTCC. Several studies have been devoted to find suitable promoters that can stabilize the oxide phase at high temperature; in particular our research has been focused on the screening of rare earth oxides added onto an alumina support as PdO stabilizers. Within this project we have tested the effect of the addition of La, Ce, Pr and Tb on a

Pd-alumina catalyst. The catalytic performance of the different catalysts has been monitored by Temperature Programmed Combustion experiments carried out in a typical lab scale microreactor for powder testing. The effluent gases have been measured qualitatively and quantitatively downstream of the reactor on a Hiden Analytical HPR-20 Mass Spectrometer. The comparison of the curves representing methane conversion and/or CO₂ production has been used for the evaluation of the effectiveness of the different catalyst formulations. On these curves the loss in conversion due to PdO decomposition followed by a recovery due to Pd re-oxidation at lower temperature are clearly distinguishable.



Hiden Analytical HPR-20 Mass Spectrometer in the Lab

Our Reference: AP0136

PROJECT SUMMARY BY:



Sara Colussi &
Alessandro Trovarelli

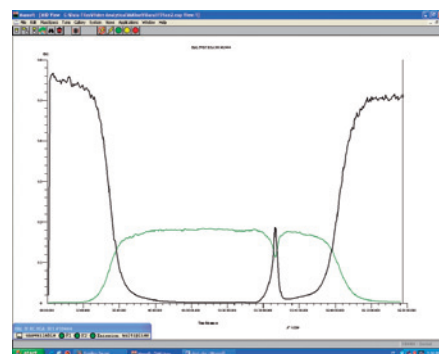
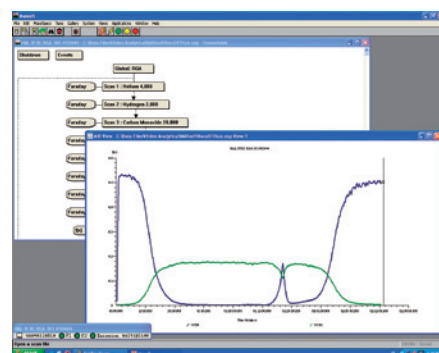
Dipartimento di Chimica, Fisica e
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Cotonificio 108, 33100 UDINE, ITALY

PAPER REFERENCE:

S. Colussi, A. Trovarelli, C. Cristiani, L.
Lietti, G. Groppi (2012) "The influence
of ceria and other rare earth
promoters on palladium-based
methane combustion catalysts"
Catalysis Today **180** (1), 124-130

HIDEN PRODUCT:

HPR-20 QIC Real time Gas Analyser



Regeneration mechanism of Lean NO_x Trap (LNT) catalyst in the presence of NO investigated using isotope labelling techniques

NO_x Storage and Reduction (NSR) or Lean NO_x Trap (LNT) catalysts are considered to be one of the most promising technologies for NO_x removal from lean burn engine exhausts. In the NSR reaction NO_x is stored under lean conditions and then reduced by H₂ or CO or hydrocarbons to N₂ during a short rich period. However, the reaction mechanism is not well-understood especially when using typical reaction conditions.

The current study highlights the effect of using NO in both lean and rich periods during the NSR reaction over a 1.2 wt% Pt/15 wt%Ba/Al₂O₃ catalyst. The transient kinetic switches, using ¹⁴NO during the storage period and isotopically labelled ¹⁵NO during the regeneration, allows us to analyse for nitrogen and ammonia formed from the reduction of stored nitrates. The evolution of gas phase species was monitored by a Hiden Analytical HPR-20 mass spectrometer. Three different routes are proposed for nitrogen formation based on the different masses detected during regeneration, i.e. ¹⁴N₂ (m/e=28), ¹⁴N¹⁵N (m/e=29) and ¹⁵N₂

(m/e=30) may take place. The formation of nitrogen via Route 1 involves the reaction between hydrogen and ¹⁴NO_x to form mainly ¹⁴NH₃. Then, ammonia further reacts with ¹⁴NO_x located downstream to form ¹⁴N₂. In Route 2 it is postulated that the incoming ¹⁵NO reacts with hydrogen to form ¹⁵NH₃ in the reactor zone where the trap has been already regenerated. This isotopically labeled ammonia travels through the catalyst bed until it reaches the regeneration front where it participates in the reduction of stored nitrates (¹⁴NO_x) to form ¹⁴N¹⁵N. The formation of ¹⁵N₂ via Route 3 is believed to occur by the reaction between incoming ¹⁵NO and H₂.

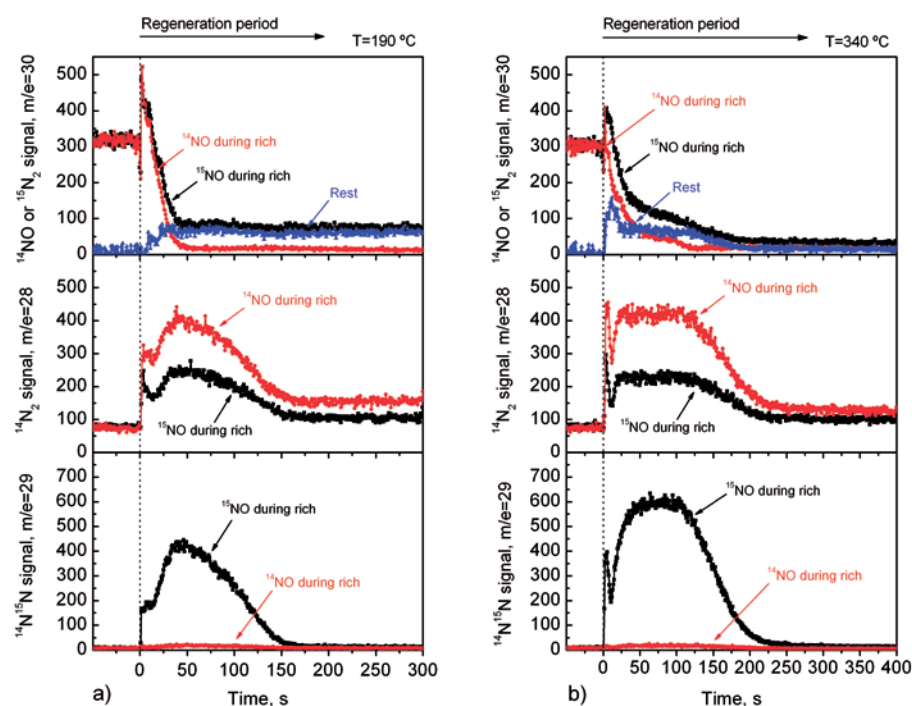


FIGURE 1 Evolution of ¹⁵N₂ or ¹⁴NO (m/e=30), ¹⁴N₂ (m/e=28) and ¹⁵N¹⁴N (m/e=29) during LNT regeneration, in the presence of ¹⁴NO (red points) or ¹⁵NO (black points). (a) 190 °C; (b) 340 °C.

Our Reference: AP0316

PROJECT SUMMARY BY:



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PAPER REFERENCE:

Beñat Pereda-Ayo et al. (2012) "Regeneration mechanism of a Lean NO_x Trap (LNT) catalyst in the presence of NO investigated using isotope labelling techniques" *Journal of Catalysis* **285** (1), 177-186

HIDEN PRODUCT:

HPR-20 QIC TMS Transient MS

Glucose production from hydrolysis of cellulose over a novel silica catalyst under hydrothermal conditions

Catalytic hydrolysis of cellulose over solid acid catalysts is one of efficient pathways for the conversion of biomass into fuels and chemicals. In this study, we synthesized a novel silica catalyst by an evaporation-induced self-assembly method (EISA) and tested its activity for the catalytic selective hydrolysis of cellulose to glucose. This silica catalyst exhibited a higher catalytic activity than other oxides, such as ZrO_2 , TiO_2 , and Al_2O_3 etc., prepared with the same method. The 73.3% cellulose conversion with 50.1% glucose yield was achieved over this novel silica catalyst under hydrothermal conditions without hydrogen gas (Table 1).

Entry	Catalyst	Conversion (%)	Yield (%)						Unknown products
			Cellohexose	Cellopentaose	Cellobetraose	Cellobiose	Glucose	Unknown products	
1	Blank	4.5	1.3	–	–	0.3	0.2	–	2.7
2	ZrO_2^b	15.8	–	–	–	0.1	0.3	9.0	6.4
3	TiO_2^b	15.4	1.9	–	0.8	1.0	2.0	2.2	7.5
4	$Al_2O_3^b$	17.0	5.3	–	1.2	0.1	1.3	0.1	9.0
5	SBA-15	4.0	1.2	–	0.2	0.3	0.5	1.4	0.4
6	HZSM-5 (25)	12.8	–	1.9	1.5	1.1	0.8	1.6	5.9
7	HZSM-5 (38)	12.3	–	1.9	1.4	1.1	0.8	1.8	5.3
8	SiO_2	73.3	1.8	–	1.0	1.8	4.0	50.1	14.6

TABLE 1 Cellulose conversion and yield of products over different catalysts at 433 K for 12 h^a

a. Reaction conditions: 12 hr reaction time, 10 mL H_2O , 0.05 g cellulose, 0.15 g catalyst.

b. The preparation of catalysts were carried out under the identical experimental conditions to that of entry 8.

Temperature-programmed desorption of ammonia (NH_3 -TPD) using a mass spectrometer (HPR-20, Hiden Analytical, Warrington, UK) was used to characterize the acidic properties of the tested samples. The amount of acid sites was estimated by

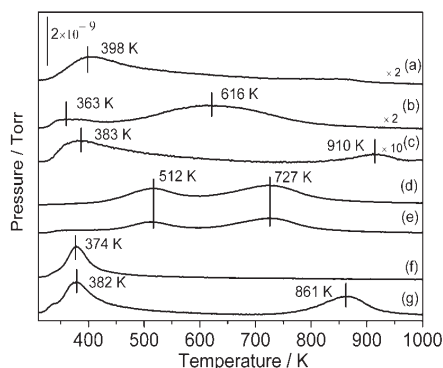


FIG. 1 Temperature-programmed desorption of ammonia (NH_3 -TPD) profiles for various samples of (a) ZrO_2 , (b) TiO_2 , (c) Al_2O_3 , (d) HZSM-5(25), (e) HZSM-5(38), (f) SBA-15, and (g) SiO_2 (EISA).

the conventional acid–base titration method. The results of NH_3 -TPD (Fig. 1) indicated that the acidic properties of the SiO_2 sample were much stronger than those of the other samples. In addition, the SiO_2 sample presented a much higher acid amount than other samples. The textural properties (BET) indicated that the SiO_2 sample has an appropriate average pore diameter (3.512 nm) that could facilitate the transportation of oligosaccharides and thus enhances the chances of oligosaccharides interacting with acid sites. It is concluded that the synergistic effect between the strong acidity and a suitable pore diameter of silica catalyst is one of the reasons for its high activity. In addition, the catalyst was recyclable and showed the excellent stability during the recycle catalytic runs.

Our Reference: AP0357

PROJECT SUMMARY BY:



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PAPER REFERENCE:

Wang H., Zhang C., He H., Wang L. (2012) "Glucose production from hydrolysis of cellulose over a novel silica catalyst under hydrothermal conditions" *Journal of Environmental Sciences* **24** (3), 473-478

HIDEN PRODUCT:

HPR-20 QIC Real time Gas Analyser

Catalytic CH₄ reforming with CO₂ over activated carbon based catalysts

The objective of this study is to compare the performance of several activated carbon (AC) based catalysts for CH₄ reforming with CO₂, including raw AC and AC modified with HNO₃ and NaNO₃, designated as AC-HNO₃ and AC-NaNO₃, respectively. CH₄-CO₂ reforming experiments were conducted in a fixed-bed reactor at temperatures from 700 to 1,000°C. The catalysts were characterized by various techniques, including Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) analysis, CO₂ chemisorption, temperature programmed oxidation-CO₂ (TPO-CO₂), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). The catalytic activities of the three catalysts are considerably different at low temperature, although they are similar at high temperature. At 700°C, the average conversions of CH₄ and CO₂ over AC-NaNO₃ are 17.7% and 29.7%, respectively, which are 2.4 and 3.2 times higher than those over AC. At 1,000°C, the conversions of CH₄ and CO₂ exceed 90% over these three catalysts. In addition, the mole ratio of H₂/CO increases with temperature for all the catalysts. The mole ratio of H₂/CO over AC-HNO₃, which is from 0.76 to 0.94 at different temperatures, is closer to 1 than that over the other two catalysts. Based on the characterization results, NaNO₃ is more instrumental to the formation of mesopores, surface oxygenated groups, and the reduction of deposited carbon. Hydroxyl group plays an important role in CH₄-CO₂ reforming. According to TPO-CO₂ observations, two types of deposited carbon are formed during reforming reaction. The apparent activation energies of the CH₄-CO₂ reforming reactions catalyzed by AC, AC-HNO₃, and AC-NaNO₃ are 202 kJ/mol, 227 kJ/mol, and 123 kJ/mol.

TPO-CO₂ of the used catalyst was done using the same TA along with a mass spectrometer (Hiden, HPR-20 QIC TMS). The used catalyst was heated in 100 ml/min CO₂ from room temperature to 1,200°C at the rate of 5°C/min, while the generation of CO was measured by the online MS. The electron ionization voltage of the MS was 0-220 eV.

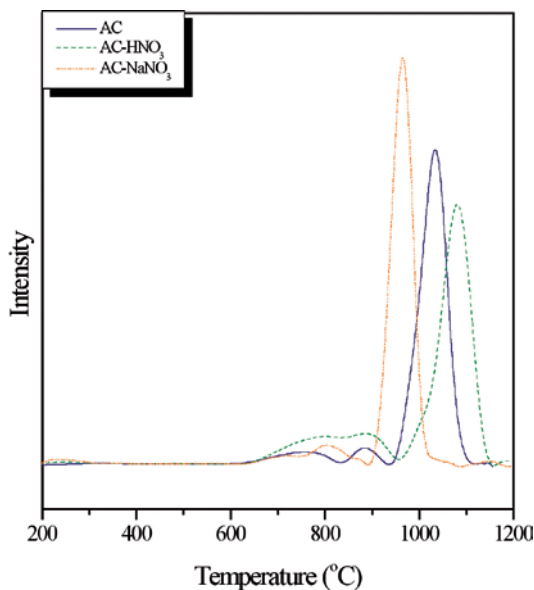


FIGURE 8. TPO-CO₂ profiles of the used catalysts [Catalyst weight: 0.3 g; Inlet flow rate: 20 ml/min; Inlet CH₄:CO₂ mole ratio: 1; Temperature: 900°C; Reaction time: 240 min]

Our Reference: AP0757

PROJECT SUMMARY BY:



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PAPER REFERENCE:

L. Xu et al. (2014) "Catalytic CH₄ reforming with CO₂ over activated carbon based catalysts" *Applied Catalysis A: General* **469**, 387-397

HIDEN PRODUCT:

HPR-20 QIC TMS Transient MS

Using Mass Spectrometry in Combination with Electrochemical Methods to Understand the Effect of Hydrogen Impurities on the Performance of a Polymer Electrolyte Membrane Fuel Cell

The majority of all hydrogen gas produced in the world today is produced from hydrocarbons, by, e.g., reforming of natural gas, fossil fuel or biomass. The result of this process is not pure hydrogen, but rather a gas mixture, referred to as reformat. In addition to hydrogen, the mixture typically contains nitrogen (N_2), carbon dioxide (CO_2), water and carbon monoxide (CO). It can also contain various other impurities, such as H_2S , NH_3 and hydrocarbons. Some of these impurities are highly poisonous to the catalyst of the fuel cell, while others have a moderate effect or are more or less harmless. In order to optimise the purification procedure, knowledge of how and to what extent the presence of different impurities in the hydrogen feed gas affects the performance of the fuel cell is important. Using mass spectrometry combined with electrochemical techniques, such as stripping cyclic voltammetry, electrochemical impedance spectroscopy, potentiostatic and galvanostatic experiments, gives us information on not only on how the cell performance is affected, but an indication of why.

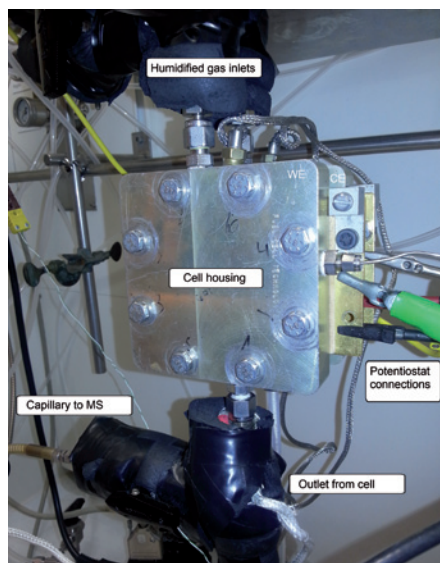


FIGURE 1: Cell Housing

Using ethene as an example, three different CVs are depicted in the top graph of figure 1a); a base CV, recorded in inert gas, a CV recorded in a continuous flow of 100 ppm ethene contaminated argon, and a stripping CV, where the electrode has been exposed to ethene contaminated argon for some time followed by purging the system prior to recording the CV. The origin of the differences between the different CVs can be interpreted with the aid of mass spectrometry. The measurements were made with a Hiden (HPR-20 QIC) Mass

Spectrometer and a PAR 273A potentiostat.

Figure 2a), bottom, shows the $m/z = 44$ signal attributed to CO_2 , which corresponds nicely with the oxidation peaks around 0.6 V (30 s and 145 s in the continuous case) indicating that adspecies originating from ethene are oxidised to CO_2 at potentials > 0.35 V vs RHE. In figure 2b) we can see the signals $m/z = 15$ and 30 appear around the hydrogen

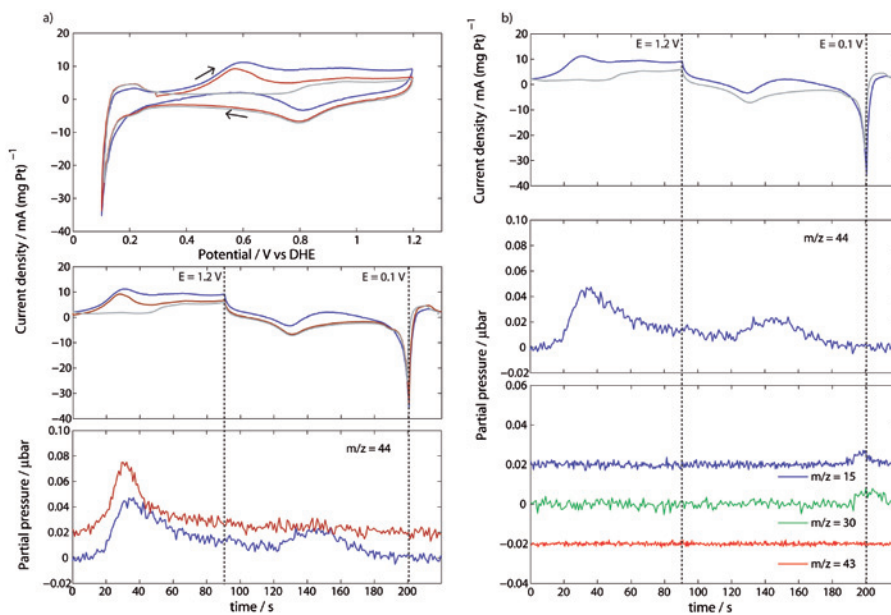


FIGURE 2: Cyclic Voltammograms recorded in a fuel cell at 80°C and 90%RH, at a scan rate of 10 mV s^{-1} and selected m/z signals. Colour codes: CVs recorded in pure argon (grey), 100 ppm ethene/argon (blue), stripping CV (red) after 10 min adsorption of 100ppm ethene at 0.3 V and. All three signals in b) bottom are recorded in 100 ppm ethene/argon.

Our Reference: AP0443

PROJECT SUMMARY BY:



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PAPER REFERENCE:

K. Kortsdottir, R. W. Lindström, G. Lindbergh (2013) "The influence of ethene impurities in the gas feed of a PEM fuel cell" *International Journal of Hydrogen Energy* **38** (1), 497-509

HIDDEN PRODUCT:

HPR-20 QIC Real time Gas Analyser

evolution peak, indicating the formation of methane and ethane at these low potentials.

The presence of hydrogen, either in gas phase or adsorbed on the surface in the ethene contaminated gas was found reduce the amount of adspecies formed on the catalyst surface. Therefore, traces of ethene in the hydrogen feed were found to have a minimal effect on the performance of PEM fuel cell.

Related Products:

HPR-20 QIC R&D - for Advanced Research

Real time gas analyser for multiple species gas and vapour analysis. Compact bench top analysis system for production and research applications:

- ▶ Process Monitoring
- ▶ In-Situ Analysis
- ▶ Catalysis Studies/Reaction Kinetics
- ▶ Environmental Gas Analysis
- ▶ CVD / MOCVD / ALCVD
- ▶ Contamination Studies
- ▶ Thermal Analysis Mass Spectrometry



QGA – for Real time Gas & Vapour Analysis

A compact bench top analysis system for real time gas and vapour analysis:

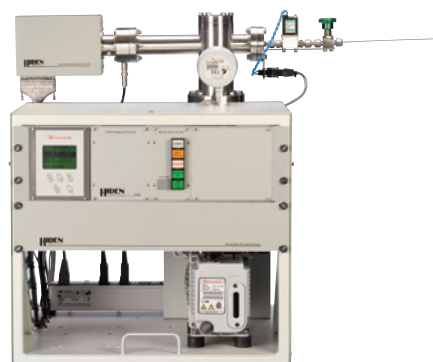
- ▶ Gas Reaction Studies
- ▶ Fuel Cell Reaction Studies
- ▶ Contamination Studies
- ▶ Fermentation Analysis
- ▶ Environmental Gas Analysis
- ▶ Thermal Analysis Mass Spectrometry
- ▶ Catalysis Studies/Reaction Kinetics



HPR-40 DSA – for Analysis of Gases, Vapours & VOCs in Liquids

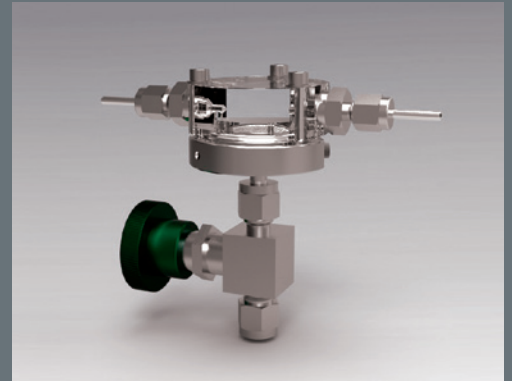
A compact bench-top gas analysis system for real-time quantitative analysis and monitoring of dissolved/evolved gases in solution and other diverse environments:

- ▶ Dissolved Species Analysis
- ▶ Fermentation Process Analysis
- ▶ Environmental Monitoring
- ▶ Soil Core Analysis
- ▶ Groundwater Contamination Studies
- ▶ Water Analysis in Estuary, River or Reservoir
- ▶ Methane Production Control
- ▶ Microbiological/Enzyme Activity Studies



OUR REFERENCE: HAPR0098

Hiden HPR-40 Membrane Inlet Dissolved Gas Monitor



The Hiden MIMS Membrane Inlet Mass Spectrometer series now feature an extended range of submersible insertion probes and flow-through cuvette-style interfaces specifically engineered for measurement of dissolved gases and vapours in aqueous solution. All incorporate a semi-permeable membrane interface selected for operation in diverse environments with optimum transition rate for the gaseous species of interest.

The systems provide real-time analysis of biological and physical processes within aquatic and marine processes, with interfaces refined for specific applications including bio-fuel development, soil analysis, water quality determination, fermentation culture monitoring and photo-responsive processes.

The compact mass spectrometer module is bench-top and cart-mounting compatible, with comprehensive control and data analysis programs for both automated and manual operation. Multiple sampling lines can be accommodated for automated sequential multi-media sampling, the QIC BioStream variant currently operating with up to 80 sample streams. A custom-design service is available to assist with interface design for specific R&D projects.

For further information on these or any other Hiden Analytical products please contact Hiden Analytical at info@hiden.co.uk or visit the main website at www.HidenAnalytical.com

If you would like to submit a project summary for consideration in our next Newsletter, please email a brief summary (approx. 500 words) and corresponding images to marketing@hiden.co.uk

Hidden **APPLICATIONS**

Hidden's quadrupole mass spectrometer systems address a broad application range in:

GAS ANALYSIS

- ▶ dynamic measurement of reaction gas streams
- ▶ catalysis and thermal analysis
- ▶ molecular beam studies
- ▶ dissolved species probes
- ▶ fermentation, environmental and ecological studies



SURFACE ANALYSIS

- ▶ UHV TPD
- ▶ SIMS
- ▶ end point detection in ion beam etch
- ▶ elemental imaging - surface mapping

HIDDEN

ANALYTICAL

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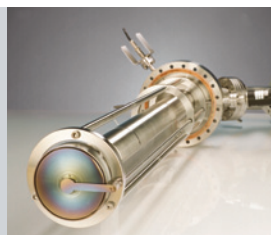
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PLASMA DIAGNOSTICS

- ▶ plasma source characterisation
- ▶ etch and deposition process reaction kinetic studies
- ▶ analysis of neutral and radical species



VACUUM ANALYSIS

- ▶ partial pressure measurement and control of process gases
- ▶ reactive sputter process control
- ▶ vacuum diagnostics
- ▶ vacuum coating process monitoring

