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## Article

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# Field continuous measurement of dissolved gases with a CF-MIMS: Applications to the physics and biogeochemistry of groundwater flow

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**Keywords:** *Dissolved gases, Noble gases, Groundwater, Tracer test, Noble Gas Temperature, Residence time, biogeochemical reactivity, MIMS.*

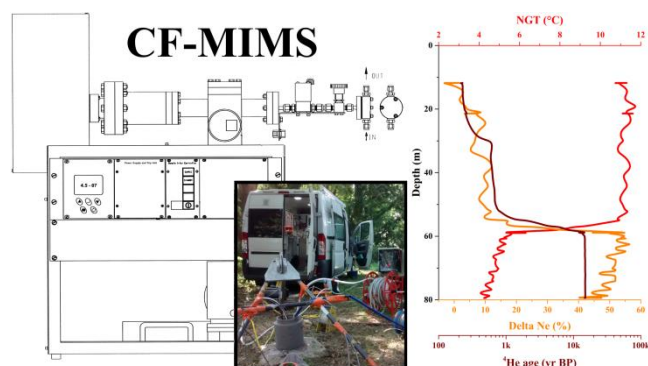
## **Abstract**

In the perspective of a temporal and spatial exploration of aquatic environments (surface and ground water), we developed a technique for field continuous measurements of dissolved gases with a precision better than 1% for N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, He, Ar, 2% for Kr, 8% for Xe, and 3% for CH<sub>4</sub>, N<sub>2</sub>O and Ne. With a large resolution (from 1×10<sup>-9</sup> to 1×10<sup>-2</sup> ccSTP/g) and a capability of high frequency analysis (1 measure every 2 seconds), the CF-MIMS (Continuous Flow Membrane Inlet Mass Spectrometer) is an innovative tool

allowing the investigation of a large panel of hydrological and biogeochemical processes in aquatic systems.

Based on the available MIMS technology, this study introduces the development of the CF-MIMS (conception for field experiments, membrane choices, ionisation) and an original calibration procedure allowing the quantification of mass spectral overlaps and temperature effects on membrane permeability.

This study also presents two field applications of the CF-MIMS involving the well-logging of dissolved gases and the implementation of groundwater tracer tests with dissolved  $^4\text{He}$ . The results demonstrate the analytical capabilities of the CF-MIMS in the field. Therefore, the CF-MIMS is a valuable tool for the field characterisation of biogeochemical reactivity, aquifer transport properties, groundwater recharge, groundwater residence time and aquifer-river exchanges from few hours to several weeks experiments.



## Introduction

Dissolved gas concentrations in groundwater originate mainly from atmosphere-water equilibria existing at the water table during aquifer recharge. These equilibria are governed by physical laws allowing the calculation of dissolved gas equilibrium concentrations (solubilities) as a function of the gas partial pressure in the air ( $z_i$ ), the atmospheric pressure ( $P$ ), the water temperature ( $T$ ) and salinity ( $S$ )<sup>1-8</sup>. Therefore, the combined determination of any dissolved gas concentration unaltered from recharge equilibrium enables the reconstruction of recharge conditions ( $T$ ,  $S$ ,  $P$ ) as long as the gas partial pressures

at the time of recharge are known. Consequently, several studies have been using dissolved noble gases<sup>9–11</sup> sometimes combined to dissolved nitrogen<sup>12,13</sup> to derive past and present climatic conditions through the determination of noble gas temperatures (NGTs i.e. recharge temperatures), the extent of the excess air phenomenon (EA) and recharge elevations. Therefore, dissolved noble gases (and dissolved nitrogen) are valuable tools for the study of groundwater origins, paleoclimates and climate changes.

Contrary to other noble gases, dissolved  $^4\text{He}$  concentrations in groundwater can increase quite rapidly (over a hundred years) due to *in situ* production by radioactive decay of uranium and thorium rich minerals of aquifer rocks. As a result, dissolved radiogenic  $^4\text{He}$  accumulates over time in aquifers and its production creates an excess He that can be typically quantified for residence time larger than hundred years. The determination of dissolved radiogenic He concentrations enables the characterisation of groundwater residence times as long as  $^4\text{He}$  production rates are known<sup>14–17</sup>.

Dissolved reactive gases ( $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{H}_2$ ) originate initially from atmospheric equilibria. However, their concentrations in natural waters can be significantly altered by biogeochemical reactions that typically occur in aquatic environments<sup>18</sup>. Therefore, the measurement of these reactive dissolved gases is critical to the understanding of the biogeochemical reactivity of aquatic environments<sup>19–25</sup>.

All these applications need precise dissolved gas measurements with various requirements in terms of spatial and temporal distribution in the field. Currently, most of the available analytical techniques are based on field sampling and laboratory analysis performed from a few hours or several days after sampling. Therefore, ensuring sample preservation and representativeness is crucial for the determination of accurate actual dissolved gas concentrations. For instance, groundwater sampling in wells is not an easy task due to the risk of sample contamination with atmospheric air, the mixing processes naturally occurring in the well (natural flows) or induced by the sampling process (renewal of the well water, pumping, movement of mobile samplers) that would bias water samples<sup>26</sup>. Furthermore, preservation of dissolved gas samples is a crucial stake particularly for the measurement of dissolved reactive gases such as  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{H}_2$  in reactive environments.

In order to solve the issues related to sampling, field measurement techniques such as Membrane Inlet Mass Spectrometers (MIMS) received great attention from environmental scientists for their capacity of rapid evaluation of dissolved gases in water <sup>27–32</sup>. MIMS technology was first developed for the measurement of organic compounds in environmental water samples <sup>33,34</sup>. Later, Ketola et al <sup>35</sup> proposed a review of the applications and improvements of this technique. Kana et al <sup>36</sup> optimised a MIMS for quasi-continuous determination of major dissolved gases (O<sub>2</sub>, N<sub>2</sub>, Ar) in water samples in order to study biological activity <sup>37–40</sup>. MIMS systems were also miniaturised for oceanographic studies in order to create dissolved gas profiles in seawater <sup>41–44</sup>. Recently, developments of MIMS have been realised for groundwater studies. Mächler et al <sup>45</sup> developed a portable GE-MIMS for field and laboratory measurements. This stand-alone system allows the quasi-continuous monitoring of dissolved He, Ar, Kr, N<sub>2</sub> and O<sub>2</sub> every 12 minutes over several days. Similarly, Visser et al <sup>46</sup> developed also their own portable NG-MIMS for quasi-continuous measurements of the whole suite of dissolved noble gases. However, the NG-MIMS remains sensitive to the sampling conditions as it requires the collection of water samples that are sequentially analysed (every 5 minutes). Furthermore, the available field quasi-continuous techniques (GE-MIMS and NG-MIMS) do not allow so far the measurement of all major dissolved gases.

We propose here a new approach for the continuous field measurement of dissolved gases in aquatic environments with a CF-MIMS (Continuous Flow Membrane Inlet Mass Spectrometer). Through this technique, natural waters (surface water or groundwater) are directly brought to a semi-permeable membrane at a constant flow rate for the continuous measurement of dissolved gases. With an original calibration procedure, the CF-MIMS allows the continuous monitoring of dissolved noble and reactive gases (He, Ne, Ar, Kr, Xe, N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) over a large concentration range. After presenting the details of the analytical development, the capabilities of the CF-MIMS are evaluated through two field applications: two groundwater tracer tests with dissolved <sup>4</sup>He and a well-logging of dissolved gases.

Method

System description

Many MIMS systems are currently available on the market for different applications. The design and conception of the CF-MIMS (HPR-40) was carried out by the private supplier Hiden Analytical. According to the specification requirements, the instrument dimensions (0.150 m<sup>3</sup>), weight (55 kg) and shielding (reinforced frame mounted on Silent Bloc<sup>®</sup>) make the CF-MIMS a mobile and resistant tool designed for field experiments.

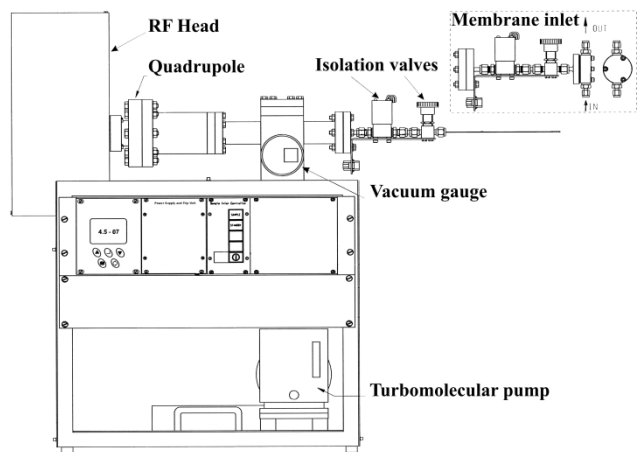


Figure 1: Representation of the CF-MIMS adapted from Hiden Analytical HPR40 manual.

Although its robustness, the CF-MIMS consists in a leading-edge analytical instrument for dissolved gas measurements. Equipped with a membrane inlet connected to the vacuum of a Quadrupole Mass Spectrometer (QMS around 10<sup>-5</sup> Torr), the CF-MIMS shown in figure 1 allow the direct permeation of dissolved gases from liquids to the mass spectrometer. Inside the QMS, dissolved gases are ionised using an oxide coated iridium filament allowing the selection of ionisation energies (between 4 and 150 eV) and emission intensities (between 20 and 5000  $\mu$ A). Once ionised, dissolved gases are separated by the quadrupole according to their mass to charge ratios (m/z ratios). Then, the detection of dissolved gases is performed either by a Faraday cup or a single channel electron multiplier (SCEM). Finally, the CF-MIMS

allows a direct and continuous measurement of dissolved gases at the high frequency of 1 dissolved gas measurement every 2 seconds.

## Optimisation techniques

### Membrane

The originality of MIMS systems lies in the inlet that uses a semi-permeable membrane to measure directly the dissolved gases of the water. The choice of a suitable membrane is therefore essential to ensure the maximal permeation of the targeted dissolved gases. Laboratory experiments have been carried out at Hiden Analytical to select or create the best membrane for our purposes by comparing different types of membrane (PDMS, Biaxially oriented PET, X44<sup>®</sup> polymer). With an enhanced noble gas permeability and a suitable gas exchange surface (16 cm<sup>2</sup>), the membrane X44<sup>®</sup> has been selected for our CF-MIMS. This membrane inlet system (figure 1) allows a continuous flow measurement of dissolved gases.

### Water vapour entrapment

In order to enhance the sensitivity of MIMS systems to low abundant gases a water trap can be installed just between the membrane inlet and the mass spectrometer <sup>46</sup>. However, the water trap requires a long stabilisation time to remove the totality of the water vapour from the signal and uses lots of electrical power that is hardly available in the field. Since this water entrapment did not significantly enhance signal/noise ratios in our CF-MIMS we chose not to use it.

### Ionisation

Inside the mass spectrometer, optimisation of ionisation procedures can be performed to improve the signal/noise ratio by optimisation of the emission intensity (flow of ionising electrons) or, to a lower extent, by experimental determination of optimal ionisation energies. In the CF-MIMS, the standard ionisation procedure (250  $\mu$ A, 70 eV) has been optimised by increasing the emission intensity in order to enhance the sensitivity to low abundant gases such as Kr and Xe (see Supporting Information).



## Calibration

In order to convert the partial pressures measured by the CF-MIMS into gas concentrations it is necessary to define a proper calibration procedure. In order to account for the different membrane interactions with dissolved gas concentrations, the system is directly calibrated on water flows of known concentration. For the purpose, a calibration chamber has been built in order to saturate a water volume with different standard gas mixtures of known composition while preventing from any atmospheric exchange (see Supporting Information). The Standard Gas Equilibrated Water (SGEW) is continuously brought from the calibration chamber to the membrane using a low voltage impeller pump allowing the monitoring of water saturation until equilibrium is reached.

Measured partial pressures for each gas can be converted into gas concentrations using either an internal or external calibration procedure. The internal calibration consists in the calculation of dissolved gas equilibrium concentrations of different SGEWs using the laws of gas solubility in water<sup>1-8</sup>. The parameters required for the calculation of equilibrium concentrations such as air pressure, water temperature and salinity are continuously monitored in the calibration chamber. In addition, the calibration chamber includes an outlet valve allowing an external calibration by sampling each SGEW for control analysis using classical gas-chromatography techniques (GC-TCD or GC-MS).

The calibration procedure is performed after connecting the membrane inlet to the mass spectrometer and should be implemented when the partial pressure baselines are stable (requiring almost 2 hours to establish an equilibrium between the permeation of gases through the membrane and the mass spectrometer vacuum). Calibration temporal stability has been investigated through a laboratory test that did not indicate any sign of instrumental drift over the 38 hours experiment. Therefore, when the calibration is achieved and as long as the membrane inlet remains connected, the CF-MIMS does not require any additional calibration. Nevertheless, regular sampling (for analysis with classical techniques) always ensures the validity of the calibration for long-term monitoring experiments.

The CF-MIMS calibration is performed at the same flow and temperature as the measurements because membrane permeability to dissolved gases depends on water temperature and flow. Water flow is controlled by an impeller/submersible pump serving the membrane (Q: 4L/min). Calibrations and measurements are performed in a mobile laboratory conditioned at a controlled temperature close to the temperature of the monitored water. However, when natural waters (in a river or in a borehole) show temperature variations while monitoring, the signals measured with the CF-MIMS must be corrected from temperature effects on the membrane permeability.

### Temperature sensitivity

Laboratory experiments have been carried out to determine the influence of the water temperature on the permeability of the membrane X44<sup>®</sup>. The results (see Supporting Information) show that the membrane permeability to gases increases substantially with temperature. Small temperature variations ( $\Delta T \pm 2^\circ\text{C}$ ) can modify the signal acquired at  $17^\circ\text{C}$  from 2.5% to 11.0% depending on the gas considered (He is less sensitive than  $\text{H}_2\text{O}$  to temperature variations). However, the fitted curves allow the calculation of effective permeability coefficients  $\beta_T^i$  of the gas  $i$  at the temperature  $T$  of measurement expressed in equation (1) as the ratio of the partial pressure of the gas  $i$  at the temperature  $T$  on the partial pressure of the same gas  $i$  at the temperature of calibration ( $T_{\text{calib}}$ ).

$$\beta_T^i = \frac{P_T^i}{P_{T_{\text{calib}}}^i} \quad (1)$$

The effective permeability coefficients are used when post-processing the data to correct temperature effects on the membrane permeability for the different gases measured with the CF-MIMS.

### Spectral Overlaps

In MIMS systems, the simplest case consists in measuring dissolved gases directly at their corresponding  $m/z$ . For instance, the partial pressures of He, Ar, Kr, Xe and  $\text{O}_2$  can be respectively associated to the  $m/z$

at 4, 40, 84, 132 and 32. However, in mass spectrometry, spectral overlaps are issues frequently encountered.

The objective of the CF-MIMS is to measure the full suite of noble gases (He, Ne, Ar, Kr, Xe) as well as the most common dissolved gases (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O). These dissolved species coexist in natural waters and unfortunately some of them occur at m/z ratio overlapping with other gases as shown in table 1. Most of the time, the overlapping gases are also among the targeted ones which inhibits the use of traps and getters<sup>46</sup> to remove the overlapping N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and Ar.

**Table 1: Spectral overlaps occurring at measured mass-to-charge ratios.**

m/z	Targeted gas	Main overlap	Second overlap
12	CO <sub>2</sub>	CH <sub>4</sub>	-
14	N <sub>2</sub>	N <sub>2</sub> O	-
15	CH <sub>4</sub>	N <sub>2</sub>	-
20	Ne	Ar	H <sub>2</sub> O
22	Ne	CO <sub>2</sub>	N <sub>2</sub> O
28	N <sub>2</sub>	N <sub>2</sub> O	CO <sub>2</sub>
44	CO <sub>2</sub> /N <sub>2</sub> O	-	-

Without traps and getters, the other way to remove overlapping species at a particular m/z ratio is to optimise ionisation energies. For instance, laboratory tests have been carried out to distinguish Ne signals from <sup>20</sup>(Ar<sub>(II)</sub>) and <sup>20</sup>(H<sub>2</sub>O) or from <sup>22</sup>(CO<sub>2(II)</sub>) and <sup>22</sup>(N<sub>2</sub>O<sub>(II)</sub>) using lower ionisation energies to avoid the second ionisation of overlapping gases at m/z 20 and 22 respectively. Although <sup>20</sup>Ne and <sup>20</sup>(Ar<sub>(II)</sub>) could be separated from <sup>20</sup>(H<sub>2</sub>O), the attempts to fully discriminate (with ionisation energies) Ne signals from <sup>20</sup>(Ar<sub>(II)</sub>), <sup>22</sup>(CO<sub>2(II)</sub>) or <sup>22</sup>(N<sub>2</sub>O<sub>(II)</sub>) were unsuccessful despite the information reported in other works on similar QMS systems<sup>47,48</sup>.

Therefore, we choose to overcome the issue of spectral overlaps by calibrating the CF-MIMS with a variety of suitable standard gases allowing the quantification of these overlaps. The idea here is to quantify the distribution of a given gas on the different m/z ratios of interest. For instance, CO<sub>2</sub> is found at

m/z 12, 22, 28 and 44 (table 1) and its distribution over each of these m/z ratios can be measured and expressed as polynomials (see Supporting Information). This is performed by monitoring the partial pressures at these m/z ratios when saturating a volume of water in the calibration chamber with pure CO<sub>2</sub> and desaturating it with another pure gas (N<sub>2</sub>, Ar, He, etc.). The same rationale applies for N<sub>2</sub> at m/z 14, 15, 28 and for Ar at m/z 20 and 40. The polynomials linking the partial pressures  $P_k^i$  and  $P_l^i$  of the gas  $i$  measured respectively at m/z  $k$  and  $l$  are expressed in equation 2:

$$P_k^i = f(P_l^i) = \sum_{n=0}^N \alpha_n (P_l^i)^n \quad (2)$$

Once fitted to the data, the resulting polynomials allow the determination of relationships between each m/z ratios due to each gas (CO<sub>2</sub>, N<sub>2</sub> and Ar) over a large concentration range. As a result, any significant partial pressure change away from the fitted polynomials indicates an overlap attributable either to Ne, N<sub>2</sub>O or CH<sub>4</sub> depending on the considered m/z. In this case, the partial pressure ( $P_k^j$ ) attributed to the overlapping gas  $j$  can be calculated as the difference between the total partial pressure ( $P_k$ ) measured at m/z  $k$  and the partial pressure ( $P_k^i$ ) of the gas  $i$  at m/z  $k$  as expressed in equation 3:

$$P_k^j = P_k - P_k^i = P_k - \sum_{n=0}^N \alpha_n (P_l^i)^n \quad (3)$$

This method relies on multiple measurements at different m/z ratios of the same targeted gas to guarantee a better precision (the gas is measured twice or thrice) and a better confidence respect to overlaps (the different m/z ratios of a gas usually do not undergo the same overlap).

After calibration and measurement, the data files provided by the CF-MIMS are post-processed using a data processing program implemented in Matlab<sup>®</sup> that calculates the partial pressure  $P_{m/z}^i$  of the gas  $i$  at m/z using the spectral overlap polynomials and the effective permeability coefficients  $\beta_T$  following equation 4:

$$P_{m/z}^i = \beta_T^i * \left[ P_{m/z} - \sum_j \left( \beta_T^j * \sum_{n=0}^N \alpha_n (P_{m/z}^j)^n \right) \right] \quad (4)$$

Dissolved gases undergoing overlaps are hence calculated as the difference between the measured partial pressure at a given  $m/z$  and the sum of partial pressures produced by the overlapping species  $j$  weighted by their effective permeability coefficients ( $\beta_T^j$ ). Therefore, it is essential to properly assess the different overlap polynomials.

Finally, the data processing program calculates and compiles the partial pressures of each gas free from overlaps, determines internal or external calibration coefficients for each gas and provides the dissolved gas concentrations that are delivered as a spreadsheet.

**Analytical performances**

For each dissolved gas, laboratory experiments have been carried out to evaluate the analytical precisions of the CF-MIMS (expressed as the relative standard deviation, RSD) and the detection limits (DL) for reactive ( $N_2$ ,  $O_2$ ,  $CO_2$ ,  $CH_4$ ,  $N_2O$ ) and noble (He, Ne, Ar, Kr, Xe) gases. Table 2 shows the details of the analytical performances of the CF-MIMS measured from three series of monitoring (2 hours) of an AEW kept at a constant temperature ( $17^\circ C$ ). The analytical frequency of the instrument allows the measurement of a  $m/z$  ratio every two seconds (the measurement of gas can require more than one  $m/z$  measurement). Therefore, a measurement cycle of the 10 gases listed in the table 2 takes about 26 seconds.

**Table 2: Experimental assessment of the CF-MIMS gas measurement precisions (RSD) and estimated detection limits (DL). Asterisks refer to DL estimations performed on the basis of  $3 \times RSD$  of the most abundant gas at the measured  $m/z$  for typical concentrations obtained with an AEW ( $CO_2 = 4.3 \times 10^{-4}$  ccSTP/g;  $N_2 = 1.4 \times 10^{-2}$  ccSTP/g).**

Gas	RSD (%)	DL ( $\times 10^{-9}$ ccSTP/g)
$N_2$	0.3	750
$O_2$	0.3	2
$CO_2$	0.3	2000
$CH_4$	2.0	800*
$N_2O$	0.3	900*
He	1.0	0.01
Ne	2.5	6*
Ar	0.3	200
Kr	1.2	0.5

Xe	7.5	4
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As Ne, CH<sub>4</sub> and N<sub>2</sub>O are measured at overlapped m/z ratios, their detection limits depend also on the analytical uncertainty of the main overlapping gas at these m/z ratios (respectively <sup>22</sup>(CO<sub>2</sub>), <sup>15</sup>(N<sub>2</sub>) and <sup>44</sup>(CO<sub>2</sub>)). Table 2 displays an example of the detection limits calculated for Ne, CH<sub>4</sub> and N<sub>2</sub>O for an air equilibrated water ([CO<sub>2</sub>]<sub>atm</sub>=0.04% and [N<sub>2</sub>]<sub>atm</sub>=78.08%) expressed as three RSD of the main overlapping gas. As a result, higher levels of N<sub>2</sub> or CO<sub>2</sub> would increase proportionally the detection limits of Ne, CH<sub>4</sub> and N<sub>2</sub>O.

## Field Applications

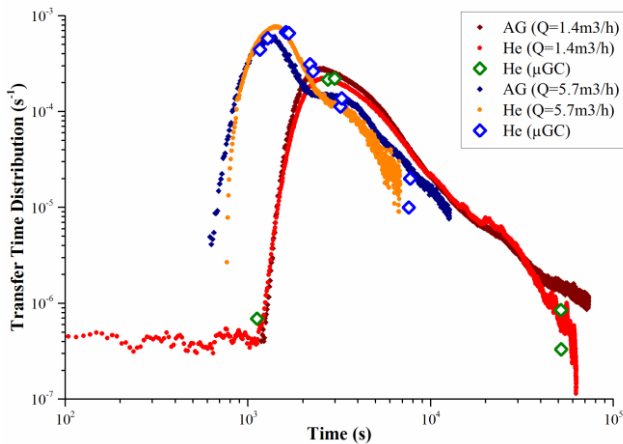
### Groundwater tracer test with dissolved <sup>4</sup>He

In hydrogeology, groundwater introduced tracer tests are usually performed with salts or fluorescent dyes in order to derive the transport properties of aquifers<sup>49–51</sup>. Although little used so far in tracer tests, dissolved noble gases are inert tracers of the physical processes governing conservative transport in aquifers such as advection, dispersion and diffusion<sup>52–55</sup>. Where classical tracers may possibly entail flaws such as toxicity, sorption, degradation or density effects<sup>56–58</sup>, dissolved noble gases can represent a valuable alternative especially when implementing tracer tests in drinking water supply areas<sup>59</sup>. As a result, we decided to evaluate the potential of the CF-MIMS to perform continuous and field measurements through a groundwater tracer test using dissolved <sup>4</sup>He.

The groundwater tracer test was carried out in a fractured aquifer located at the experimental site of Ploemeur (H+ observatory network, Brittany, France) at the contact zone between a granitic formation and the overlying micaschist<sup>60</sup>. This vertical tracer test was performed in a single well (B3) and consisted in the combined pulse injection of dissolved <sup>4</sup>He (60 L of He saturated water) and a fluorescent dye called amino-G acid (7-Amino-1,3-naphthalenedisulfonic acid) in a fracture crossing the borehole at 44.9m (B3.2) while pumping in an hydraulically connected fractured zone (B3.1) found in the same well at

34.0m. Tracer path was constrained into the fracture network using low flow injections (6 L/min) below a single packer placed in the borehole between the two connected fractures.

Figure 2 shows the  $^4\text{He}$  and amino-G acid (AG) breakthrough curves produced respectively by the CF-MIMS and the fluorimeter over two tracer tests performed with two pumping rates (1.4 and 5.9 m<sup>3</sup>/h). For these short tracer tests,  $^4\text{He}$  and AG show similar breakthrough curves (although  $^4\text{He}$  systematically peaks late) as well as similar fitted transport parameters (see Supporting Information) using a semi analytical solution developed by Becker and Charbeneau<sup>49</sup>. For longer tracer tests, the differences between the two breakthrough curves are expected to increase with time due to a higher He diffusion.



**Figure 2:**  $^4\text{He}$  and AG acid breakthrough curves obtained with two different pumping conditions (1.4 and 5.9 m<sup>3</sup>/h). The transfer time distribution curves (s<sup>-1</sup>) refer to the tracer mass flux (g/s) divided by the recovered mass of tracer (g).

This groundwater tracer tests show that the CF-MIMS is able to measure dissolved gas concentrations *in situ* over experiments of several hours and to record ~~instantaneously~~ large concentration gradients with high temporal resolution. The CF-MIMS measurements are directly validated by control sampling performed during the two tracer tests and indirectly by AG breakthrough curves produced by the fluorimeter.

## Well-logging of dissolved gases

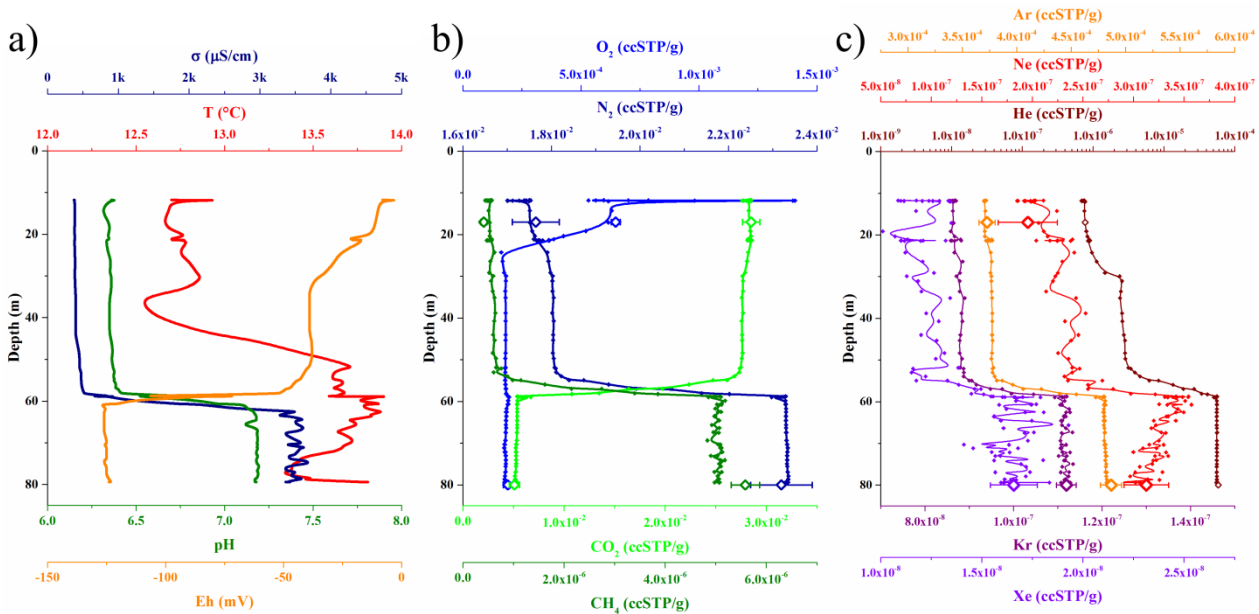
Classically, a first order characterisation of groundwater geochemistry is achieved using a multi-parameter probe allowing the vertical measurement of the field parameters in wells (temperature, electrical conductivity, pH, redox potential and dissolved oxygen). More detailed investigations require additional measurements that are usually performed through the sampling of targeted dissolved species (gases, ions, stable isotopes, etc.). The results of such geochemical characterisation are hardly available on the field and rely inherently on substantial uncertainties associated to sampling (representativeness, contamination and preservation of the sample). Besides, due to practical constraints the exhaustiveness (number of measured parameters, spatial and temporal distribution) of classical geochemical characterisation is often limited in view of the variety and variability of biogeochemical processes in time and space.

In order to test the method developed here, we have investigated the potential of performing a well-log of dissolved gases with the CF-MIMS in a borehole (Pz6) drilled in a schist bedrock and located nearby our laboratory in Rennes (H<sup>+</sup> observatory, Brittany, France). The transportation and power supply of the CF-MIMS has been made possible thanks to the mobile laboratory arranged in an all-terrain truck (CRITEX Lab). This simple experiment consisted in coupling a multi-parameter probe (OTT<sup>®</sup> Hydrolab) to the well-pump (Grundfos<sup>®</sup> MP1) serving the CF-MIMS in order to measure the evolution with depth of dissolved gases concentrations (He, Ne, Ar, Kr, Xe, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>), temperature (T), pH, electrical conductivity ( $\sigma$ ) and redox potential (Eh). The pumping rate (3 L/min) and the logging velocity (2.5 m/min) have been adjusted to the borehole diameter, the number of measured dissolved gases and hence to the measurement frequency of the CF-MIMS (12 m/z every 24 s for 1 measure every meter).

The figure 3 shows the profiles that were obtained at Pz6 for the field parameters (figure 3a), the reactive dissolved gases (figure 3b) and the dissolved noble gases (figure 3c). This well-log consists in two contrasted groundwater bodies and two transition zones: (80-60m) high pH and conductivity, high reactive and noble gas concentrations except CO<sub>2</sub> and low Eh and O<sub>2</sub>; (60-55m) a mixing zone where almost all the parameters change; (55-30m) lower pH, conductivity and dissolved gas concentrations except CO<sub>2</sub> that



increases, low O<sub>2</sub> and higher Eh. The shallowest part of the well (30-12m) shows a transition towards an atmospheric dissolved gas composition.



**Figure 3:** Well-logs performed at Pz6 for (a) water temperature (T), electrical conductivity ( $\sigma$ ), pH and redox potential (Eh); (b) reactive dissolved gases (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>); (c) dissolved noble gases (He, Ne, Ar, Kr, Xe). The large dots in b) and c) refer to samples collected at 17m and 80m. Continuous lines refer to a spline fit of the data points shown as small dots in the figure.

During the well-logging experiment discrete samples were collected and analysed using accepted analytical protocols<sup>46,61,62</sup>. A comparison of these analyses with the CF-MIMS measurements is shown in table 3. Both measurements agree for all dissolved gases analysed within the error of the respective methods.

**Table 3:** Comparison of CF-MIMS measurements with measurements of dissolved gases in Pz6 conducted either (\*) at the University of Rennes by gas-chromatography<sup>61,62</sup> or (#) *in situ* by mass-spectrometry with a NG-MIMS<sup>46</sup>.

Depth (m)	Gas <sup>*#</sup>	Sample (ccSTP/g)	Sample RSD (%)	CF-MIMS (ccSTP/g)	CF-MIMS RSD (%)	Relative difference (%)
17	N <sub>2</sub> <sup>*</sup>	1.76×10 <sup>-2</sup>	3.0	1.75×10 <sup>-2</sup>	0.3	0.5
	O <sub>2</sub> <sup>*</sup>	6.48×10 <sup>-4</sup>	3.0	6.21×10 <sup>-4</sup>	1.3	3.0
	CO <sub>2</sub> <sup>*</sup>	2.85×10 <sup>-2</sup>	3.0	2.84×10 <sup>-2</sup>	0.3	0.5

	<b>CH<sub>4</sub>*</b>	$4.11 \times 10^{-7}$	15.0	$5.29 \times 10^{-7}$	3.0	17.5
	<b>He*</b>	$7.75 \times 10^{-7}$	3.0	$1.19 \times 10^{-6}$	3.5	1.0
	<b>Ne*</b>	$1.96 \times 10^{-7}$	10.0	$2.11 \times 10^{-7}$	5.0	5.5
	<b>Ar*</b>	$3.73 \times 10^{-4}$	2.5	$3.71 \times 10^{-4}$	0.1	0.5
<b>80</b>	<b>N<sub>2</sub>*</b>	$2.32 \times 10^{-2}$	3.0	$2.33 \times 10^{-2}$	0.1	0.5
	<b>O<sub>2</sub>*</b>	$1.90 \times 10^{-4}$	10.0	$1.77 \times 10^{-4}$	0.6	5.0
	<b>CO<sub>2</sub>*</b>	$5.09 \times 10^{-3}$	10.0	$5.24 \times 10^{-3}$	2.1	2.0
	<b>CH<sub>4</sub>*</b>	$5.59 \times 10^{-6}$	5.0	$5.05 \times 10^{-6}$	0.7	7.0
	<b>He<sup>#</sup></b>	$5.88 \times 10^{-5}$	2.0	$5.82 \times 10^{-5}$	1.3	3.0
	<b>Ne<sup>#</sup></b>	$3.13 \times 10^{-7}$	6.5	$3.04 \times 10^{-7}$	4.8	2.0
	<b>Ar<sup>#</sup></b>	$4.87 \times 10^{-4}$	2.0	$4.83 \times 10^{-4}$	0.1	0.5
	<b>Kr<sup>#</sup></b>	$1.12 \times 10^{-7}$	2.0	$1.12 \times 10^{-7}$	0.7	0.5
	<b>Xe<sup>#</sup></b>	$1.66 \times 10^{-8}$	6.5	$1.66 \times 10^{-8}$	5.2	0.5

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296 The field measurement of dissolved noble gas concentrations allow to derive profiles of groundwater

297 recharge conditions <sup>63</sup> and the amount of non-atmospheric <sup>4</sup>He produced by radiogenic U and Th of the

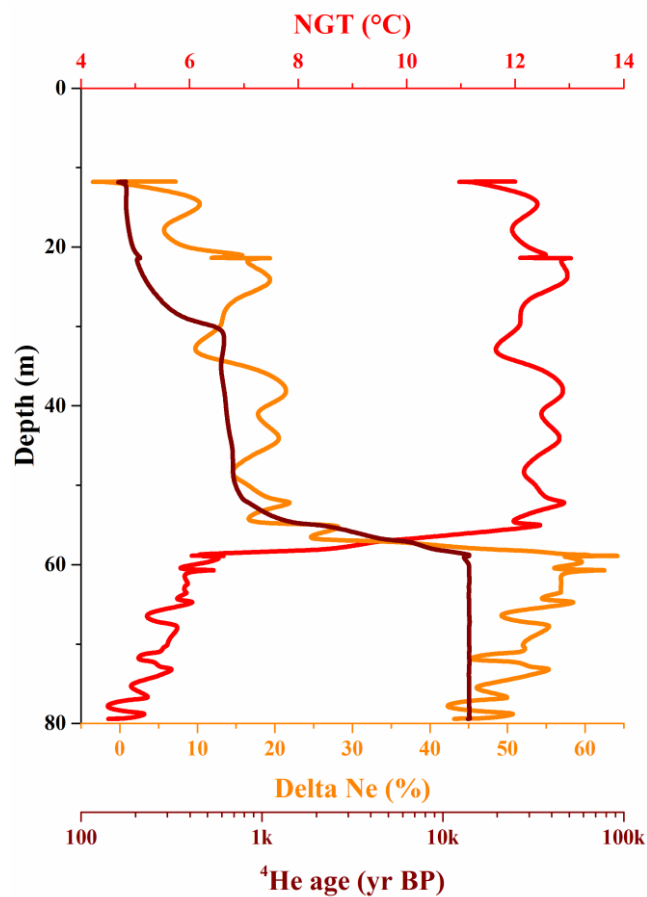
298 rocks. With no mantle He and using a production rate of  $4 \times 10^{-9}$  ccSTP/g/yr for <sup>4</sup>He calibrated on <sup>14</sup>C ages

299 <sup>64</sup>, the groundwater residence time can be assessed for regional groundwater circulations using <sup>4</sup>He dating

300 <sup>17</sup>. Figure 4 shows the field determination of the distribution with depth of noble gas temperatures (NGTs

301 i.e. recharge temperatures), amounts of excess air (commonly expressed as the  $\Delta\text{Ne} = ((\text{CNe}_{\text{meas}}/\text{CNe}_{\text{eq}}) -$

302  $1) \times 100$ ) and <sup>4</sup>He ages.



**Figure 4: Profile of noble gas temperature (NGT),  $\Delta\text{Ne}$  and  $^4\text{He}$  age distribution with depth.**

Similarly to the previous profiles, the figure 4 shows three groundwater layers: (80-60m) low NGTs ( $\approx 5^{\circ}\text{C}$ ) associated with large  $\Delta\text{Ne}$  ( $\approx 50\%$ ) and  $^4\text{He}$  ages ( $\approx 14,000$  yr BP); (60-55m) mixing zone; (55-12m) NGTs around  $11^{\circ}\text{C}$  associated with smaller  $\Delta\text{Ne}$  ( $\approx 10\%$ ) and  $^4\text{He}$  ages ( $\approx 500$  yr BP). The shallowest part of this layer (30-12m) shows decreasing  $\Delta\text{Ne}$  (0% in average) and  $^4\text{He}$  ages ( $\approx 200$  yr BP) towards the water table.

This field experiment illustrates the usefulness of field measurements of dissolved gases for the characterisation of groundwater chemistry and the determination of groundwater origins. The field continuous measurements performed with the CF-MIMS make available a quantity of valuable distributed information so far inaccessible during field works.

## Discussion

### Calibration

Precise dissolved gas measurements with a CF-MIMS can only be achieved with a proper calibration procedure which is not so trivially accomplished because it is performed on SGEWs (a precise determination of their composition is essential) with a water flow and temperature dependent membrane permeability (a precise determination of these effects is also necessary). In addition, calibration of Ne, CH<sub>4</sub> and N<sub>2</sub>O require a special care (use of additional SGEWs) in order to overcome spectral overlap issues.

When the calibration procedure is properly achieved and as long as the membrane inlet remains connected to the mass spectrometer, the CF-MIMS allow a continuous monitoring of dissolved gases over relatively long experiments (days or weeks) without additional calibration (standard bracketing). The latter would alter the benefits of the continuous measurements since the CF-MIMS measurements require as much stability as possible. For long monitoring experiments we thus recommend a regular sampling to ensure the validity of the calibration. So far, biogeochemical clogging of the membrane has not been observed which might be explained by the nature of the membrane X44<sup>®</sup>.

### Capabilities of the CF-MIMS

First, the dissolved gas tracer tests demonstrate the ability of the CF-MIMS to perform field dissolved gas measurements accurate enough to produce appropriate breakthrough curves during groundwater tracer tests. This experiment exhibits the instrument capabilities for high-frequency measurements and its rapidity to quantify large concentration gradients. The CF-MIMS offer new perspectives for groundwater tracer tests enabling the use of new tracers (noble and reactive gases) and allowing a combined injection of several tracers of different nature (salts, fluorescent tracers, dissolved gases, etc.).

As for tracer tests, the well-logging experiment demonstrates the ability of the CF-MIMS to work at high-frequency *in situ* and provide accurate environmental measurements allowing in this case the determination of groundwater recharge conditions, groundwater residence time and redox conditions profiles. These field continuous measurements do not only solve the problems associated to sampling (representativeness, contamination or preservation of samples) but also, taken as a whole, improve the quality of the information carried by each value of the dataset (enhanced representativeness with distributed measurements and enhanced precision with several replicates). Therefore, the CF-MIMS gives access to spatially and temporally distributed data of great significance that represents an important breakthrough for environmental measurements.

In addition, the CF-MIMS ability to produce field continuous measurements allows the scientist to visualise and interpret the data directly on site allowing a better definition of field experiment strategies and a higher flexibility when implementing them. Finally, the rationale behind the CF-MIMS technology consists in bringing back environmental scientists on the field to get a much more thorough understanding of the site structure and properties all along the experiments.

### Potential Applications

Once installed in the mobile laboratory, the CF-MIMS has the required mobility to perform *in situ* measurements in a large diversity of accessible areas (boreholes, rivers, vadose zone, sea or lake shores, wetlands). In these sites, the high-frequency and multi-tracer measurements offered by this instrument allow the observation of a variety of stable to highly-transitory physical, chemical or biological phenomena modifying dissolved gases concentrations (water flow, mixing, degassing, biochemical consumption/production of one or more gas(es)). Therefore, the CF-MIMS is a valuable tool for the field characterisation of biogeochemical reactivity in aquatic systems, aquifer and river transport properties, groundwater recharge conditions, groundwater residence time ( $^4\text{He}$ ,  $^{40}\text{Ar}$ ) and aquifer-river exchanges.

## Associated Contents

## Supporting Information

Measurement settings, Instrumental drift, Temperature Sensitivity, Calibration standard gases, Overlap extents, Tracer test details, Part List. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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