HIDEN ANALYTICAL

Dissolved Species Analysis Applications

INTRODUCTION
Dissolved Species Analysis Application

MIMS APPLICATIONS

Membrane Inlet Mass Spectrometry (MIMS) is an analytical technique used for direct sampling of dissolved gases in liquids and volatile compounds from bulk samples via a semipermeable membrane material. This technique enables real-time analysis of multiple gas and vapour species with dynamic range from sub-ppb to 100% and requires little to no sample preparation or pre-treatment.

Hiden offers MIMS capabilities in the form of a benchtop HPR-40 DSA system for laboratory-based research and the portable case mounted *p*QA for applications that favour in-situ measurements in the field. Both of these systems are supplied with a choice of membrane material and user-changeable sample inlets to provide application specific enhancements for a variety of common applications.

INLET OPTIONS

Direct Membrane Inlet Probe.
The probe inlet is a membrane inlet that can be submerged in any liquid or slurry sample. It is used for a wide range of applications.

Large Circular Membrane Cell.
Dissolved species flow-through membrane cell with optional integrated thermocouple. Includes liquid flow connections, ideal for circulation applications and rare earth gases.

Enzyme Kinetics Probe.
The Enzyme Kinetics Probe was specifically developed to be submerged in enzyme containing samples. All wetted parts are made of glass to avoid sample contamination and side reactions.

Cuvette.
The Cuvette Cell is designed to allow temperature and illumination control of a liquid sample - e.g. for algae studies.

Flow-Through Dissolved Species Probe.
The Flow-Through Probe is directly mounted on the MS with two ports to allow flow from an external reservoir. It is used for a wide range of dynamic applications.

Denitrification Probe.
Flow-through probe with a low flow design for denitrification studies.

Micro-flow Inlet.
Flexible capillary inlet for OEMS, on-line electrochemical MS, evolved gas analysis, where evolved gas flow is extremely limited.

Contents

Oceanic Trace Gas Measurements

PPT LEVEL DETECTION OF VOLATILES IN WATER

The Hiden HPR-40 DSA is proven to be a versatile, effective product for the analysis of dissolved species, it is unsurpassed for extremely low-level detection of trace gases, for example Dimethylsulphide (CH_3SCH_3), known as DMS. This is a naturally produced trace substance, evolved from certain marine micro-organisms, such as plankton. Detection of fluctuations in the DMS concentration in seawater therefore gives crucial information about the abundance of these life forms, which are widely believed to be important in global climate regulation.

Successive dilution was used to reduce the concentration of DMS in the sample. The strongest peak at 62 amu was used for the measurements and correlating this DMS peak signal intensity with the DMS concentration level provides quantitative information on the DMS detection levels. As can be seen in **Figure 1**, the linear relationship gives a high degree of confidence regarding the detection levels. Further experiments could extend this detection level down to lower partial pressures. The detection limit of the spectrometer is 5 x 10^{-15} Torr.

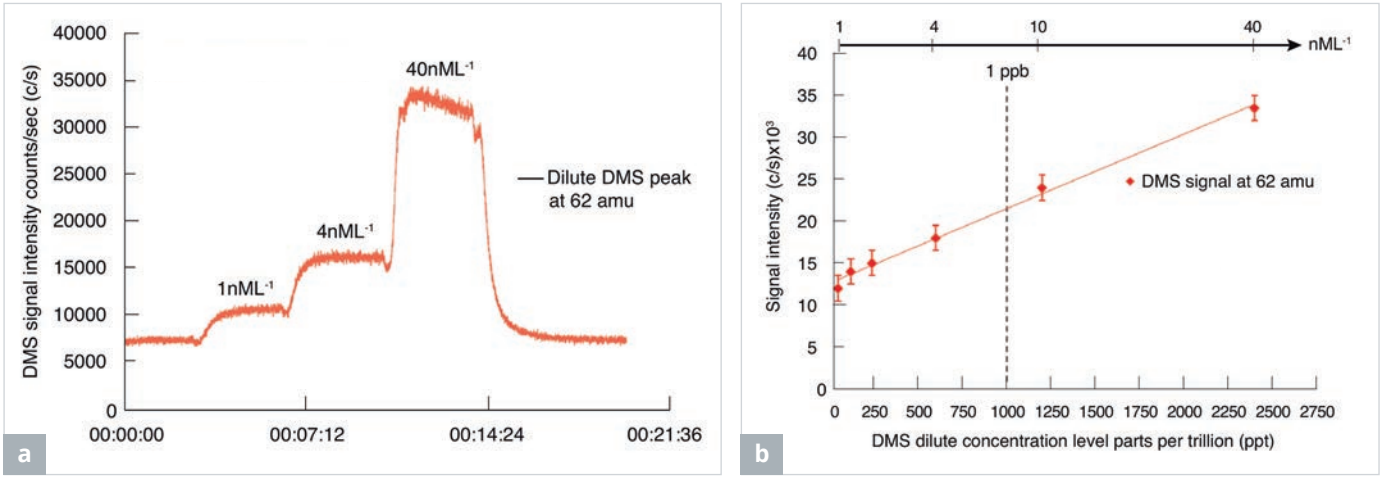
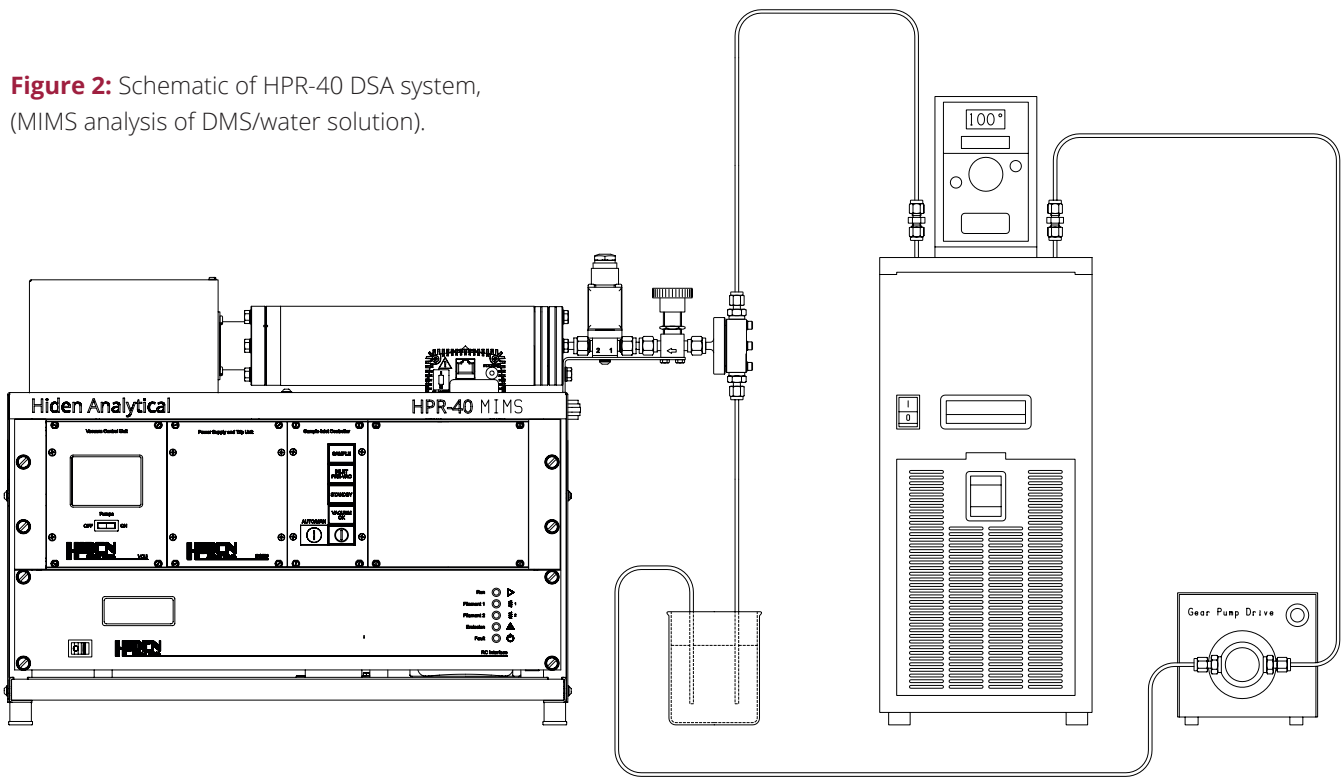


Figure 1 (a & b): Mass scan of dilute concentration levels of DMS and the concentration levels (ppt) derived from DMS partial pressure at 62 amu.

PROCEDURE

Current research in this area has been performed using a Hiden HPR-40 DSA (HAL101/3F, SEM detector) system. **Figure 2** shows a schematic of the setup. In the schematic, the DMS aqueous solution is circulated around the system to allow continuous monitoring of the DMS concentrations over time. This data was obtained after first preparing the dilutions of the DMS solution to produce the desired DMS concentrations relative to water. To maintain consistency with seawater conditions, the samples are kept at 10°C using a chiller system, then pumped across the membrane inlet pre-configured reduce the possibility of air bubble contamination.

Figure 2: Schematic of HPR-40 DSA system, (MIMS analysis of DMS/water solution).



Denitrification Studies

REAL-TIME ANALYSIS OF BACTERIAL RESPIRATION IN ANOXIC ENVIRONMENTS

Denitrification is a process carried out by numerous genera of bacteria and in anoxic environments, where the concentration of dissolved and freely available oxygen is depleted, can be used as an alternative to aerobic respiration. Where nutrients are limited, bacteria enter a state of stress and begin to use nitrate (NO_3^-) or nitrite (NO_2^-) as a terminal electron acceptor in place of oxygen, producing nitrogen, nitric oxide and nitrous oxide gases. Both of the latter gases are ozone-depleting substances and greenhouse gases that can have a considerable influence on global warming. Better understanding how the process conditions affect the rate of denitrification could lead to improved wastewater treatment methods and reduce the leaking of harmful gases into the atmosphere.

MIMS is an ideal method for simultaneously monitoring the consumption and production of gases involved in denitrification. Varying the concentrations of carbon, denitrifying bacteria and nitrate/nitrite in sterile lake water microcosms can demonstrate how the dynamics of the denitrification pathway under nutrient-limited conditions are different to those found in a nutrient-rich medium.

Continuous real-time measurement of gases enabled the dynamics of the process to be investigated. Concentrations of 17 mmol/L nitrate and 10 mmol/L nitrite were identified as optimal for denitrification under nutrient-limited conditions (i.e., produced the highest concentrations of N_2). Available carbon was the major rate-limiting factor in lakewater when nitrate or nitrite was present. No stratification of the process with depth was observed, and aerobic denitrification was apparent under all the conditions employed. See **Figure 3**, below.

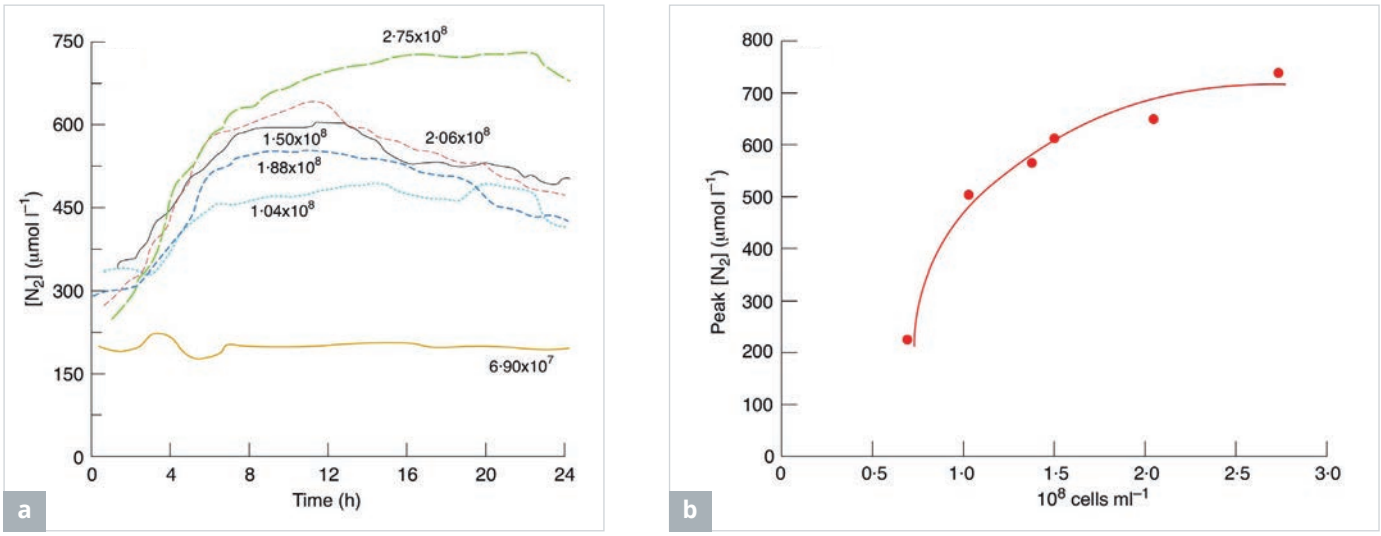


Figure 3 (a & b): Data showing denitrification by Pseudomonas stutzerl in a sterile lake water microcosm supplements with succinate and nitrate.

Swimming Pool Water Analysis

CHARACTERISATION OF CONTAMINANT SPECIES IN SWIMMING POOL WATER

Swimming pools include reactive compounds, including the disinfectants, cleaning compounds and several species released by bathers to form disinfection by-products (DBPs). Medical studies, including incidence and distribution of infectious diseases have shown adverse effects on health associated with the exposure to DBPs present in indoor swimming pool atmosphere. DBP analyses require a combination of techniques in order to identify the molecules of interest and the measurement process itself is challenging due to the low stability of several compounds and the lack of specificity of certain methods.

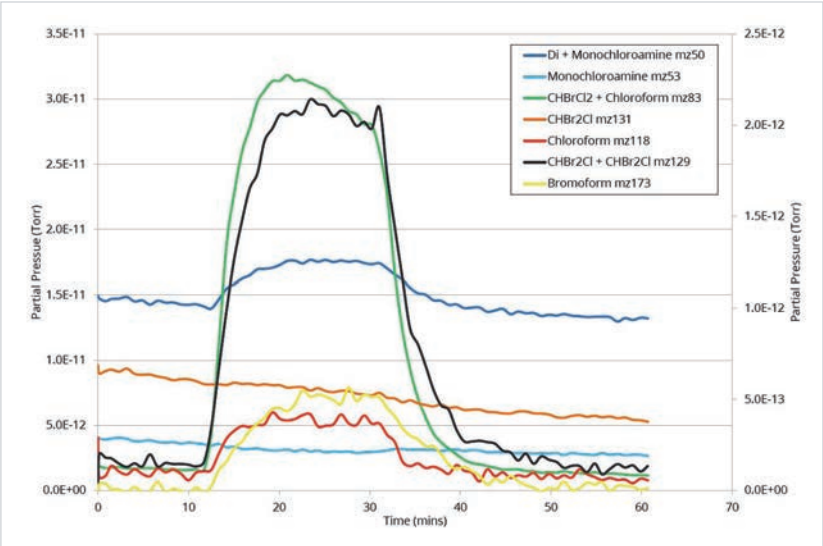


Figure 4: Example MS data showing dissolved compounds in swimming pool water.

MIMS offers a robust method for in-situ analyses of pool water DBPs with high accuracy and precision, without the need to use multiple techniques. The concentration of dissolved THMs (trihalomethanes) and chloramines can be quantified by simultaneously measuring the signals at multiple m/z values. Using a dual probe sampling system enables additional head space analysis which can be used to monitor chloroform levels as well as THMs and chloramines. Using MIMS, the determination of these by-products is not significantly influenced by the pH or ionic strength of the solution, making it an excellent method for this application. **Figure 4** shows some example data of pollutant compounds in swimming pool water.

HPR-40 DSA

Stable Isotope Analysis

QUANTIFICATION OF NITROGEN ISOTOPES FOR POLLUTION MONITORING

Nitrogen pollution in aquatic ecosystems is an urgent environmental issue in coastal waters around the world. Monitoring ^{15}N concentration levels has become an increasingly common method of distinguishing between land derived and natural sources of nutrients. Waste-water nitrate has higher concentrations of ^{15}N than occur naturally and the bacteria present in sewage systems favourably consume ^{14}N resulting in an even higher ratio of ^{15}N:^{14}N in the water reaching the aquifer. The inorganic nitrogen is usually found in the form of $^{15}NH_4^+$ and in recent decades, increased nitrogen input from fertilisers has caused environmental problems including coastal eutrophication, seasonal hypoxia and harmful algae blooms. Traditional methods to determine nitrogen isotope ratios of dissolved ammonium are generally time consuming whilst also requiring large samples and costly equipment.

MIMS provides an efficient and cost-effective alternative to traditional methods. By oxidizing the dissolved $^{15}NH_4^+$ using hypobromite iodine to form nitrogen gas, MIMS can be used to determine the concentrations of $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$ present in the sample, **Figure 5** depicts this procedure. This method requires only small sample volumes of water or sediment slurries and is rapid, convenient, accurate, and precise over a range of salinities and ^{15}N:^{14}N ratios, as shown in **Figure 6**. The effectiveness of this technique makes it a great method to analyse nitrogen transformation in agricultural systems and surrounding waters including lakes, rivers and coastal regions.

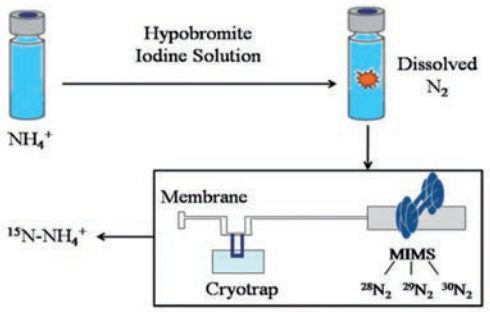
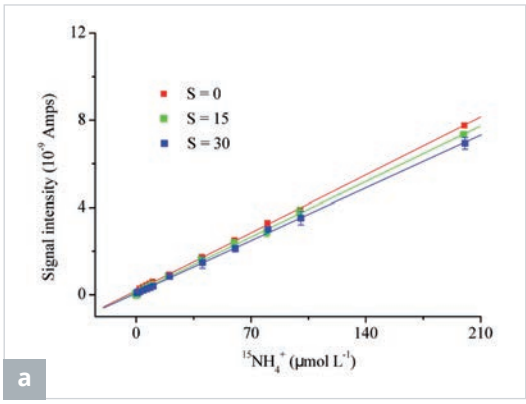


Figure 5: A typical experimental procedure used to perform MIMS analysis of ^{15}N:^{14}N ratios.



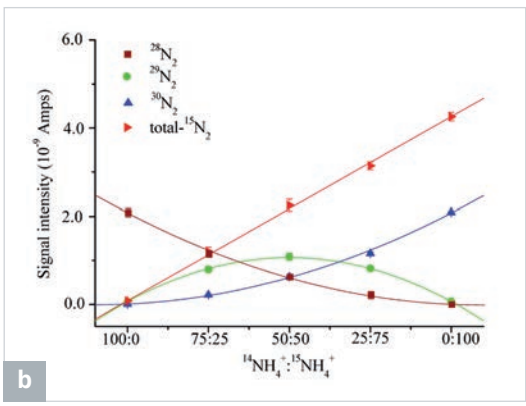


Figure 6 (a & b): Relationships of the known $^{15}NH_4^+$ concentrations under different salinity conditions and the known $^{14}NH_4^+$/$^{15}NH_4^+$ ratios with measured signal intensities of $^{28}N_2$, $^{29}N_2$, $^{30}N_2$ and total $^{15}N_2$ at a NH_4Cl concentration of 100 µmol L^{-1}.

Enzyme Activity Studies

REAL-TIME ANALYSIS OF DISSOLVED GASES IN ENZYMATIC REACTIONS

A major advantage of using membrane inlet mass spectrometry is the ability to simultaneously monitor the concentrations of reactants and products in real time, whilst a reaction is taking place. Due to the high sensitivity and rapid response time of MIMS analysis, the catalytic conversion rate of dissolved gas species can be optimised by measuring it using a range of catalyst concentrations.

In this example, **Figures 7-9**, the real time nature of MIMS analysis allows researchers to pinpoint what changes lead to the initiation of a desired reaction. Here the 2 mL reaction was initiated by the addition of recombinant CsOxOx to a final concentration of 0.12 µm at 2 minutes. The reaction is characterised by the production of CO_2 and consumption of O_2 (in arbitrary ion currents) from mesoxalate catalysed by CsOxOx.

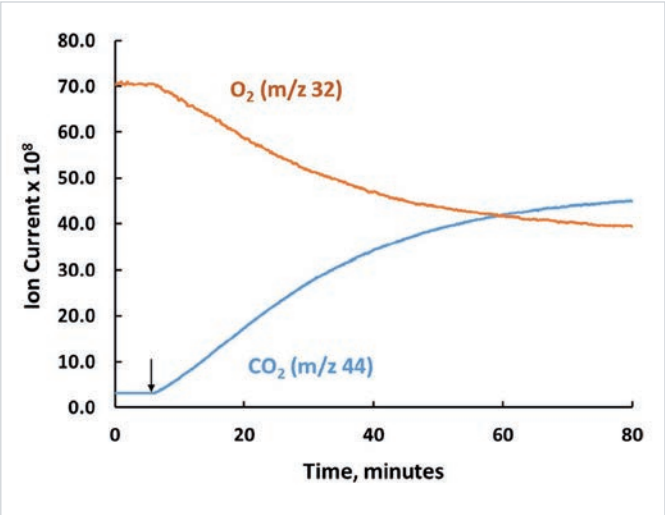


Figure 7: Data showing CO_2 production from mesoxalate catalysed by CsOxOx.

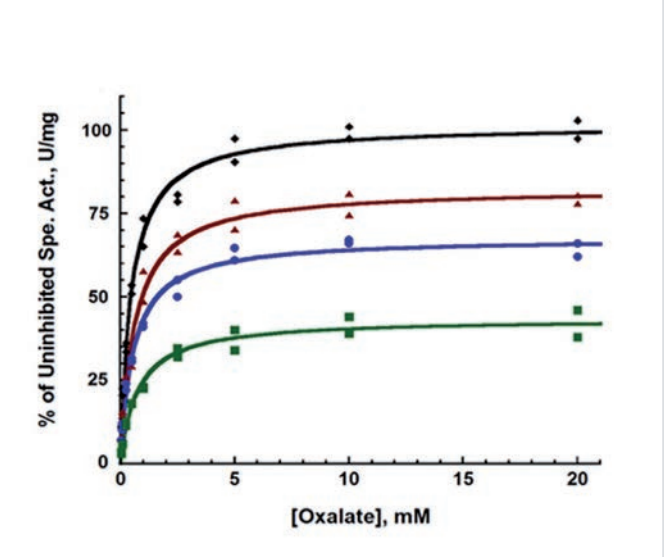


Figure 8: Data showing hydrogen peroxide inhibition of bicupin oxalate oxidase.

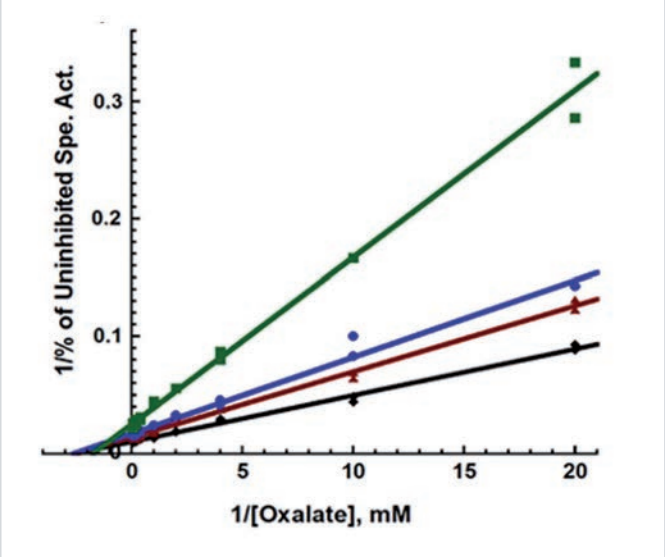


Figure 9: Data showing hydrogen peroxide inhibition of bicupin oxalate oxidase.

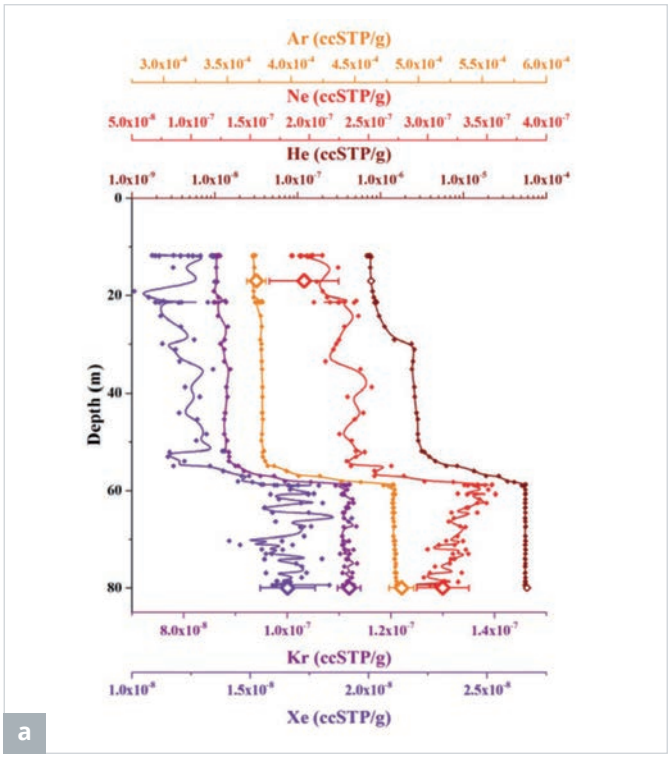
Groundwater Studies

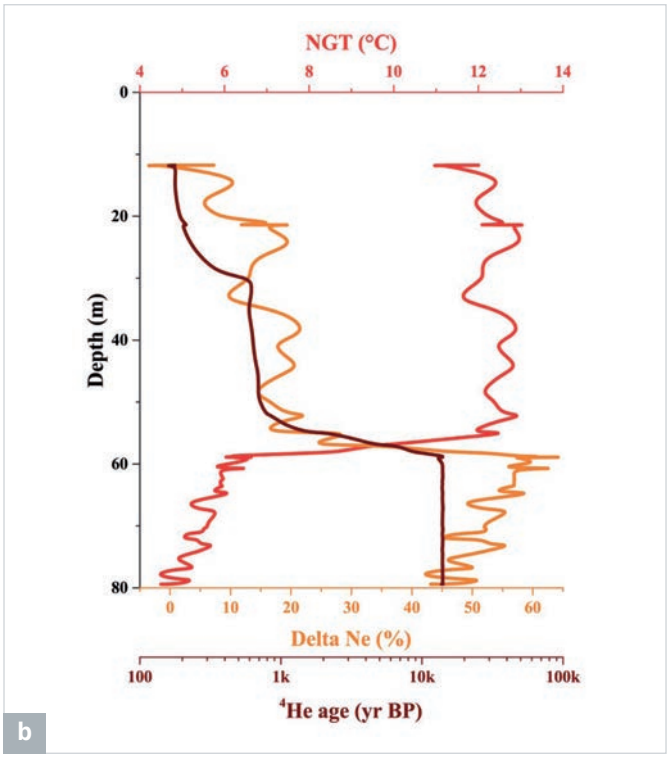
MONITORING OF WATER QUALITY IN GROUNDWATER SYSTEMS

Groundwater is water, found in soil pores and fractures in rock formations beneath Earth's surface, that accumulates over time to form vast underground reservoirs, the depth at which these are found is known as the water table. Where there is a sufficient quantity of water for it to be extracted and used, these water-filled voids are called aquifers. Surface discharge of groundwater can occur naturally at springs, oases and wetlands however, groundwater is often cheaper, more convenient and less prone to pollution than surface water making it a reliable freshwater supply particularly in dry climates that receive limited or intermittent rainfall.

It is important to study the distribution and movement of ground water over time as well as monitoring the impurity levels found in aquifers. Groundwater pollution can often be less visible and harder to remove than surface water contaminants due it commonly originating from industrial and household chemicals, pesticides and landfills. Effective analysis of contaminants in aquifer samples as well as the sources of recharge such as streams and rivers are essential to ensure the high quality and sustainability of the extracted fresh water.

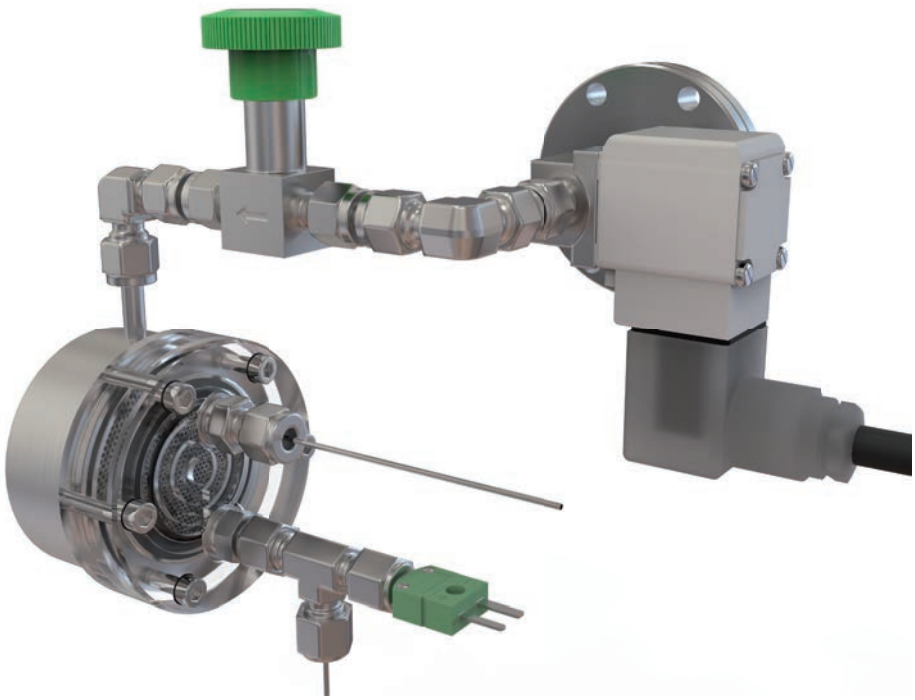
Figure 10 (a & b): Field continuous measurements of dissolved gases with a CF-MIMS





METHOD

The Flow-Through Dissolved Species Probe enables continuous real-time measurement of dissolved gases directly from aqueous solutions. The choice of a suitable membrane is essential to ensure the maximal permeation of the targeted dissolved gases. With enhanced permeability to noble gases and a suitable gas exchange surface, the Large Circular Membrane Cell has been selected for our CF-MIMS. This membrane inlet system allows a continuous flow measurement of dissolved gases.



Large Circular Membrane Cell

Wastewater and Sludge Analysis

THERMAL AND THERMO-CHEMICAL PRE-TREATMENT OF WASTE RESIDUE

The rate-limiting step in the anaerobic digestion of solid matter is the hydrolysis. Thermal hydrolysis has been deeply investigated with temperatures between 60˚C and 180˚C and several types of pre-treatments have been studied in order to accelerate this step. A series of low temperature pre-treatments at less than 100˚C showed an increase in biogas production, whilst wet oxidative (WO) pre-treatment involves higher temperatures and an oxidising agent such as oxygen or peroxide but it can reduce solid waste volume and generate valuable organic compounds like acetic acid. The membrane inlet mass spectrometry (MIMS) allows to monitor the change in the volatile components during pre-treatment.

Here, in **Figure 11**, MIMS was used to follow oxygen consumption and carbon dioxide production during thermal pre-treatment process in four different substrates: coal, Kraft pulp solids, chicken feathers and chicken processing waste. In the graphs is possible to see the variations in O_2 and CO_2 at 200˚C (a), total O_2 consumption (b), total CO_2 production in oxidative (c) and inert atmosphere (d).

The research group was also able to observe the production of acetic acid in oxidative (e) and inert (f) atmosphere.

Moreover, the methane yield increased after pre-treatment at 140˚C but decreased at higher temperature (200˚C).

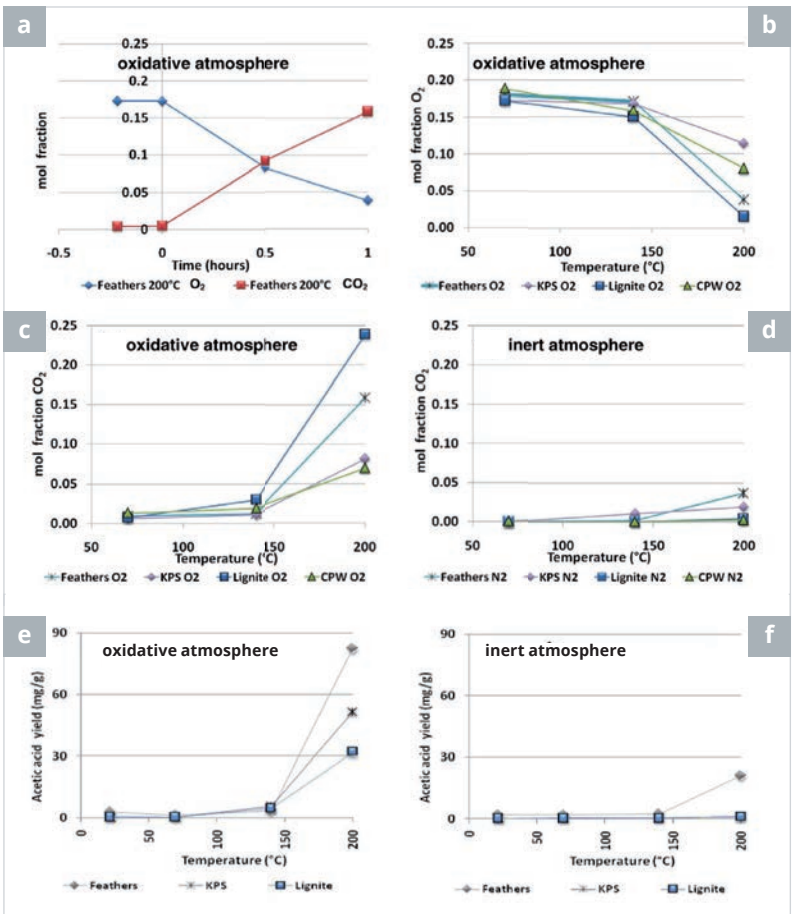


Figure 11 (a-f): Changes in O_2 and CO_2 when feathers are treated at 200˚C (a), total O_2 consumption (b) and total CO_2 production for all substances after 1h under oxidative atmosphere (c) and inert atmosphere (d) at various temperature. Acetic acid production under an oxidative (e) and inert atmosphere (f) up to 200˚C.

Environmental Research

VOLCANIC GAS, WATER AND SEDIMENT ANALYSIS

An important application for MIMS analysis is the monitoring of volcanic activity. Through the analysis of gas, liquid and soil samples, on-site or in the laboratory, researchers around the world can collect important information on the levels of rare earth gas isotopes such as Ar, Ne and He and other gases like H_2S and SO_2. Trace gases like H_2 and He for example, are in low concentration in the atmosphere and have low solubility in water, however, the high concentration in aquifers indicates the dissolution of volcanic gases.

The variation of concentration of dissolved gases in groundwater in relation to seismic events, helps to understand the layout of the underground waters. The charts show the data collected between April 2016 and June 2020 from two different sites in Tenerife. The increase in dissolved CO_2 and He content, and the variation in He/CO_2 and He/N_2 ratios after a seismic event in 2016, confirmed a connection between groundwater and the hydrothermal system.

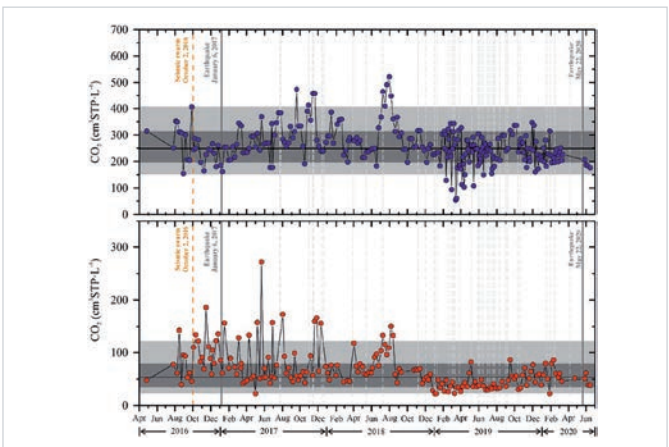


Figure 12: Temporal evolution of dissolved CO_2 of ground water from Fuente del Valle (blue) and San Fernando gallery (red) in Tenerife, Spain from 2016 to 2020.

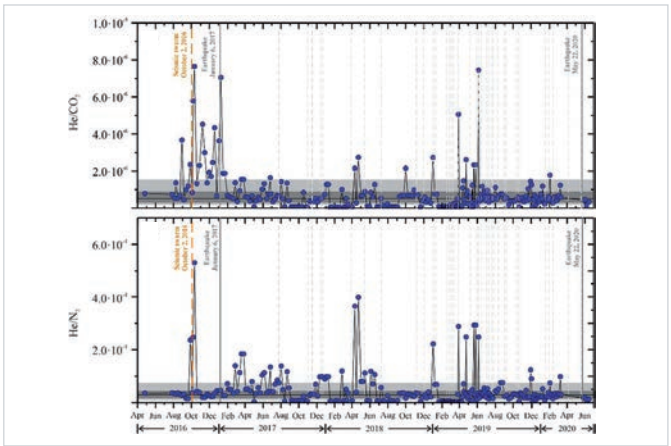


Figure 13: Temporal variation of He/CO and He/N_2 of ground waters collected from Fuente del Valle gallery (Tenerife, Spain) from 2016 to 2020.

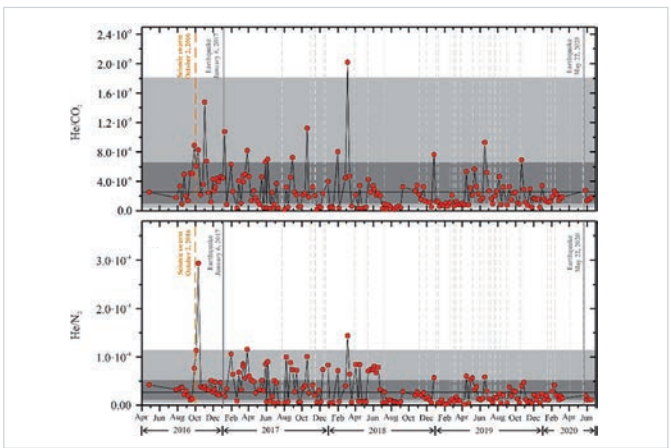


Figure 14: Temporal variation of He/CO and He/N_2 of ground waters collected from San Fernando gallery (Tenerife, Spain) from 2016 to 2020.

Standard deviation values are shown as thick grey lines. Seismic swarm are shown as vertical pale grey dotted lines and the orange line is the event of 2016. The vertical grey lines are the largest seismic events since 2004.

The Hiden HPR-40 DSA dissolved species analyser is a bench mounted or mobile cart mounted module for analysis of dissolved species in fermentation cultures, soil samples, and general applications where analysis of dissolved species in liquid sample is required. The *p*QA portable gas analyser is a versatile mass spectrometer, offered with a range of interchangeable sampling inlets to suit a broad application range. The system is supplied in a Pelican case, and can be powered by a 12 V supply for field use or a 220 V supply for laboratory use. Both systems are suited to gas analysis applications, where sample volume is small, and for environmental applications where detection of low concentration levels is required. Each is configured with a mass range of 200 amu (300 amu option) and sub ppb detection levels.

THE SYSTEMS INCLUDE

- Quadrupole mass spectrometer system from the RGA series or high performance 3F series (HPR-40 DSA only), with mass range options 200 or 300 amu.
- Mass spectrometer analyser manifold and UHV pump set with a manually valved dissolved species probe with silicone rubber membrane.
- Total pressure gauge and interlocks to provide protection for the mass spectrometer in case of over pressure.
- Fast acting shut off valve between the dissolved species probe and mass spectrometer manifold to protect the mass spectrometer in case of membrane failure. The valve is interlocked with the integral UHV pressure gauge.

HPR-40 DSA – MIMS

***p*QA Portable Quadrupole Analyser**

CONTRIBUTORS

- Council of Scientific & Industrial Research (CSIR), Rafi Marg, New Delhi, 110 001, India
- Green Processing Unit, Sustainable Design, Scion, Private Bag 3020, Rotorua 3046, New Zealand
- Instituto Volcanológico de Canarias (INVOLCAN), 38320 San Cristóbal de La Laguna, Santa Cruz de Tenerife, Spain
- Monterey Bay Aquarium Research Institute (MBARI), 7700 Sandholdt Road, Moss Landing, CA 95039, USA
- Department of Chemistry and Biochemistry, Kennesaw State University, Kennesaw, GA, United States of America
- Centre Scientifique et Technique du Bâtiment, AQUASIM, 11 rue Henri Picherit, BP82341, 44323 Nantes Cedex 3, France
- Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China
- OSUR-UMR6118 Géosciences Rennes, Université de Rennes 1 and Centre National de la Recherche Scientifique, Rennes, France

Hiden**APPLICATIONS**

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

GAS ANALYSIS

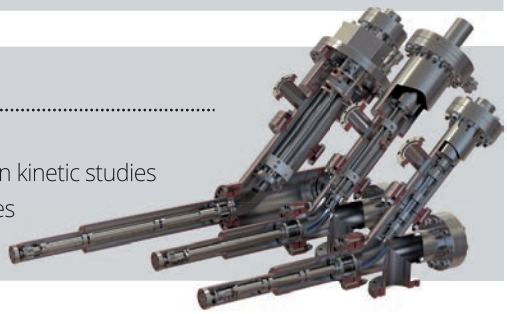
- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

SURFACE ANALYSIS

- UHV TPD
- ToF qSIMS and SIMS analysers
- end point detection in ion beam etch
- elemental imaging – 3D mapping

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

HIDEN ANALYTICAL

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

T +44 [0] 1925 445 225
F +44 [0] 1925 416 518
E info@hiden.co.uk
W www.HidenAnalytical.com

Sales Offices:

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