HPR-40

Parts Per Trillion (ppt) Concentration Level Detection of CH_3SCH_3 (Dimethylsulphide) Volatiles in Water

Summary

The Hiden HPR-40 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 has been used to specifically tackle specialist applications. This application note details the detection of low level, down to 60 parts per trillion (≥60ppt) concentrations of CH_3SCH_3, Dimethylsulphide (DMS). This is a trace substance naturally evolved from micro-organic species in oceanic waters, and is implicated in global climate change and regulation.

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Introduction

The Hiden HPR-40 is a powerful monitoring and diagnostic instrument for use in many aspects of liquid environmental monitoring. The semi-permeable membrane interface allows dissolved species to be analysed, whilst preventing the bulk liquid from entering the QMS vacuum chamber.

The basic principle of the membrane inlet has been optimised and various refinements have been developed to serve particular applications including soil analysis, fermentation cultures and water quality monitoring.

One particular sample cell has been developed in conjunction with Dr. Philippe Tortell of the University of British Columbia, Canada. The Hiden Analytical HPR-40 system using HAL 101/3F is shown in Figure 1.

Figure 1: HPR-40 (HAL 101/3F, with chiller system; MIMS analysis of DMS to ≤ 60ppt concentration levels.

The HPR-40 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.

DMS is a simple chemical. It is volatile and dissolves easily in aqueous solution. A summary of the main peaks of the cracking pattern from the NIST database is seen in Table 1.

Mass/amu	Intensity / %	Ionic Species
62	99.9	$CH_3SCH_3^+$
47	95.4	CH_3S^+
45	40.8	CHS^+
46	36.1	CH_2S^+
61	33.3	$CH_3SCH_2^+$
35	32.2	SH_3^+
27	20.7	CH_2CH^+

Procedure

The HPR-40 system is designed for detection of volatile species, such as DMS, dissolved in aqueous sample media. The membrane permeability to volatile organic species is higher than the permeability to non-volatile inorganic species.

Current research in this area has been performed using a Hiden HPR-40 (HAL 101/3F, SEM detector) system [1].

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 concentrates over time.

Example results are shown in figures 3 and 5. 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^{o}C using a chiller system, then pumped across the membrane inlet pre-configured reduce the possibility of air bubble contamination. For the following two experiments, the Hiden QMS of the HPR-40 system was operating in analogue SEM mode for the first set of data (figure 3), and then in PIC SEM mode for the second set of data (figure 5).

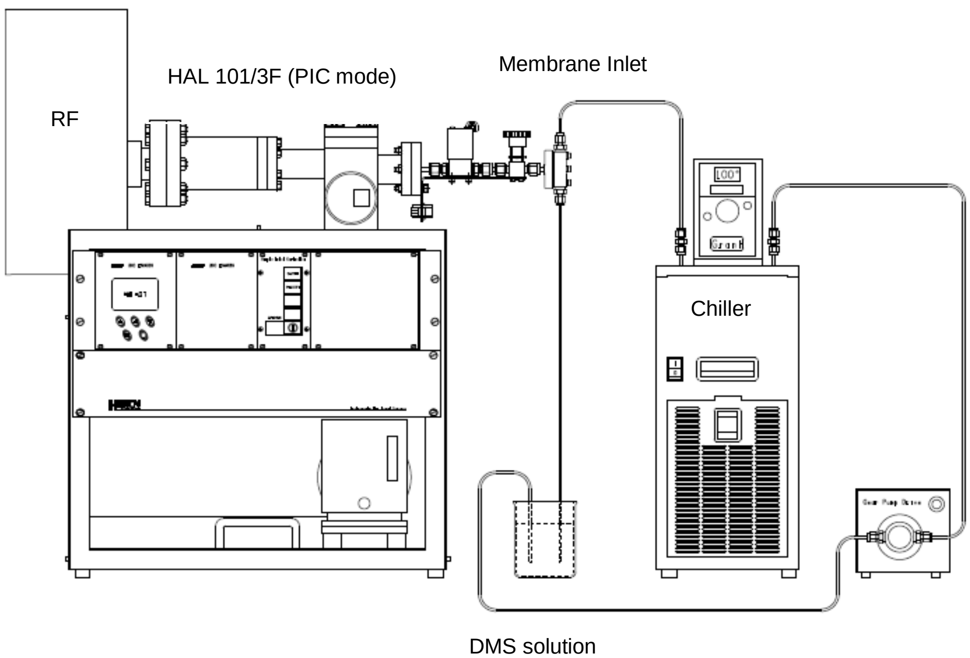

Figure2: Schematic of HPR-40 system, (MIMS analysis of DMS/water solution)

Test Data

The strongest peak at mass 62 (amu) was used for the measurements. Figure 3 shows an example mass scan for a range of DMS concentrations at 62 amu. The concentrations range from 4-20nML^{-1}.

Correlating the DMS peak signal intensity at 62 amu with the DMS concentration level provides quantitative information on the DMS detection levels, shown in figure 4.

The high degree of linearity shown in figure 4 indicates a high level of confidence in the detection characteristics of the HPR-40 system into the ppb range.

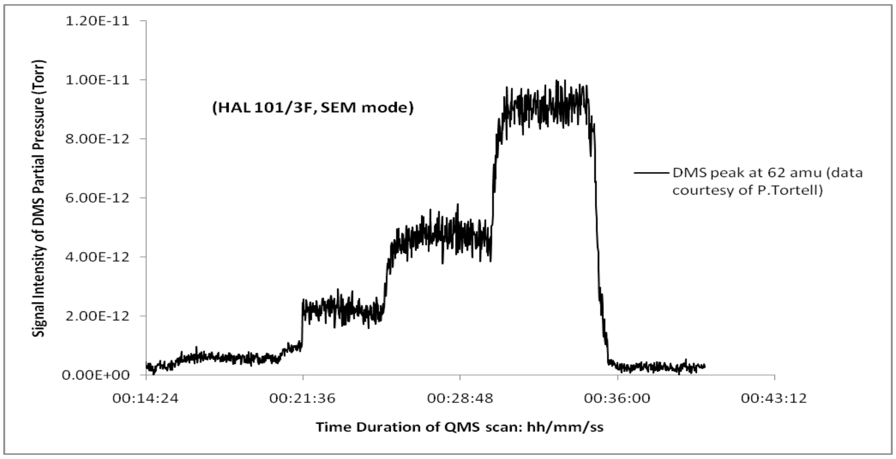

Figure 3. Mass scan of dilute concentration levels of DMS at 62 amu, analogue SEM configuration

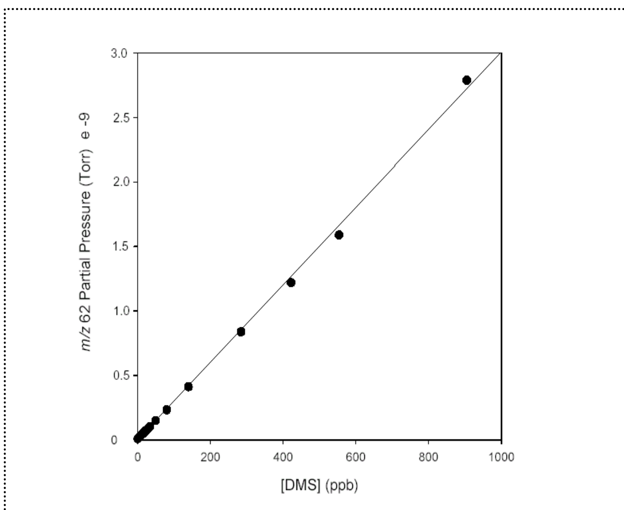

Figure 4: DMS concentration levels (ppb) derived from DMS partial pressure at 62 amu, analogue SEM detection configuration

An important aim in this area of current research is the desire for increased detection sensitivity, with ≤ $2nML^{-1}$ detection levels the target, corresponding to sub 0.1 ppb detection levels of DMS.

Taking this research forward, Hiden Analytical has introduced improvements to certain aspects of the HPR-40 system.

Figure 5 shows a mass scan for DMS at 62 amu obtained with a HAL 101/3F QMS configured with the alternative Pulse Ion Counting (PIC) mode.

Enhanced peak transmission sensitivity at 62amu is evident. Figure 6 details detection levels attainable in the parts per trillion range (ppt). Signal peaks due to DMS concentration levels of ≤ 60 ppt can be resolved, corresponding to DMS concentration levels in water of ≤ $1nML^{-1}$.

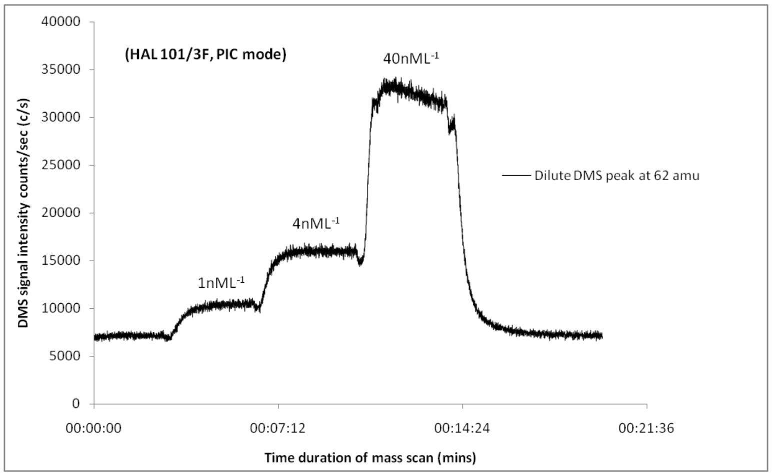

Figure 5: Mass scan of dilute concentration levels of DMS in Q-Water at 62 amu operating in PIC mode

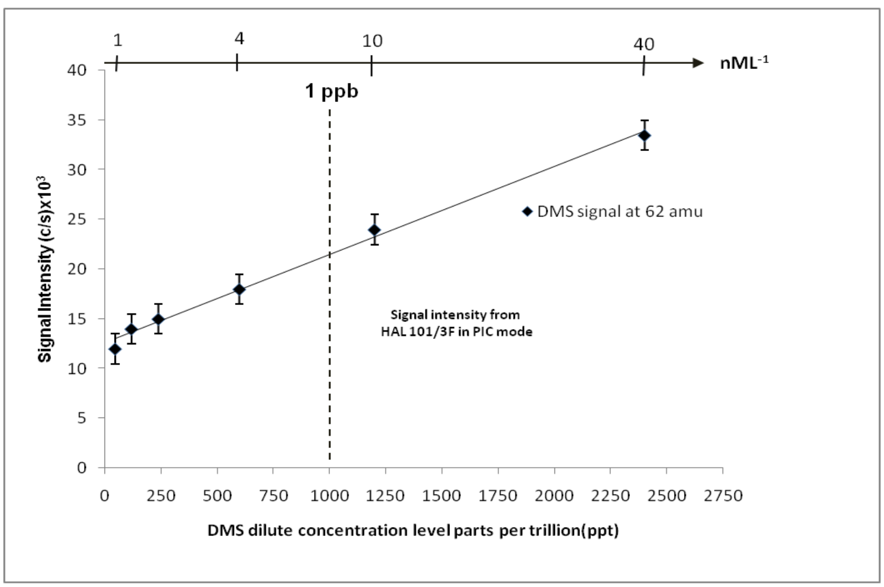

Figure 6: DMS concentration levels (ppt) derived from DMS signal count rate (PIC mode) at 62 amu

Conclusions

- The Hiden HPR-40 is proven to be the definitive product for the analysis of dissolved species.
- Very low levels of detection, crucial in this application to detect trace substance Dimethylsuphide (DMS) are achieved.
- HPR-40 configured in PIC mode provides detection levels into the parts per trillion (ppt) range.
- Current research in this area is striving for detection levels of DMS <2nML^{-1}.
- The specific application detailed in this report shows levels of ≈ 60 ppt are attainable, corresponding to dilute DMS concentrations of ≤1nML^{-1}.

References

[1] Tortell, P. *Limnol. Oceanogr.: Methods 3, 2005, 24–37 © 2004, by the American Society of Limnology and Oceanography, Inc.*