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

HPR-40 DSA

MIMS Application in Fast Response, High-Precision Determination of N_2 and Ar Levels in Marine Biological Denitrification Processes

Summary

The Hiden HPR-40 DSA is proven to be a versatile, effective product for the analysis of dissolved species. This technique is often referred to as membrane inlet mass spectrometry (MIMS).

The HPR-40 DSA has been used to perform fast response, high precision measurements of dissolved N_2 and Ar in water. The deviation of the N_2, Ar concentrations from equilibrium are known to be indicative of the important biological and physical processes taking place in the marine and aquatic biological environments. The HPR-40 DSA has measured the precision (co-efficient of variance) of N_2, Ar and the N_2 /Ar ratio as: $Cv(N_2) \leq 0.26\%$, $Cv(Ar) \leq 0.25\%$, and $Cv(N_2/Ar) \leq 0.058\%$ respectively.

Such high-precision measurements are important, in particular, in the study of the sensitive marine biological process of denitrification: $NO_3^- \rightarrow N_2$.

Introduction

The Hiden HPR-40 DSA is a powerful monitoring and diagnostic instrument for use in many aspects of liquid environmental monitoring. The semi-permeable membrane inlet allows dissolved species to be analysed, whilst preventing the bulk liquid from entering the QMS vacuum chamber. For safety and protection against system overpressure a Penning gauge is fitted as standard. Although the basic principle of the membrane inlet has been kept, various improvements have been developed to serve particular applications including soil analysis, fermentation cultures and water quality monitoring.

Dissolved gases play an important role in marine and aquatic science. Deviations from equilibrium concentrations are common and reflect biological activity and physical processes acting on the system. Of the three most concentrated gases in aerobic waters, N_2 and O_2 are affected by both biological and physical processes, whereas Ar is affected strictly by physical processes. In some cases, only small fractional (<1%) deviations from equilibrium occur and it is therefore necessary to measure these dissolved gases with high precision.
A typical Hiden Analytical bench-top HPR-40 DSA system with this membrane inlet is shown in Figure 1.

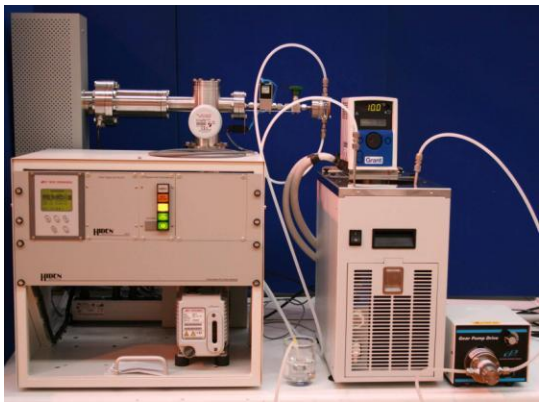

Figure 1: HPR-40 (MIMS analysis of high precision N_2/Ar ratios for denitrification processes in marine and aquatic biology (shown with chiller system in line)

Previous studies have measured the precision of N_2 and Ar extracted from water. Gas chromatography (GC) offers a precision in the range 0.3 – 1%, while standard off-line mass spectrometry yields a much higher precision of <0.1% ***[1]***. However, both GC and MS require introduction of a gas sample that has been previously extracted from a water sample in a separate process. This step adds time and can compromise the precision of the gas analysis.

Procedure & Test Data

The HPR-40 DSA MIMS system is unique to these other techniques in that it analyses the water sample directly. The degassing of the water is done automatically via the membrane inlet interface, with the gas analyzed by the quadrupole mass spectrometer. Response time is rapid, allowing for quick sample turn-around.

Previous research in this area has shown factors in obtaining highest precision measurements require control of the stability of water flow across the membrane, temperature control of the water, pre-sample treatment and preparation. It has also been shown that cyro-trapping of the water vapor to reduce the interference of other species, such as CO_2, on the detection of the gases of interest can improve precision. ***[2]***

In certain circumstances, it may not be possible or straightforward to accommodate for these factors when obtaining sample measurements, for example when rapid "out in the field" high volume sample analysis is required.

The following measurements were made to establish the level of precision attainable under these circumstances.
In this study, a MIMS Hiden Analytical HPR-40 DSA (using standard HAL 201) dual faraday/SEM mass spectrometry system was used.

Sample analysis of standard DI- water with HPR-40 DSA at typical room temperature, with the water temperature measured at ~ 21°C.

The method of inlet sampling technique is a unique Hiden variable powered circular membrane inlet, water sample analysis was performed without particular experimental constraints in place:

- no preparation or pre-treatment of sample water
- no temperature control of water bath,
- no in-situ (liquid nitrogen) cryogenic trapping

The HPR-40 DSA was setup to:

- Detect masses 28 and 40 sequentially at ~ 1.5Hz
- Hiden MASsoft© was setup to calculate σ, μ and ratio data in real time
- QMS operated in multiple ion detection mode (MID scan)
- Figure 2 shows the empirical data tabulated along with time resolved mass scans (28 & 40). The time resolved data was analysed using a boxcar moving average method over 30-60secs duration periods.

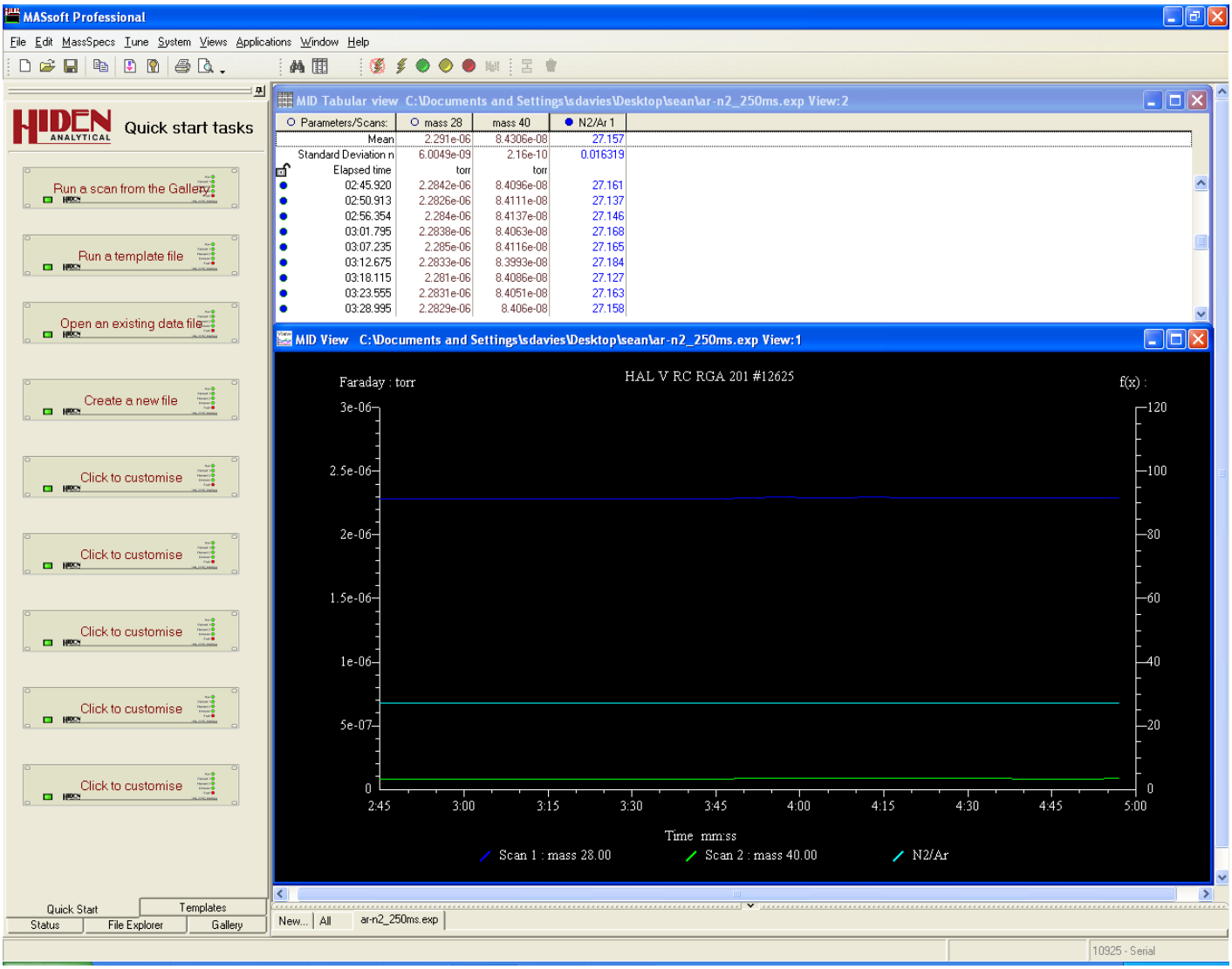

Figure 2. MASsoft Professional tabular and graphical output data from HPR-40: N_2, Ar and N_2/Ar precision from MIMS sampled water

Precision is defined;

Co-efficient of variance (C_v) = standard deviation (σ)/mean value(μ), where:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \overline{x})^2}.$$

Taking examples from the tabulated data show typical precision values of C_v= σ/μ:

N_2: $C_v(N_2)$ = $6.00X10^{-9}/2.29X10^{-6}$= 0.0026
Ar: $C_{v(Ar)}$ = $2.16X10^{-10}/8.43X10^{-8}$= 0.0025

N_2/Ar ratio:
C_v (N2/Ar) = 0.016/27.157 = $5.89x10^{-4}$
Therefore the co-efficient of variance of N_2 , Ar and the N_2/Ar ratio:

- $C_v(N_2) \leq 0.26\%$
- $C_v(Ar) \leq 0.25\%$
- $C_v(N_2/Ar) \leq 0.058\%$
-

These values compare well with results published by Kana *et al, (1994)* ***[2]***, were the authors of that study quoted the Cv for N_2 and Ar
≤0.5%, with the Cv for N_2/Ar ≤ 0.08% using the MIMS technique at room temperature.

Conclusions

- The Hiden HPR-40 DSA is proven to be the definitive product for the analysis of dissolved species.
- High precision ratio data is obtained for N_2/Ar levels in water at room temperature.
- This remains viable without the need for sample pre-treatments, temperature control or cryo-trapping of the sample water prior to the dissolved gas interaction in the quadrupole mass spectrometry system.

- With the HPR-40 DSA, co-efficient of variance of N_2, Ar and the N_2/Ar ratio:
  - $C_v(N_2) \leq 0.26\%$
  - $C_v(Ar) \leq 0.25\%$
  - C_v $N_2/Ar) \leq$ 0.058%
- These values compare well with results published by Kana *et al (1994)*[3], were the authors of that study quoted the C_v for N_2 and Ar ≤0.5%, with the C_v for N_2/Ar ≤ 0.08% using the MIMS technique at room temperature.

References

[1] Craig. H; Howard. T;Science 1987, 235,199-202

[2] Kana, T.M; Darkangelo, C; Duane Hunt, M; Oldham, J.B; Benett, G.E; Cornwell J.C; Anal. Chem. 1994, 66, 4166-4170