



Dissolved Species Analysis Applications

INTRODUCTION

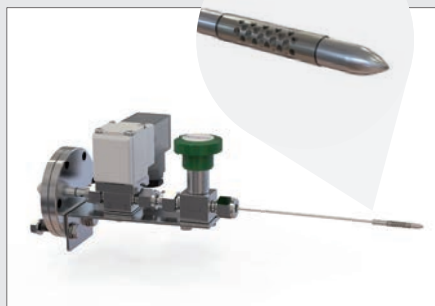
Dissolved Species Analysis Applications

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.

Hidden offers MIMS capabilities in the form of a benchtop HPR-40 MIMS 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



MIMS Probe

Designed for direct, in-situ analysis of static samples where pumping/flow isn't possible, enabling robust, flexible sampling of liquids and slurries (e.g., fermenter liquors) and other heterogeneous matrices across single or multiple sample environments.



MIMS Proximity Probe

Enables ultra-low-volume, thin-layer sampling in confined setups, delivering fast, high-sensitivity surface/interfacial measurements for inline monitoring, kinetics, droplet and biofilm studies.



MIMS MultiStream

Supports multi-point sampling with automatic sequential measurement, enabling high-throughput vial and batch workflows while maintaining consistent, repeatable results.

FLOW THROUGH SERIES



FT-Standard

Flow-through inlet for continuous environmental water analysis, designed for stable routine monitoring across ground, sea, and wastewater samples.



FT-Low Volume

Low-volume inlet delivering high sensitivity with minimal dead volume for improved temporal resolution, ideal for vial analysis, denitrification studies, and dynamic environmental measurements.



FT-High Sensitivity

Flow-through inlet optimised for enhanced analyte transfer in challenging matrices, compatible with alternative membranes for targeted species analysis in wastewater, slurries, solvents, oils, and silicone-incompatible media.

GAS SAMPLING CAPILLARY INLET



Micro-flow Inlet

2 m microflow capillary for atmospheric-pressure gas sampling, providing ~12.5 $\mu\text{L}/\text{min}$ (air) flow with ~16 s response time.

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- 8. Groundwater Studies
- 9. Biophotovoltaic & Photosynthetic Research
- 10. Wastewater, Sludge and Soil Core Analysis
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Oceanic Trace Gas Measurements

PPT LEVEL DETECTION OF VOLATILES IN WATER

The Hiden HPR-40 MIMS 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 5×10^{-15} Torr.

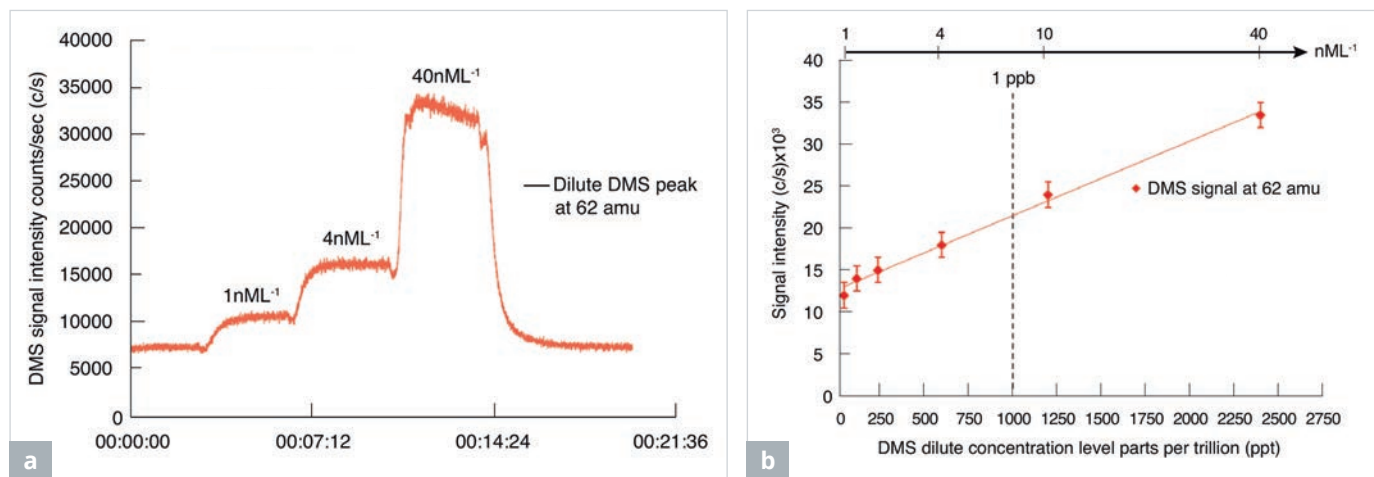


Figure 1 (a & b): Mass scan of dilute concentration levels of DMS and the concentration levels (ppt) derived from DMS partial pressure at 62 amu. Data obtained with assistance from P. D. Tortell, Department of Botany, University of British Columbia.

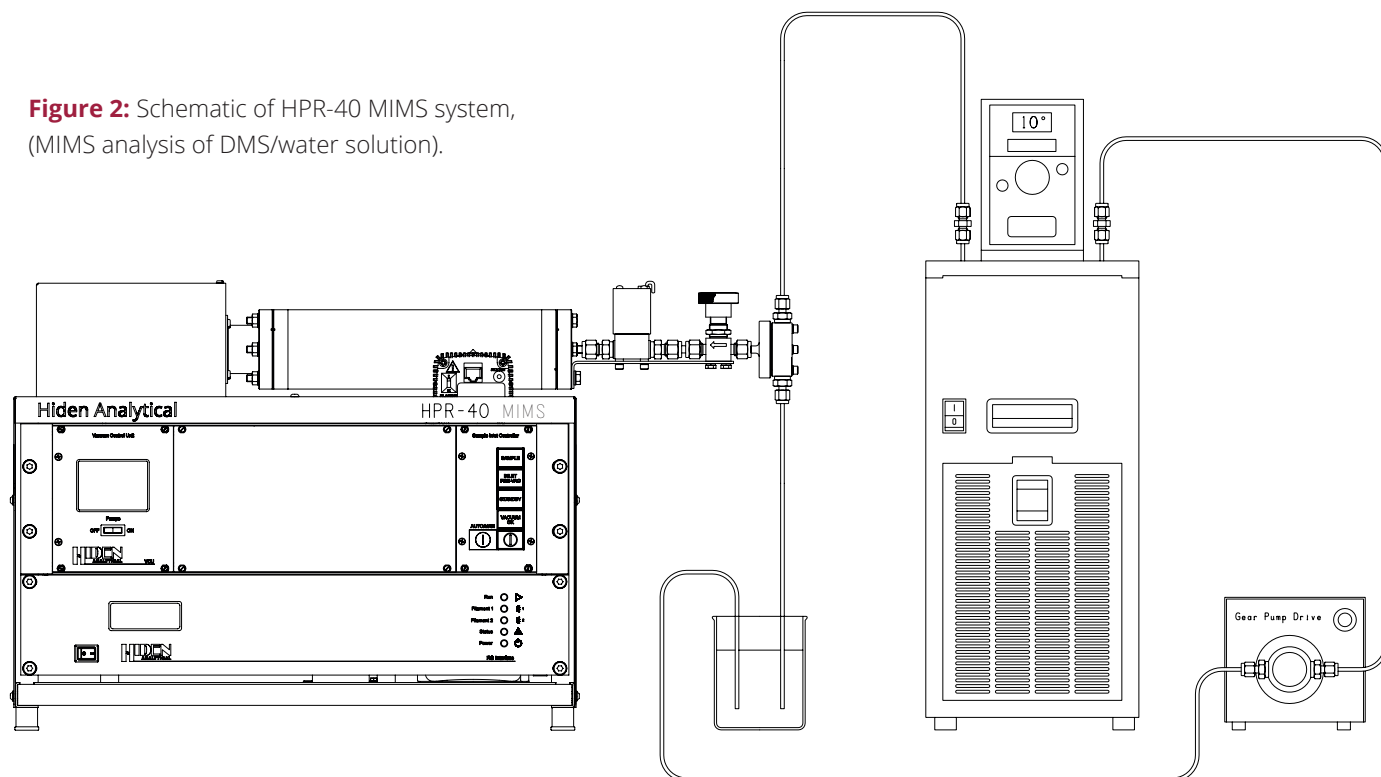
Reference: Data obtained with assistance from P. D. Tortell, Department of Botany, University of British Columbia.



PROCEDURE

Current research in this area has been performed using a Hidden HPR-40 MIMS (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 MIMS 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.

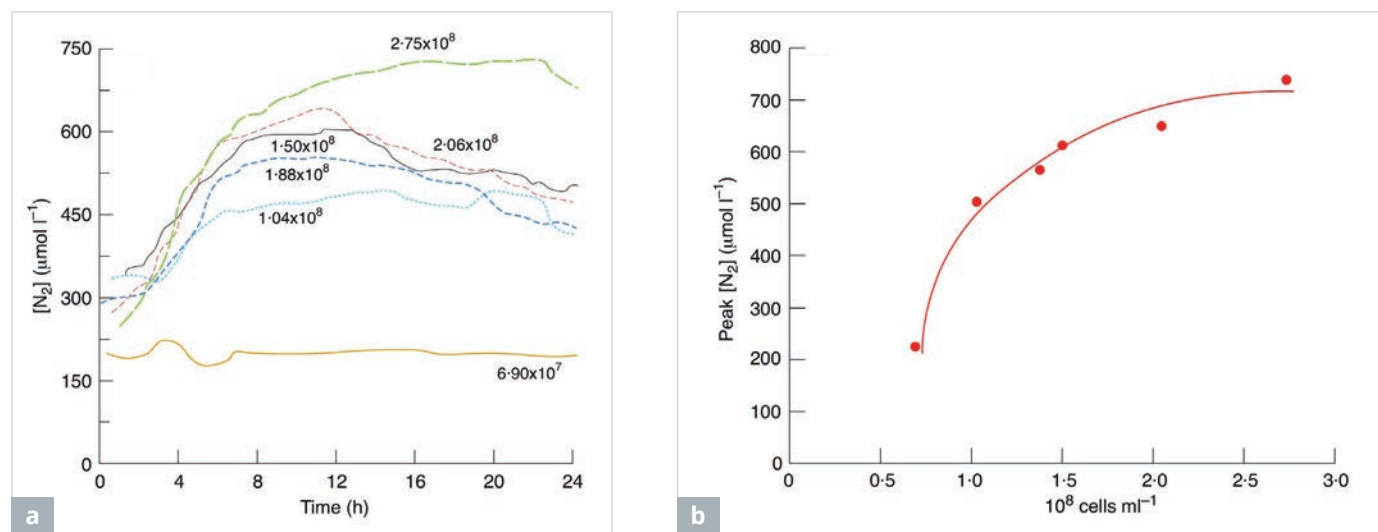


Figure 3 (a & b): Data showing analysis of denitrification by *Pseudomonas stutzeri* under nutrient-limited conditions using membrane inlet mass spectrometry.

Reference: *Journal of Applied Microbiology* (2000) 88, 5, 853-859.

Swimming Pool Water Analysis



CHARACTERISATION OF CONTAMINANT SPECIES IN SWIMMING POOL WATER

Swimming pools contain 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.

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 multi 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.

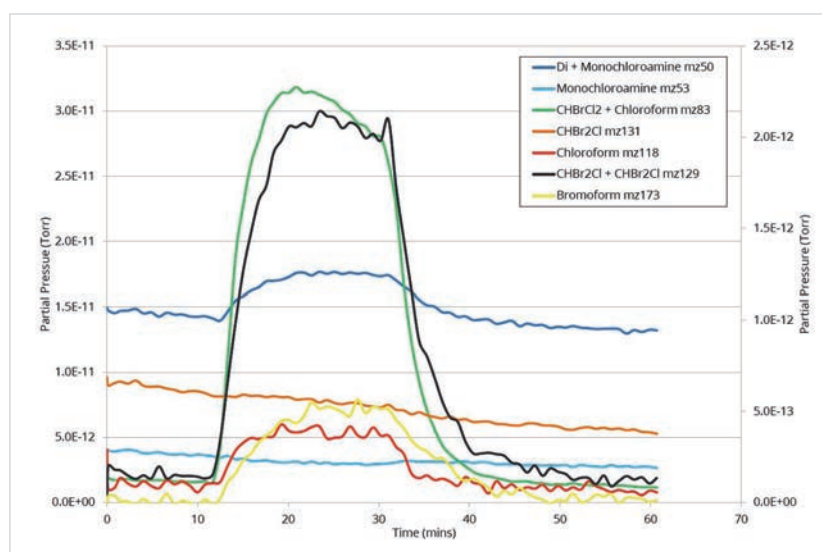


Figure 4: Example MS data showing dissolved compounds in swimming pool water.



HPR-40 MIMS

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 $^{15}\text{N}:^{14}\text{N}$ in the water reaching the aquifer. The inorganic nitrogen is usually found in the form of $^{15}\text{NH}_4^+$ 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 $^{15}\text{NH}_4^+$ using hypobromite iodine to form nitrogen gas, MIMS can be used to determine the concentrations of $^{14}\text{N}_2$, $^{14,15}\text{N}_2$, and $^{15}\text{N}_2$ 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 $^{15}\text{N}:^{14}\text{N}$ 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.

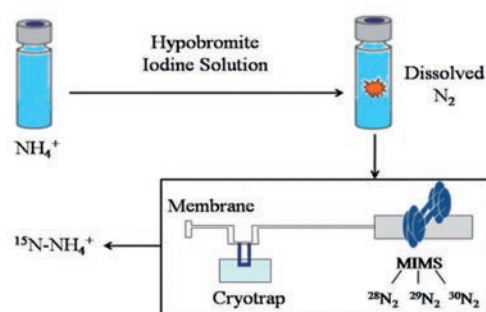


Figure 5: A typical experimental procedure used to perform MIMS analysis of $^{15}\text{N}:^{14}\text{N}$ ratios.

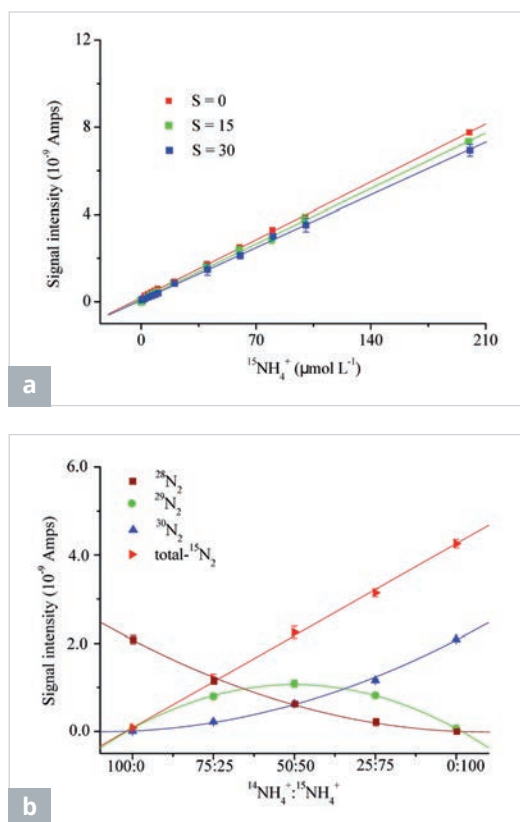


Figure 6 (a & b): Relationships of the known $^{15}\text{NH}_4^+$ concentrations under different salinity conditions and the known $^{14}\text{NH}_4^+/:^{15}\text{NH}_4^+$ ratios with measured signal intensities of $^{14}\text{N}_2$, $^{14,15}\text{N}_2$, $^{15}\text{N}_2$ and total $^{15}\text{N}_2$ at a NH_4Cl concentration of $100 \mu\text{mol L}^{-1}$.

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, 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 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 Oxalate oxidase from *Ceriporiopsis subvermisporea* (CsOxOx) to a final concentration of $0.12 \mu\text{M}$ 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.

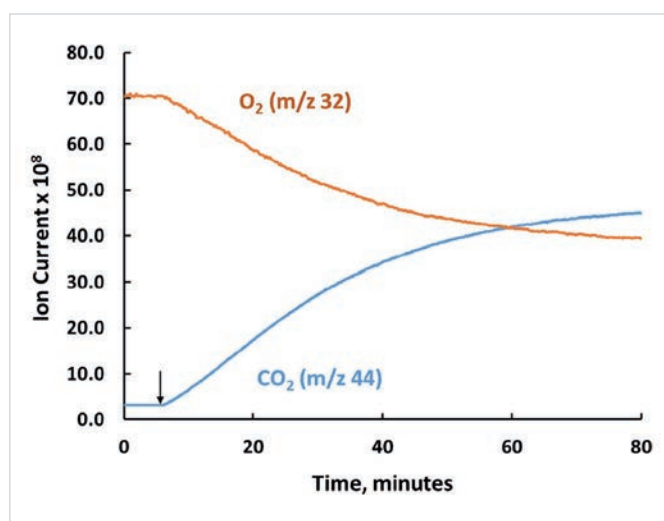


Figure 7: Data showing CO_2 production from mesoxalate catalysed by CsOxOx.

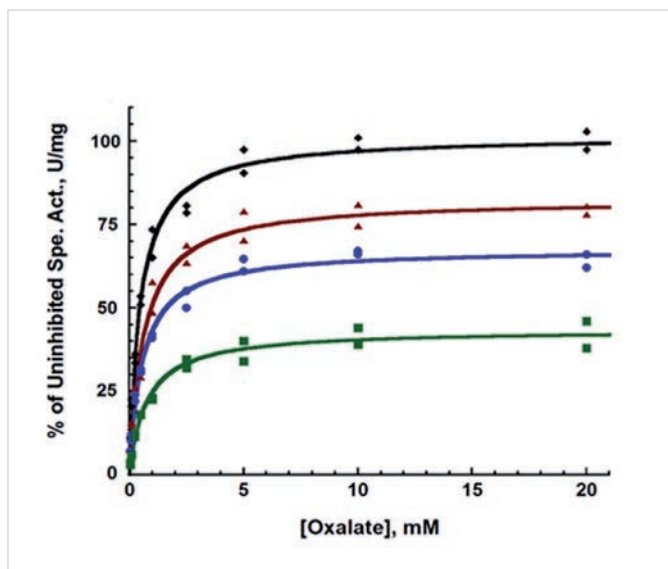


Figure 8: Data showing hydrogen peroxide inhibition of bicupin oxalate oxidase.

Reference: *PLoS ONE* (2017) 12, 5, e0177164.

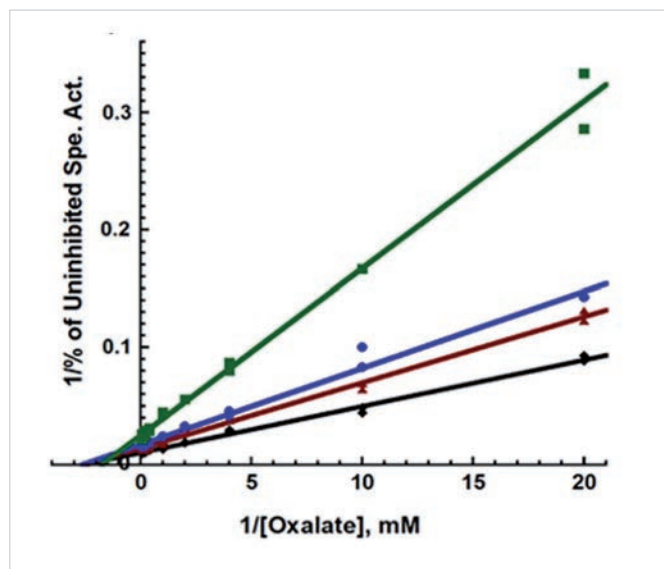


Figure 9: Data showing hydrogen peroxide inhibition of bicupin oxalate oxidase.

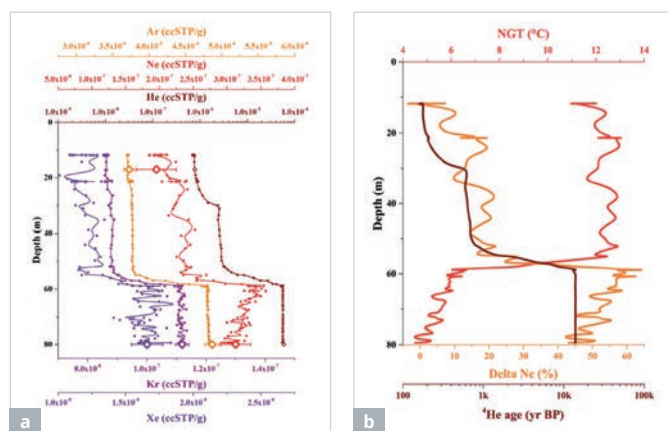
Groundwater Studies



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.

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

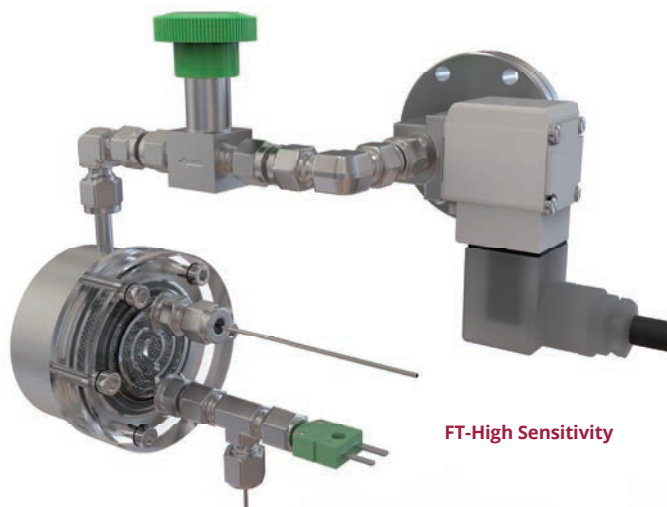


Reference: *Environmental Science & Technology* (2017) 17, 846-854.

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.

METHOD

FT-Standard 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 FT-High Sensitivity has been selected for our Continuous Flow Membrane Inlet Mass Spectrometer. This membrane inlet system allows a continuous flow measurement of dissolved gases.



FT-High Sensitivity

Biophotovoltaic & Photosynthetic Research



REAL-TIME MOLECULAR DYNAMICS OF PHOTOSYNTHETIC ELECTRON FLOW

Biophotovoltaics (BPV) represents an innovative biohybrid technology that couples electrochemistry with oxygenic photosynthetic microbes to harness solar energy and directly convert it into clean electricity. Central to the optimization of BPV systems is understanding how microbes perform extracellular electron transfer (EET) to an anode. Investigating these sub-cellular pathways requires an analytical technique capable of isolating complex gas exchange behaviours—such as separating metabolic respiration from true photosynthetic oxygen evolution—without disrupting active electrochemical processes.

Membrane Inlet Mass Spectrometry (MIMS) provides a non-invasive, highly sensitive method for the simultaneous tracking of dissolved gases inside living bio-electrochemical systems. By introducing stable isotope tracers into the liquid matrix, MIMS allows researchers to cleanly decouple overlapping cellular mechanisms in real time.

Recent studies have utilized a **Hidden HPR-40 MIMS system** configured with a high-precision multi-stream selector and direct insertion membrane probes to monitor the cyanobacterium *Synechocystis sp. PCC 6803* inside a ferricyanide-mediated BPV reactor. Online tracking of dissolved CO_2 , $^{16}\text{O}_2$, and $^{18}\text{O}_2$ revealed that while EET actively competes for electrons with native flavodiiron proteins (flv1/3), it operates safely downstream of photosystem I without diminishing cell growth, respiration, or carbon fixation efficiency.

Reference: *Environmental Science and Ecotechnology* (2025) 23, 100519.

PROCEDURE

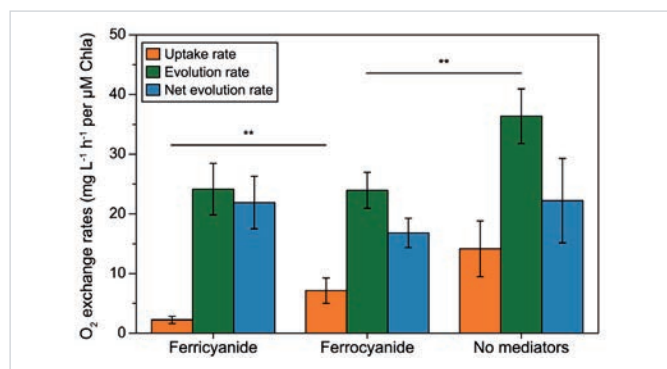
Experimental profiling is conducted using a **Hidden HPR-40 MIMS system** coupled with an eight-way multi-stream selector (MIMS MultiStream). Multi-probe manifolds are fitted with 500 mm MIMS Probes, which are submerged directly into the working electrode chamber of the BPV reactors.

To precisely isolate dynamic photosynthetic oxygen exchange from simultaneous respiratory oxygen consumption, the reactor liquid is enriched with a stable isotope ($^{18}\text{O}_2$). The mass spectrometer continuously monitors parallel ion current channels:

- **m/z 32 ($^{16}\text{O}_2$)** to calculate true oxygen evolution from water splitting at photosystem II.
- **m/z 36 ($^{18}\text{O}_2$)** to monitor light-induced oxygen consumption and Mehler-like reactions.
- **m/z 44 (CO_2)** to record real-time carbon fixation kinetics under shifting light and electrical loads.

This multi-inlet setup guarantees automated, continuous, and highly reproducible data acquisition directly from active, sterile liquid volumes without physical sample extraction.

Figure 11: HPR-40 MIMS measurement of photosynthetic O_2 uptake, evolution and net evolution rates in *Synechocystis sp. PCC 6803* BPV reactors under ferricyanide, ferrocyanide and no-mediator conditions.



Wastewater, Sludge and Soil Core 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 O₂ and CO₂ at 200°C (a), total O₂ consumption (b), total CO₂ production in oxidative (c) and inert atmosphere (d) at various temperature. Acetic acid production under an oxidative (e) and inert atmosphere (f) up to 200°C.

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).

Reference: *Waste Management* (2022) 32, 1669-1677.

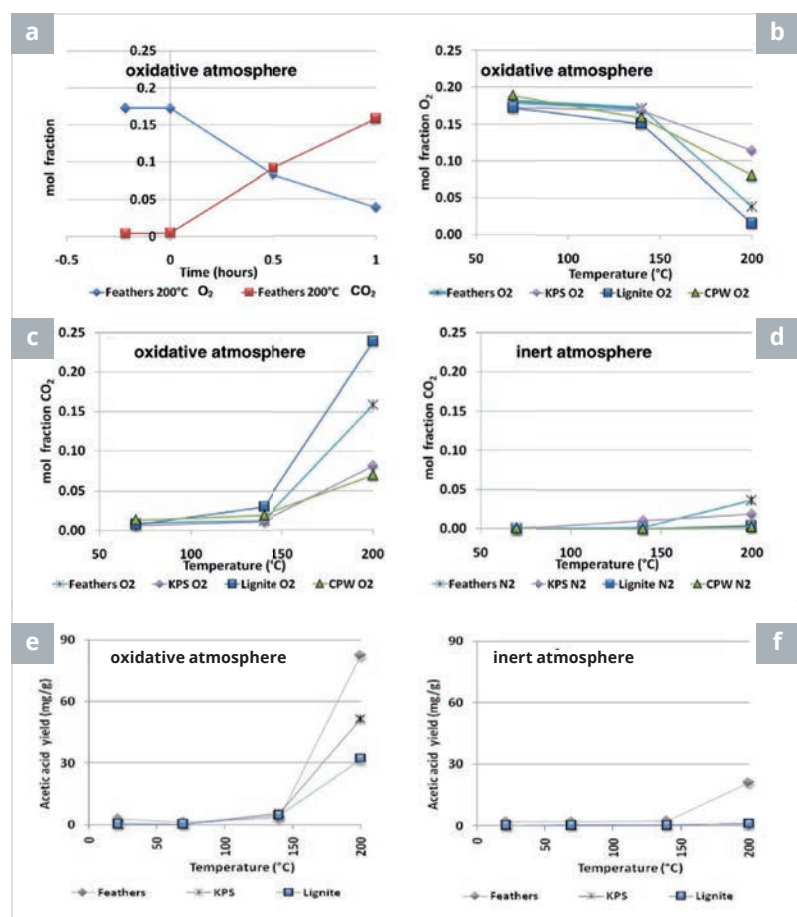


Figure 12 (a-f): Changes in O₂ and CO₂ when feathers are treated at 200°C (a), total O₂ consumption (b) and total CO₂ production for all substances after 1h under oxidative atmosphere (c) and inert atmosphere (d) at various temperature. Acetic acid production under an oxidative (e) and inert atmosphere (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.

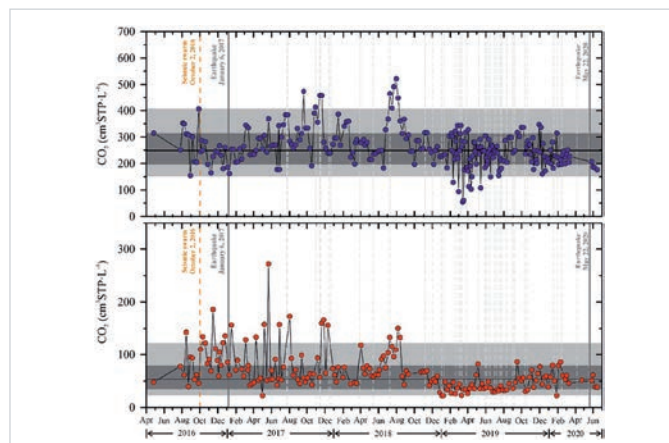


Figure 13: Temporal evolution of dissolved CO_2 of ground water from Fuente del Valle (blue) and San Fernando gallery (red) in Tenerife, Spain from 2016 to 2020.

Reference: *Journal of Volcanology and Geothermal Research* (2022) 424, 107512.

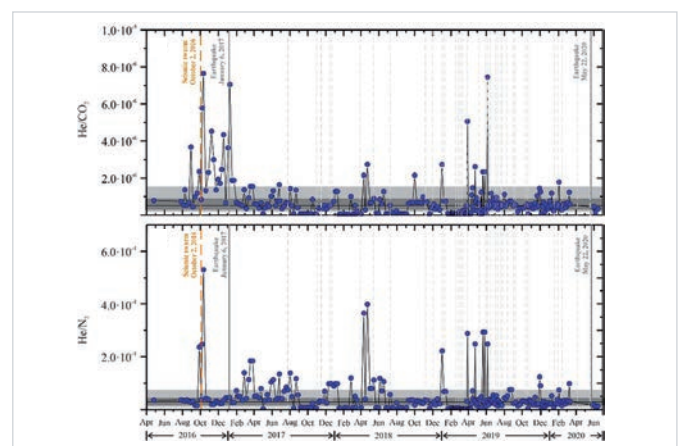


Figure 14: Temporal variation of He/CO_2 and He/N_2 of ground waters collected from Fuente del Valle gallery (Tenerife, Spain) from 2016 to 2020.

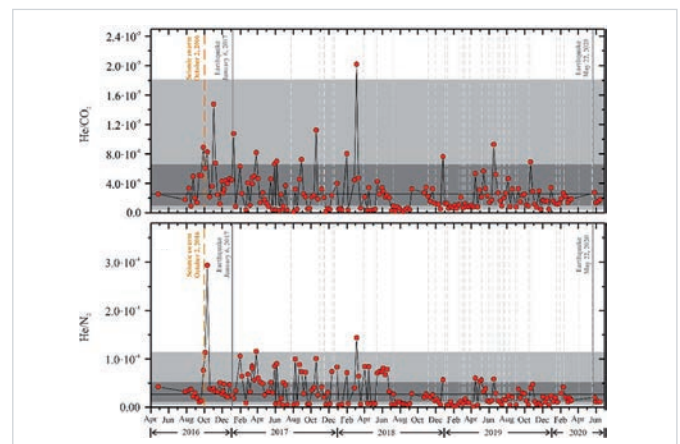


Figure 15: Temporal variation of He/CO_2 and He/N_2 of ground waters collected from San Fernando gallery (Tenerife, Spain) from 2016 to 2020.

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 MIMS dissolved species analyser is a bench-top 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 *pQA* 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 MIMS 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 MIMS



***pQA* Portable Quadrupole Analyser**

CONTRIBUTORS

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Groundwater Studies

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Biophotovoltaic & Photosynthetic Research

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Wastewater, Sludge and Soil Core Analysis

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Environmental Research

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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
- ▶ Electrochemical analysis
- ▶ Dissolved gas analysis
- ▶ Fermentation, environmental and ecological studies



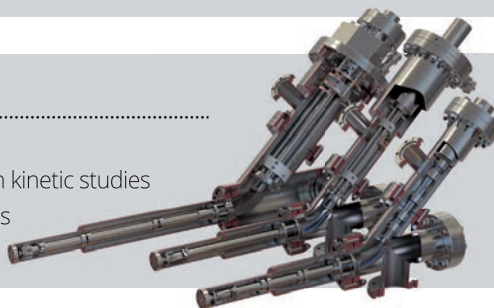
SURFACE ANALYSIS

- ▶ UHV TPD/TDS
- ▶ ToF qSIMS and SIMS analysers
- ▶ End point detection in ion beam etch
- ▶ Elemental imaging – 3D mapping
- ▶ SIMS system with simultaneous dual polarity analysis



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



HIDDEN

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