

Gas Reaction Studies & Catalysis Research



Customer Contributions:

SSITKA study of complete methane oxidation on palladium and platinum catalysts

Marek Rotko and Andrzej Machocki :: University of Maria Curie-Skłodowska

Multifunctionality of silver closo-boranes

Bo Richter & Torben R. Jensen :: Aarhus University

An experimental assessment of the ammonia temperature programmed desorption method for probing the surface acidic properties of heterogeneous catalysts

Roberto Di Chio :: University of Messina

Dehydrogenation mechanism of LiBH_4 by Poly(methyl methacrylate)

Jianmei Huang, Liuzhang Ouyang & Min Zhu :: South China University of Technology

Related Products:

HPR-20 R&D - for Advanced Research

HPR-20 EGA - for Evolved Gas Analysis

QGA - for Real-time Gas & Vapour Analysis

A very big thank you to all
who have contributed:



SSITKA study of complete methane oxidation on palladium and platinum catalysts

The catalytic process of complete methane oxidation is a highly promising alternative to flame combustion, because it makes it possible to reduce the emission of NO_x , CO and non-oxidized hydrocarbons into the Earth's atmosphere. Some of the most active catalytic materials for complete methane oxidation are supported palladium and platinum catalysts. They demonstrate very high activity and selectivity; also, their resistance to high temperature and mechanical damage is acceptable. However, for the wide application of palladium and platinum catalysts in the industry, there is still a need for clear answers to many important questions. One of the most crucial issues is the reaction mechanism of complete methane oxidation over palladium and platinum catalysts. We studied this problem by means of the SSITKA method (Steady State Isotopic Transient Kinetic Analysis).

The SSITKA method enables obtaining much unique and valuable information concerning mechanisms of various heterogeneous catalytic reactions, as well other equally important issues such as: the number of active centres on the catalyst surface, an average surface life-time and surface concentrations of reagents, intermediates and products of the catalytic reaction. However, the SSITKA study needs very high-quality and precise equipment, in particular, a system of dosing and fast switching of reagent streams as well as a mass spectrometer, which makes it possible to investigate even extremely low changes in the concentration of isotopes. In our experiments, the switches between reaction streams including $^{12}\text{CH}_4/\text{Ar}/\text{O}_2/\text{He}$ and $^{13}\text{CH}_4/\text{Kr}/\text{O}_2/\text{He}$ as well as between $^{16}\text{O}_2/\text{Ar}/\text{CH}_4/\text{He}$ and $^{18}\text{O}_2/\text{Kr}/\text{CH}_4/\text{He}$ were carried out. The examples of results for the Pd-Pt/ Al_2O_3 catalyst are included in Fig. 1.

On the basis of such results and after a comprehensive analysis (widely described in the reference paper), it has been proposed that two different kinds of active centres (α – more active, but less numerous and β – less active, but more numerous) exist on the catalyst surface and the process of methane oxidation proceeds simultaneously according to two different reaction mechanisms (by Mars-van Krevelen and Langmuir-Hinshelwood). The level of their participation in methane oxidation is different and depends on the reaction temperature. What is more, the process of methane oxidation proceeds not only simultaneously, according to two different reaction mechanisms, but also with different reaction rates determined by the type of active centres.

Our Reference: AP0898

PROJECT SUMMARY BY:

Marek Rotko and Andrzej Machocki

University of Maria Curie-Skłodowska
Faculty of Chemistry
Department of Chemical Technology
3 Maria Curie-Skłodowska Square
20-031 Lublin
Poland



UMCS
MARIA CURIE-SKŁODOWSKA UNIVERSITY
PL LUBLIN

PAPER REFERENCE:

M. Rotko, A. Machocki, G. Słowik (2014)
"The mechanism of the CH_4/O_2 reaction on the Pd-Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst: A SSITKA study" *Applied Catalysis B: Environmental*, 160-161 298-306

HIDDEN PRODUCT:

HPR-20 R&D

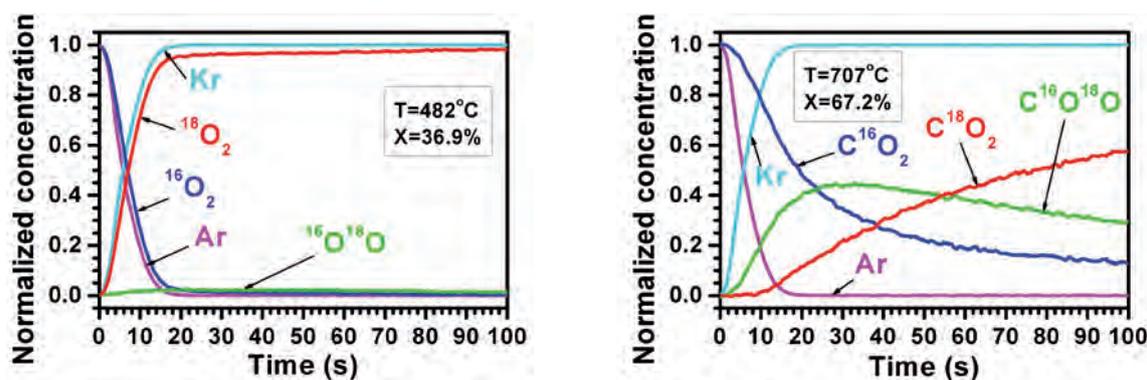


FIGURE 1: Effect of the switching between reaction streams including $^{16}\text{O}_2/\text{Ar}/\text{CH}_4/\text{He}$ and $^{18}\text{O}_2/\text{Kr}/\text{CH}_4/\text{He}$ (X is the conversion of methane).

Multifunctionality of silver closo-boranes

As a successor of research based on metal borohydrides, higher boranes are being investigated. $\text{Ag}_2\text{B}_{12}\text{H}_{12}$ and $\text{Ag}_2\text{B}_{10}\text{H}_{10}$ are synthesized and found to possess very high ion conductivities, as well as being semiconducting. In the course of decades, research on borane materials has broadened to embrace many different properties other than hydrogen storage properties. This is an example of unravelling such useful properties, serving as a basis for further property studies of related materials.

$\text{Ag}_2\text{B}_{12}\text{H}_{12}$ reduces to metallic silver, by exposure to an electron beam (TEM), and as such caught attention for further work. Silver boranes are also complexed with AgI in order to access high ion conductivities at room temperature. Synthesis is straight forward, and is achieved in water as a solvent, yielding the desired materials. It is crucial to ensure that residual water is fully removed, to perform reliable quantification of semi-conducting and ion conducting properties. For this purpose, mass spectrometry was employed, analyzing the release of any residual gases, providing assurance of completely dry and water free samples. The gas spectrum was also analyzed to determine the thermal stability of the silver boranes and understand their decomposition mechanism.

The **Hidden Analytical HPR-20** quadrupole mass spectrometer was utilized and allowed for unambiguous determination of the water content, as well as ensuring that no undesired impurities are present. At the

University of Aarhus, Department of Chemistry and iNANO center, daily investigations of e.g. borane materials are aided by analysis of residual gases released from materials studied as either classical hydrogen storage materials, or as demonstrated here, for other purposes. The information gained is valuable in evaluating synthesis methods, evaluating the purity of materials, and for studies of behavior upon thermal decomposition of materials.

Hydrogen evolution as the silver boranes decompose, is evident from the data presented in the DSC/MS figures. Both compounds decompose above 250°C, releasing an appreciable quantity of hydrogen. Heating to high temperatures for ion conductivity studies it is obvious that no decomposition or release of any gaseous species is observed. Thus, the information from the mass spectroscopy data assures that the samples are pure and that the derived properties are quantified accordingly.

Our Reference: AP-HPR-20-0006

PROJECT SUMMARY BY:

Bo Richter and Torben R. Jensen

Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Center for Materials Crystallography (CMC), Aarhus University, Denmark.

www.chem.au.dk / www.inano.au.dk



PAPER REFERENCE:

"Multifunctionality of silver closo-boranes" *Nature Communications* **8**, Article number: 15136 (2017). doi:10.1038/ncomms15136

HIDEN PRODUCT:

HPR-20 EGA

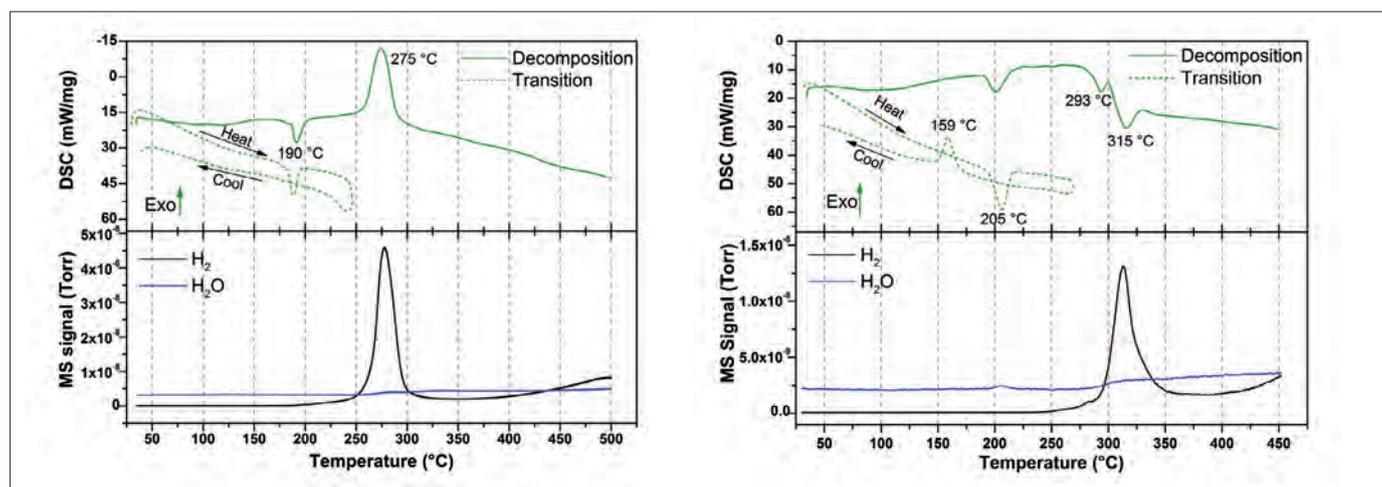


FIGURE 1: Differential scanning calorimetry (DSC) and mass spectroscopy (MS) data of $\text{Ag}_2\text{B}_{10}\text{H}_{10}$ (left) and $\text{Ag}_2\text{B}_{12}\text{H}_{12}$ (right). Two DSC measurements are shown for each material, one illustrating decomposition (solid line) and another showing the polymorphic phase transformation (dashed line). The MS trace is shown in the bottom part of the graphs.

An experimental assessment of the ammonia temperature programmed desorption method for probing the surface acidic properties of heterogeneous catalysts

The aim of this work was to study the surface acidic properties of oxide catalysts and carriers ($\gamma\text{-Al}_2\text{O}_3$, CeO_2 , ZrO_2 , SiO_2 , TiO_2 , HZSM5 zeolite), comparatively probing their surfaces by ammonia temperature programmed desorption (ATPD) measurements. ATPD is a simple and reliable technique in which a surface, after saturation with ammonia at low temperature, is subject to a temperature ramp, which causes desorption of the probe molecule along with a temperature profile. By qualitatively and/or quantitatively analyzing the desorption pattern, it is possible to obtain information about the adsorption/desorption energy and the quantity of ammonia that has been adsorbed on the surface (ammonia uptake). Since ammonia is a basic molecule, it can be used as a probe to investigate surface acidity. This information can help understand the catalytic behavior of a sample, or even help in fine tuning the synthesis of new systems. Instead of using a traditional TCD Detector for this task, we employed a Quadrupole Mass Spectrometer (Hiden **HPR-20**) connected through a heated capillary to our testing apparatus.

The use of a QMS allowed us to easily discriminate between the different species desorbing from our surfaces, without the use of any kind of chemical or physical filter and traps which could negatively affect our analyses. By properly tuning the ionization potential of our instrument, we were also able to avoid water molecule fragmentation and related interference with the ammonia m/z signal. The reliability and accuracy of the ATPD data were assessed by theoretical criteria and experimental tests highlighting

the effects of carrier gas, data acquisition mode, catalyst particle size and reactor geometry, remarking the flexibility of the technique employed. All of the studied materials featured complex ATPD patterns spanned in the range 423-873K, except for ceria which showed a narrow and resolved desorption peak, indicative of homogeneous weak acidity. Quantitative data signalled a difference of more than one order of magnitude in ammonia uptake between silica and the other materials.



FIGURE 1: The Hiden HPR-20 in the Lab used for characterisation and testing of catalytic samples.

Our Reference: **AP1036**

PROJECT SUMMARY BY:

Roberto Di Chio

Dipartimento di Ingegneria,
Università degli Studi di Messina,
Contrada Di Dio, Sant'Agata,
I-98166 Messina, Italy



PAPER REFERENCE:

Francesco Arena, Roberto Di Chio,
Giuseppe Trunfio (2015) "An
experimental assessment of the
ammonia temperature programmed
desorption method for probing the
surface acidic properties of
heterogeneous catalysts" *Applied
Catalysis A: General* **503**, 227-236

HIDEN PRODUCT:

HPR-20 EGA

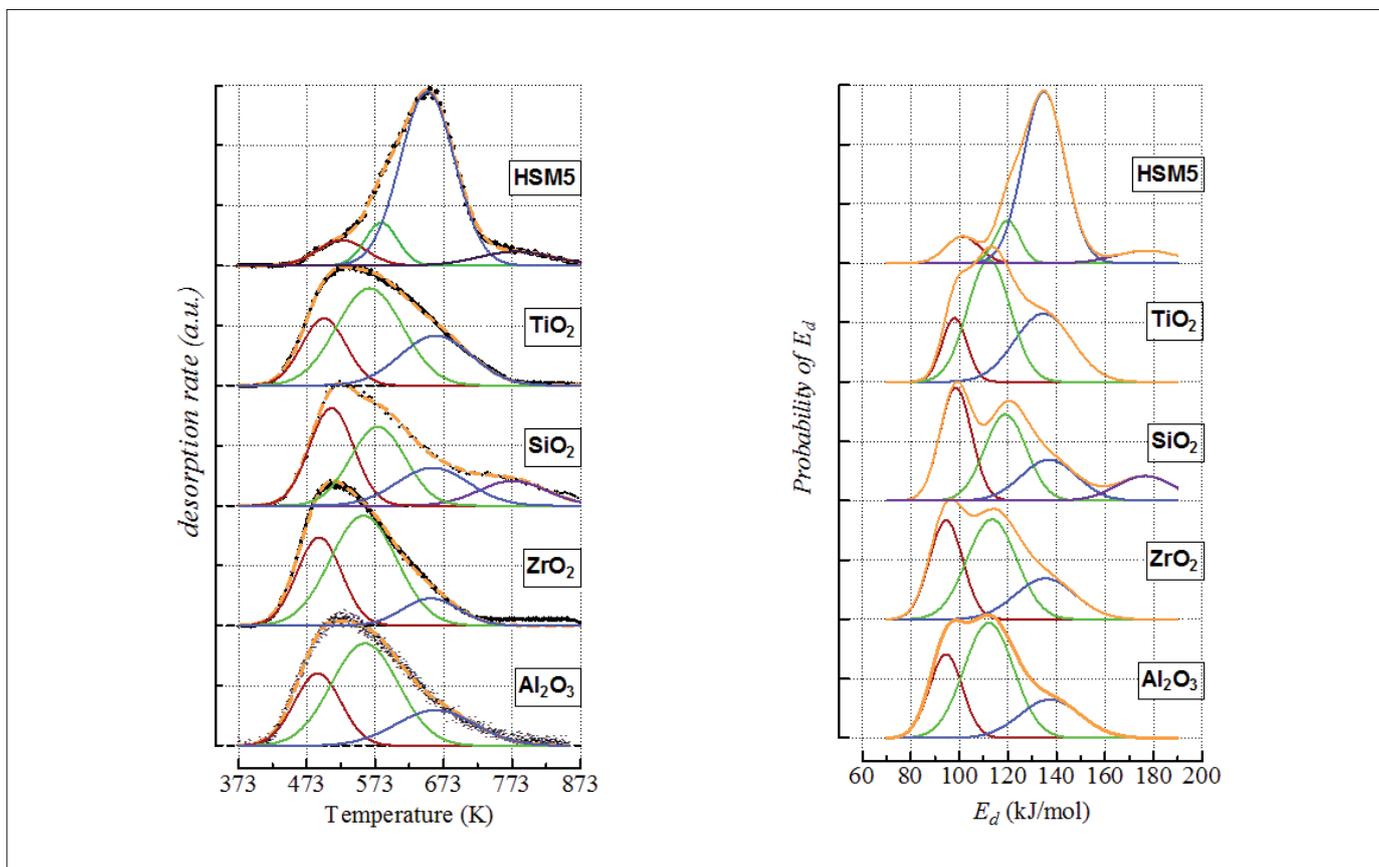


FIGURE 2: (Left) Deconvolution of ATPD profiles by Gaussian functions (dotted yellow lines depict the generated profiles, while black points are the experimental data); (Right) Energy distribution functions of ammonia desorption from the various site populations.

Since the ATPD profiles of ceria match Gaussian curves regardless of heating rate and surface coverage, the patterns of the studied materials are described as linear combinations of four Gaussian functions related to *weak, medium, strong* and *very strong* site populations. After collecting all the profiles, we were able to apply ATPD modelling analyses to get information about the energy of adsorption of the probe molecule related to each desorbing temperature. The cumulative energy site distributions indicated the following acidity scale based on the average energy (expressed in kJ/mol) value (e.g., surface coverage $\theta=0.5$)

CeO_2 (100) < $\gamma\text{-Al}_2\text{O}_3$ (111) \approx ZrO_2 (111) \approx TiO_2 (117) \approx SiO_2 (118) < HZSM5 (135)

In order to acquire additional information on the functionality of the studied materials, we performed dehydration of isopropanol to propylene as a probe reaction. The results obtained matched the ones previously uncovered by ATPD measurements in terms of abundance and strength of surface acid sites, but also let us distinguish between Brønsted and Lewis acidic sites.

Dehydrogenation mechanism of LiBH₄ by Poly(methyl methacrylate)

Hydrogen is considered as a promising alternative energy carrier owing to its high-energy density, abundance, light weight and pollution-free burning [1]. Developing a safe and efficient hydrogen storage material is one of the key challenges for the mobile application of hydrogen [2]. Due to the high gravimetric (18.5 wt.%) and volumetric (121 kg H₂/m³) hydrogen density, lithium borohydride (LiBH₄) has been acknowledged as a potential candidate for hydrogen storage materials [3]. However, due to the unfavorable high thermal stability (e.g. decomposition peak temperature of ~ 470°C), the practical utilization of LiBH₄ as hydrogen storage medium is hampered [4]. Hence, several approaches including reactant destabilization, catalyst/additive introduction, nanostructuring, and anion/cation substitution have been applied to decrease the dehydrogenation temperature and accelerate the kinetics [5].

Nanoengineering had been demonstrated to be a useful method to reduce the dehydrating/rehydrating temperature of LiBH₄ by decreasing diffusion path lengths and increasing surface areas [6]. However, nanoscale LiBH₄ is too reactive and very sensitive to the water and oxygen in the air, which impede its practical utilization. PMMA (Poly (methyl methacrylate)), with a high permeability ratio of H₂/O₂, was reported to have good gas selectivity [7]. Therefore, in this project, PMMA was applied to protect LiBH₄ from oxygen and water but let the

hydrogen get in or out freely (Scheme 1). Furthermore, the nanoconfinement of LiBH₄ in the fine network pore of PMMA and the interaction between the B atom in LiBH₄ and the O atom in C=O of PMMA resulted in a much lower hydrogen release temperature of LiBH₄. LiBH₄ PMMA composite started to dehydrogenate at 53°C and released 5.2 wt.% of hydrogen at 162°C within 1 h. This project provides a general strategy to utilize a gas-selective polymer to protect air-sensitive hydrogen storage compounds and improve their hydrogen storage properties.

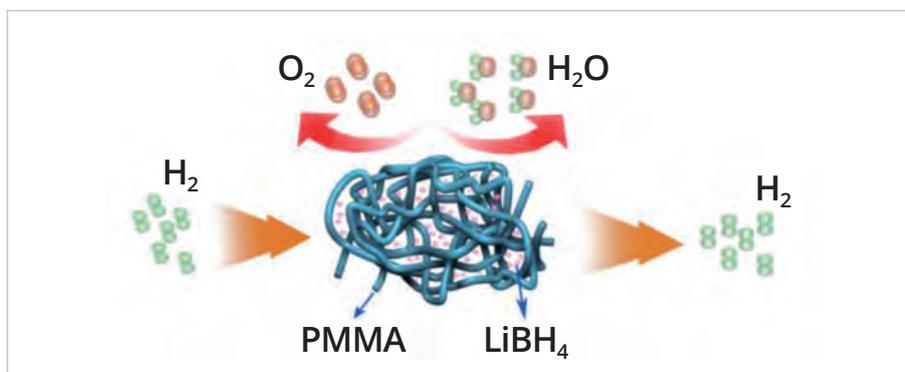


FIGURE 1: Schematic illustration of LiBH₄ protected from oxygen and water by PMMA.

REFERENCES:

- [1] Jain, I. P. *Int J Hydrogen Energ* 2009, **34**, (17), 7368-7378.
- [2] Schlapbach, L.; Züttel, A. *Nature* 2001, **414**, (6861), 353-358.
- [3] Züttel, A.; Wenger, P.; Rentsch, S.; Sudan, P.; Mauron, P.; Emmenegger, C. *J Power Sources* 2003, **118**, (1-2), 1-7.
- [4] Saldan, I. *Cent Eur J Chem* 2011, **9**, (5), 761-775.
- [5] Li, H.-W.; Yan, Y.; Orimo, S.-i.; Züttel, A.; Jensen, C. M. *Energies* 2011, **4**, (1), 185-214.
- [6] Fang, Z. Z.; Wang, P.; Rufford, T. E.; Kang, X. D.; Lu, G. Q.; Cheng, H. M. *Acta Mater* 2008, **56**, (20), 6257-6263.
- [7] K. J. Jeon, H. R. Moon, A. M. Ruminski, B. Jiang, C. Kisielowski, R. Bardhan and J. J. Urban, *Nat. Mater.*, 2011, **10**, 286.

Our Reference: AP1148

PROJECT SUMMARY BY:

Jianmei Huang, Liuzhang Ouyang,
Min Zhu

School of Materials Science and
Engineering,
Key Laboratory of Advanced Energy
Storage Materials of Guangdong
Province,
South China University of Technology,
Guangzhou 510641
People's Republic of China



PAPER REFERENCE:

Jianmei Huang *et al.* (2015)
"Dehydrogenation mechanism of LiBH₄
by Poly(methyl methacrylate)" *Journal of
Alloys and Compounds* **645** (1), S100-S102

HIDEN PRODUCT:

QGA

HPR-20 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



HPR-20 EGA – for Evolved Gas Analysis in TGA-MS

A compact benchtop gas analysis system for evolved gas analysis in thermogravimetric mass spectrometry, TGA-MS:

- ▶ Thermal Analysis Mass Spectrometry
- ▶ Catalysis
- ▶ Fuel Cells
- ▶ CVD / MOCVD / ALCVD
- ▶ Environmental Monitoring



QGA – for Real-time Gas & Vapour Analysis

A compact benchtop analysis system for real time gas and vapour analysis:

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



HiddenAPPLICATIONS

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 – 3D mapping



HIDDEN

ANALYTICAL

Hidden Analytical Ltd.
420 Europa Boulevard
Warrington WA5 7UN England

T +44 [0] 1925 445 225

F +44 [0] 1925 416 518

E info@hidden.co.uk

W www.HiddenAnalytical.com



Sales Offices:

We have sales offices situated around the globe. **Visit our website for further information.**



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

