

Article

Sensing Hydrogen Seeps in the Subsurface for Natural Hydrogen Exploration

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Abstract: The recent detection of natural hydrogen seeps in sedimentary basin settings has triggered significant interest in the exploration of this promising resource. If large economical resources exist and can be extracted from the sub-surface, this would provide an opportunity for natural hydrogen to contribute to the non-carbon-based energy mix. The detection and exploration of hydrogen gas in the sub-surface is a significant challenge that requires costly drilling, sophisticated instrumentation, and reliable analytical/sampling methods. Here, we propose the application of a commercial-based sensor that can be used to detect and monitor low levels of hydrogen gas emissions from geological environments. The sensitivity, selectivity ($K > 1000$), and stability (< 1 ppm/day) of the sensor was evaluated under various conditions to determine its suitability for geological field monitoring. Calibration tests showed that the hydrogen readings from the sensor were within $\pm 20\%$ of the expected values. We propose that chemical sensing is a simple and feasible method for understanding natural hydrogen seeps that emanate from geological systems and formations. However, we recommend using this sensor as part of a complete geological survey that incorporates an understanding of the geology along with complementary techniques that provide information on the rock properties.

Keywords: hydrogen; sensor; seeps; environmental monitoring; soil gas; geological survey



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1. Introduction

The transition to low emissions is gaining widespread acceptance, with hydrogen expected to play a major role in achieving a net zero emissions energy future. Currently, hydrogen is primarily produced via two pathways, either through thermochemical means, which involve the use of fossil fuel feedstocks, or through electrochemical means, which use an electrical current to split water into hydrogen and oxygen [1]. While the hydrogen industry and the technologies developed are scaling up [2], currently, there is no method that can be used to deliver the required quantities of hydrogen. The exploration and production of natural hydrogen, also called “white or gold” hydrogen, is one promising way to obtain potentially large quantities of green hydrogen compared with the “blue” one produced from methane [3–5]. There is significant interest in understanding natural hydrogen geological systems with a focus on seeps, as the modern history of oil and gas exploration began in the 19th century with the digging and drilling of oil seeps [6,7]. Surface emanations called “fairy circles” are often associated with high hydrogen soil gas measurement and have been described in numerous countries such as Russia, Brazil, Mali, Australia, and the United States [8–12].

Determining the hydrogen concentration and the assessment of hydrogen gas seeps in the environment is an important part of not only hydrogen exploration, but also for ensuring that any hazardous leaks are minimal. The hydrogen content of soil-gas is typically tested at the surface of natural hydrogen seeps with various analytical techniques. Commonly, air

and gas samples are collected and sent to a laboratory for analysis using techniques such as gas chromatography. Although this method can provide relatively accurate quantitative information regarding the hydrogen concentration in air samples, it is unable to deliver real-time data and is not suitable for long-term field deployment. To address the limitations associated with existing laboratory techniques, there has been increasing interest in the development of sensors and sensing materials for hydrogen detection. More importantly, a few analytical techniques and sensors have been used to monitor hydrogen leaks from geological formations [5,13,14]. Recently, it has been shown that certain portable analysers may provide more reliable information regarding the presence and absence of hydrogen near surface settings in Western Australia [12].

There are several types of sensors that are currently useful for hydrogen detection in atmospheric environments [15–17]. Electrical resistance metal oxide sensors are a very common type of gas sensor and are widely available. In these sensors, the interaction of a gas species changes the electrical resistance of a metal oxide (often SnO_2), which forms the sensor signal. Metal oxide sensors are highly sensitive and can often achieve lower detection limits of 5–10 ppm. Unfortunately, they are sensitive to humidity changes and have multiple cross sensitivities. In principle, they respond to almost any gas, including water vapour; however, when doping the metal oxide with various materials it can make the sensor more responsive to one gas molecule over another [16]. These types of sensors are often very low cost and by using a combination of sensors and appropriate data processing, it may be possible to deconvolute the response from a mixture of gases. Some types use a proprietary molecular sieve coating that prevents cross sensitivity to many other gases including methane. Electrochemical sensors that employ amperometric methods are also commonly used for hydrogen detection. These sensors comprise a miniature electrochemical cell including a working electrode (where hydrogen is oxidised) and a counter electrode allowing a reduction process to take place (typically oxygen from air) [16,18]. Most sensors use a liquid electrolyte such as sulfuric acid and a reference electrode. Electrochemical sensors are available with different concentration ranges and can typically detect hydrogen between 10–2000 ppm. Cross sensitivity to other gases is generally much lower than metal oxide sensors; however, some are strongly affected by CO and, to some extent, H_2S , NO, and ethylene. Many of the commercial sensors incorporate a filter or membrane to reduce sensitivity to certain gases such as CO. Similar to metal oxide sensors, electrochemical sensors are also strongly affected by changes in temperature. However, most manufacturers do supply a transmitter board that will compensate for temperature, provided that the sensor is used within its specified humidity range. In many cases, electrochemical sensors have the disadvantage of using a liquid acid electrolyte that can absorb or lose water depending on the humidity level. Very high humidity's (above 90–95%) can even cause the electrolyte to swell and then leak. Some electrochemical sensors use a solid polymer electrolyte, which eliminates the issue of leakage at high humidity and extends the sensor lifetime to 5 years. This may be useful for autonomous long-term monitoring equipment. In addition to metal oxide and electrochemical sensors, several other technologies exist for hydrogen detection, which involve laser-based absorption spectroscopy [19] and Raman spectroscopy [20].

Numerous small handheld gas monitors have been designed to investigate gases emerging from landfill sites. More specifically, the commercial system from Geotech (GA5000) is one such device that has recently been deployed in various natural hydrogen research projects [10,12]. The GA5000 gas analyser is relatively simple to operate and given that it is light to carry along with having the ability to provide long-term measurements, it is ideal for remote field studies. The aim of this study is to determine if a commercial-based hydrogen sensing technology is able to quantify hydrogen gas emanating from geological formations. Information on the exact hydrogen sensor used in the GA5000 is unavailable; however, it is stated by the manufacturer to be based on electrochemical detection [21]. The response of the GA5000 gas analyser was initially evaluated in the laboratory through calibration tests that comprised different gas mixtures. The second part of the investigation

involved the application and field deployment of the gas analyser for hydrogen seep detection. The primary objective of this research is to investigate its sensitivity, selectivity, and suitability for directly determining hydrogen gas emissions relevant to source rock characterisation and hydrogen resource development.

2. Materials and Methods

2.1. Sampling Site and Geology

A site located northwest of Kalgoorlie, in the Western Australian goldfield province, was selected for this natural hydrogen seep study. The site is underlain by the Yilgarn Craton, which is comprised of ancient igneous and metamorphic rocks and is in contrast to our previous work in the sedimentary North Perth Basin [12]. The area also contains numerous surface features resembling fairy circles, which, as mentioned above, have been associated with high hydrogen soil gas measurement. Figure 1 also shows that the region contains north-northeastern fault systems deeply rooted in the basement and associated with numerous gold deposits. Field measurements were conducted over 4 days in early September 2021 and were performed during daylight hours between 7 a.m.–6 p.m. No rain occurred during the field trip and daily maximum temperatures for Kalgoorlie-Boulder were between 24.1–31.4 °C (Australian Government, Bureau of Meteorology).

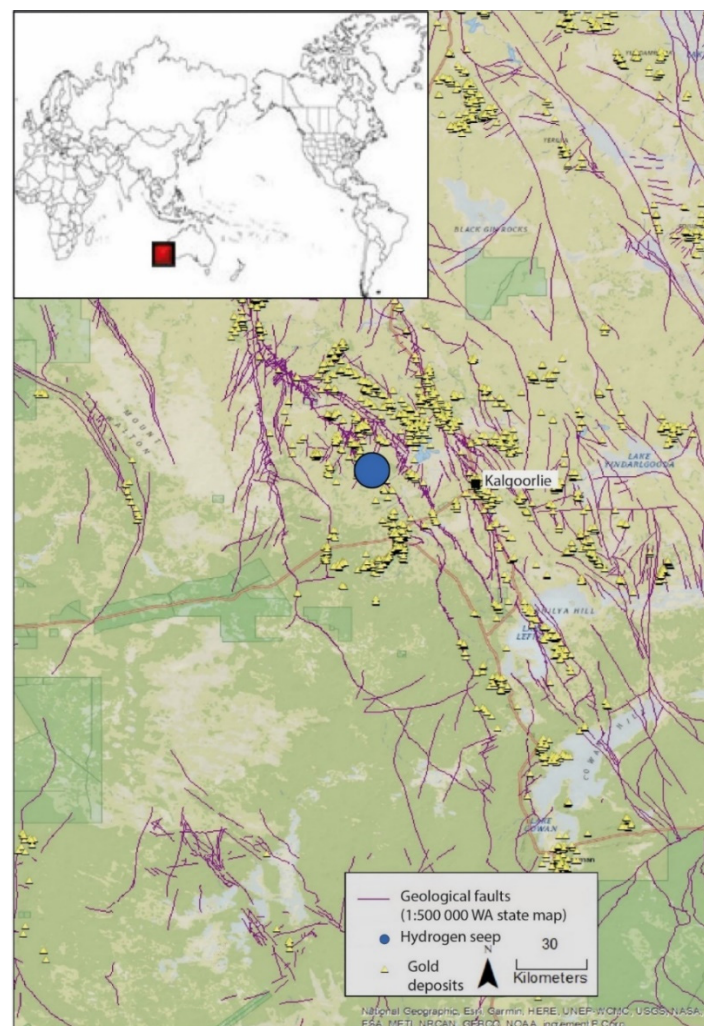


Figure 1. Field example location, northwest of Kalgoorlie, WA [22,23].

2.2. Sensor Stability

All of the hydrogen sensing measurements were performed using the GA5000 sensor (Geotech, Coventry, UK). The sensor was initially calibrated by connecting multicomponent standard (supplied by BOC 89 ppm $\pm$ 4 ppm hydrogen, 93 $\pm$ 5 ppm methane, 91 $\pm$ 5 ppm helium, 508 $\pm$ 10 ppm carbon monoxide) to the inlet via a demand flow regulator (Scientific Gas Australia Pty Ltd., Banksmeadow, Australia). Regular measurements were then made to investigate the stability of the instrument using the same gas standard. The measurements were run for long enough for the readings to stabilize ($\sim$ 90 s).

2.3. Sensor Linearity and Effect of Methane

Hydrogen gas standards were prepared by mixing with nitrogen using a flow controller and Figure 2 displays the experimental setup. To generate the reference gas, we used three cylinders each attached to its own mass flow controller (MFC). The MFCs were attached to a three to one manifold so the gas exiting the manifold was mixed according to the flow of each individual MFC.

Table 1 shows the gases used for the sensor testing and calibration, which are as follows: pure nitrogen (supplied by Coregas as 5.0 grade) (A), 5% hydrogen in nitrogen (supplied by BOC as 5 $\pm$ 0.25% H₂ in N₂ balance) (B), and 1% methane in nitrogen (supplied by BOC as 1.00 $\pm$ 0.05% methane in N₂ balance) (C). The mass flow controllers were of the red-y series from Vögtlin. The MFCs are capable of very precisely controlling the flow of gas coming out of each cylinder in the range from 0 to 1000 mL/min. By regulating the flow rates on each of the three different MFCs, the concentration of methane and hydrogen at the manifold outlet is controlled (see Table 2). The gas mixture is then sent to a buffer chamber so that the methane concentration can be measured with the methane sensor (Aeris Pico natural gas analyzer, Hayward, CA, USA). The output from the methane sensor is sent to a second buffer chamber so the GA5000 can measure the hydrogen concentration. The buffer chambers are not hermetically sealed. Positive pressure inside the chamber ensures that there is no ingress of atmospheric air, which is achieved by setting the flow from the manifold greater than the flow coming into the methane sensor, and likewise the flow coming out of the methane sensor is higher than the flow going into the GA5000. The effect of methane on the hydrogen gas reading was tested by studying the GA5000 sensor response as a function of methane concentration. In addition, studies were performed to investigate the effect of sensor drift and stability.

Table 1. Calibration gas mixtures with different amounts of nitrogen, hydrogen, and methane.

Composition of Cylinder	A	B	C
Nitrogen	100%	95%	99%
Hydrogen	0%	5%	0%
Methane	0%	0%	1%

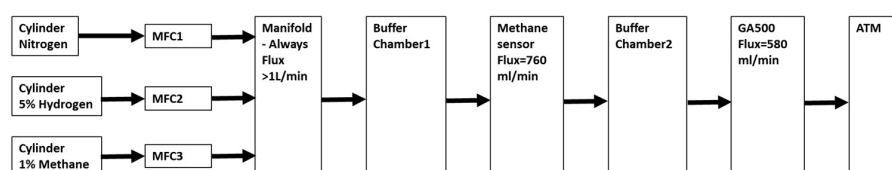
Table 2. The conditions used to generate the variable gas mixtures for sensor calibration and testing.

Experiment Number	Cylinder Flow Rates (mL/min)			Theoretical Manifold H ₂ Concentration (ppm)	Theoretical Manifold CH ₄ Concentration (ppm)
	A	B	C		
1	1000	0	0	0.0	0.0
2	1000	0	50	0.0	469.8
3	1000	0	100	0.0	897.5
4	1000	0	200	0.0	1647.2
5	1000	2	0	99.8	0.0
6	1000	2	50	95.1	468.9
7	1000	2	100	90.9	895.9
8	1000	2	200	83.4	1644.4
9	1000	4	0	199.2	0.0
10	1000	4	50	189.9	468.1
11	1000	4	100	181.4	894.2
12	1000	4	200	166.5	1641.7

Table 2. Cont.

Experiment Number	Cylinder Flow Rates (mL/min)			Theoretical Manifold H ₂ Concentration (ppm)	Theoretical Manifold CH ₄ Concentration (ppm)
	A	B	C		
13	1000	8	0	396.8	0.0
14	1000	8	50	378.3	466.3
15	1000	8	100	361.5	891.0
16	1000	8	200	331.9	1636.2
17	0	0	1000	0.0	10,000.0
18	0	2	1000	101.2	9979.8
19	0	4	1000	202.0	9959.6
20	0	8	1000	402.4	9919.5

(a)



(b)



Figure 2. (a) Experimental setup flow diagram showing different components of the setup and (b) photograph of the setup including: cylinders (bottom), mass flow controller in red, computer to control the mass flow controller, GA5000 (middle left), and methane sensor (far left).

2.4. Field Measurements

Field measurements involved the calibrated GA5000 analyser coupled with an 80 cm stainless steel tube, as presented by other authors [16]. Briefly, an 80 cm long, $\frac{1}{4}$ inch diameter stainless steel tube is attached to the inlet of the GA5000 via a 1 m long, $\frac{1}{4}$ inch diameter flexible silicone tube. An inline filter is fitted before the inlet to prevent dust from entering the instrument. The first 20 cm of the steel tube at the end farthest from the GA5000 is perforated by 2 mm holes every 5 cm. To perform a measurement, the instrument is turned on and allowed to perform its warmup cycle. A 12 mm-diameter hole is drilled into the soil using a 1 m long masonry drill bit and a battery powered drill. As a result of the variation in soil type, it was not possible to always drill to the same depth which varied between 20 cm to 1 m. If at least 20 cm could not be reached, a new hole was drilled in another location or the result was discarded. The stainless-steel tube was immediately inserted into the hole as soon the drill was withdrawn and the measurement started. The measurement was conducted until the hydrogen readings stabilized, reached a maximum value, and then began to fall, which was typically 30 to 90 s, depending on the hydrogen level. Profile measurements were made about every 10 m over a distance of 350 m.

3. Results and Discussion

3.1. Sensor Response and Stability

Although the GA5000 gas analyser was developed as a portable instrument that does not require frequent calibration, very little information exists regarding its stability and suitability over extended periods of operation and measurement. To investigate its long-term analytical performance, the instrument was tested at regular intervals, noting that the same sensor was used throughout the entire study. The GA5000 was calibrated with a multicomponent standard containing 89 ± 4 ppm hydrogen and the same standard was then measured over time. The results obtained are shown in Figure 3. The hydrogen gas readings varied between 85 ± 5 ppm over a seven-day period, which represents a variation of about 6%. Significant drift in the sensor actually occurred immediately after the calibration, but then become more stable with time. Over the total period, the response changed from 89 ppm to 81 ppm, which represents a sensor drift rate and stability less than 1 ppm per day. Evidently, the response to hydrogen gas did not deviate considerably with time, suggesting that long-term exposure does not pose any major problem for the sensor. This study shows that the GA5000 gas analyser does not undergo any significant deterioration in response over a seven-day period and that the sensor may be suitable for long-term monitoring studies in the field.

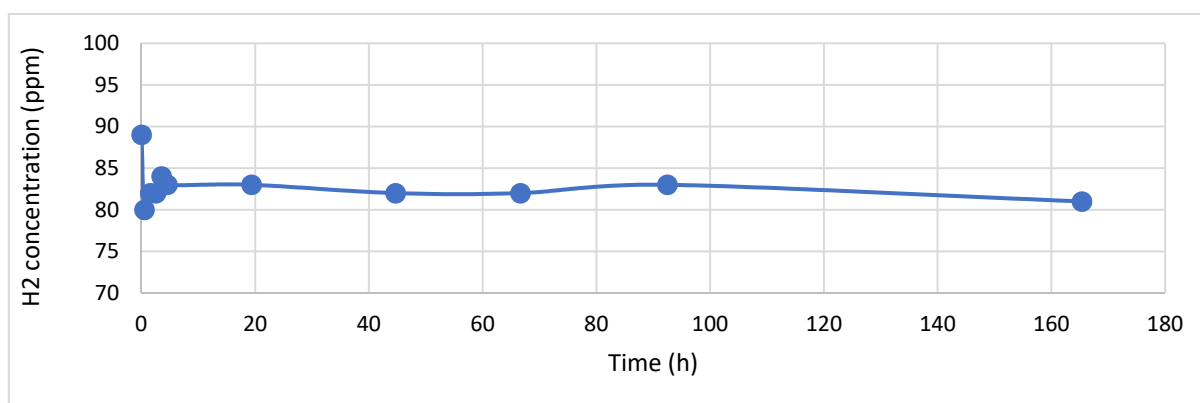


Figure 3. Evaluation of GA5000 sensor stability as a function of time. The readings were obtained by exposing the sensor to a known hydrogen gas concentration.

The response of the analyser/sensor was investigated against hydrogen standards generated with the mass flow controllers, including different levels of methane. It was

shown that the sensor responded to the hydrogen gas mixtures and Figure 4 shows a typical calibration curve where methane was also present at around 10,000 ppm. Regression analysis revealed that the sensor gives a linear response to hydrogen over the 0 to 400 ppm concentration range. Interestingly, the hydrogen concentration reading obtained from the GA5000 sensor was slightly higher than the expected/known value. However, given that the uncertainty in the original standard is 4.5%, the uncertainty of standard preparation (both cylinders B and C) is 5%, and the instrument is known to drift by around 6%, then the total uncertainty is around 20.5%. The readings from the GA5000 are therefore within the error bars.

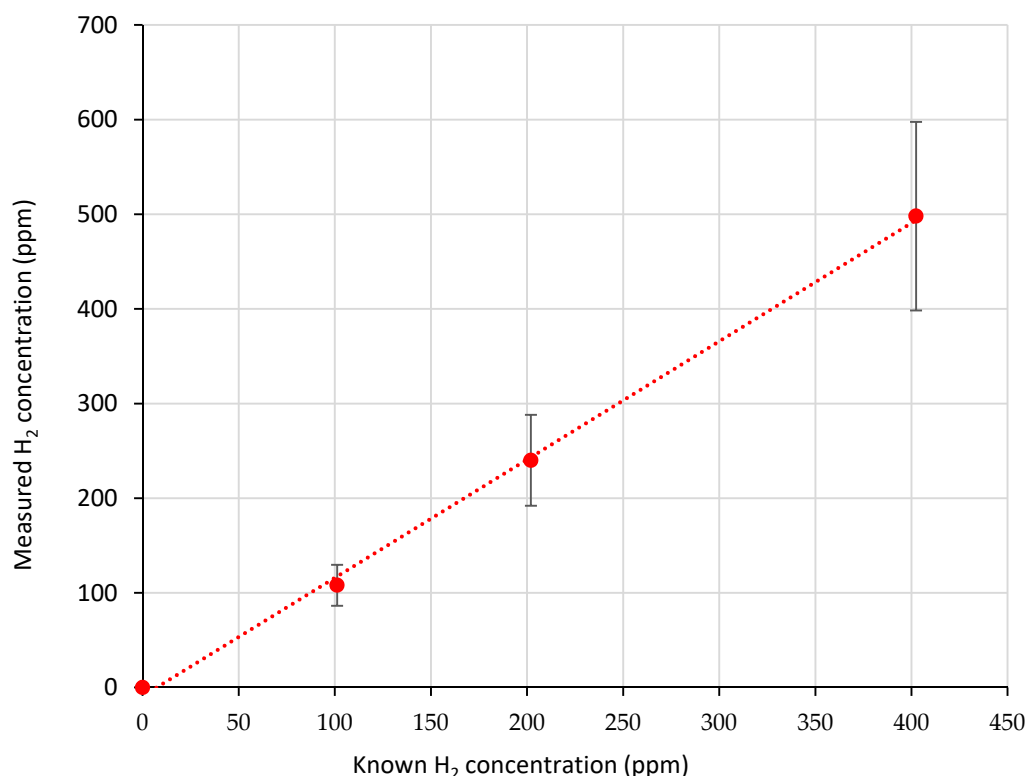


Figure 4. Measured hydrogen concentration (GA5000) vs. known hydrogen concentration (mass flow controllers) for experiments containing approximately 10,000 ppm methane (experiments 17–20).

3.2. Effect of Methane Concentration

Methane is a common gas that is also present in natural seeps and is a possible chemical interferant when sensing hydrogen. To determine the effect of methane on the hydrogen sensor response, sensor calibrations were performed in the absence and presence of different levels of methane. It is evident from Figure 5 that the hydrogen sensitivity of the GA5000 analyser did not vary significantly with different concentrations of methane. Most critically, the presence of methane did not give any false positive during hydrogen detection and measurement. In other words, the sensor did not respond to methane when no hydrogen was present. This can be seen in Figure 4, as zero hydrogen concentration gives a zero measured concentration, despite the 10,000 ppm methane present. Table 3 summarises the calibration functions/response factors and it is evident that the coefficient of determination in all cases was above 0.99. This study clearly shows that methane does not pose a significant influence on the GA5000 sensor response and this is important in the context of monitoring of hydrogen seeps in geological formations that can also contain high levels of methane. As it is known that electrochemical type hydrogen sensors generally do not have high cross sensitivity to methane, this further confirms our expectation that GA5000 used an electrochemical sensor and that methane does not pose a significant issue for using the GA5000 sensor. The sensitivity of the sensor is related to the slope of the

calibration curve. From Table 3, the calibration slope varied between 1.25 to 1.35. Sensor selectivity is typically the ratio of the targeted analyte sensitivity versus the sensitivity of a potential interferant and is represented by K , where $K = (\text{sensitivity-H}_2)/(\text{sensitivity-CH}_4)$. As the sensor did not respond to methane in the absence of hydrogen, we are unable to calculate the K value, but estimate that it is very high ($K > 1000$).

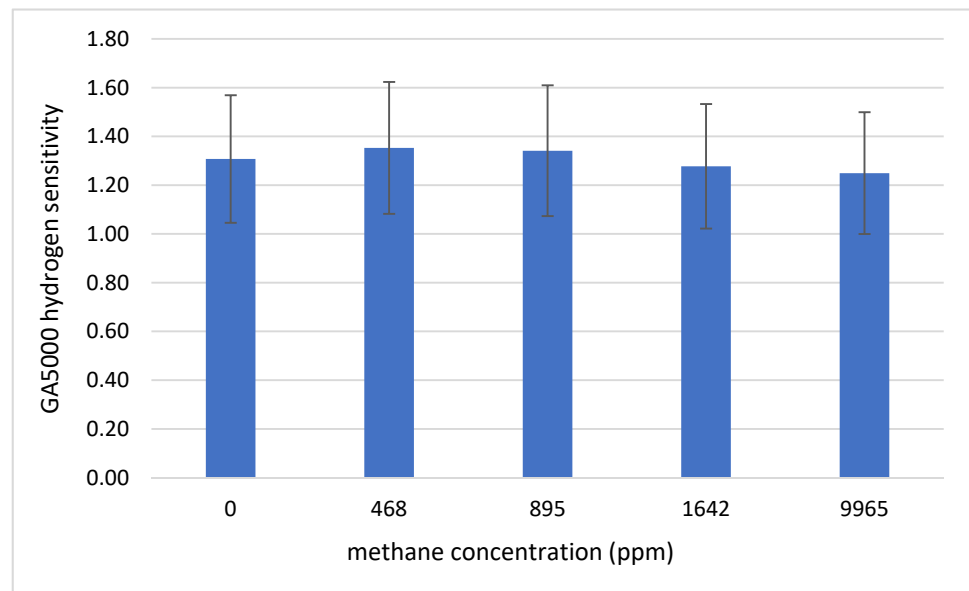


Figure 5. Sensitivity of GA5000 to hydrogen at different methane concentrations where sensitivity is the slope of the GA5000 response vs. theoretical hydrogen concentration curve.

Table 3. Results of linear regression between measured and theoretical hydrogen concentrations at different methane concentrations.

Methane Concentration	Gradient	R ²
0 ppm	1.31 ± 0.27	0.9998
468 ± 2 ppm	1.35 ± 0.28	0.9999
895 ± 3 ppm	1.34 ± 0.27	0.999
1642 ± 6 ppm	1.28 ± 0.26	0.9994
9965 ± 40 ppm	1.25 ± 0.26	0.9986

3.3. Hydrogen Seep Detection

The sensor calibration and testing revealed that the hydrogen gas readings/results from GA5000 drift by around 9% after 1 week. As a result of the use of multiple reference gases in our studies, the measurements of different mixtures created with the mass flow controllers are only accurate to within about 20%, which did encompass the theoretical concentrations of the mixtures. In addition, we established that the sensor was relatively stable over a long period of time (>1 day) with drift less than 1 ppm per day. To further evaluate the sensor under real field conditions, the GA5000 instrument was deployed on a site north of Coolgardie, which is a town located near Kalgoorlie, Western Australia. Figure 6 presents the soil-natural hydrogen gas values, which were measured at a 50 cm depth along a path cross-cutting a hydrogen seep from the centre of the feature to the edge of the surrounding vegetation ring. The record shows high hydrogen values (>100 ppm) at the centre of the seeps and in the external green vegetation ring, with a maximum hydrogen reading of 447 ppm. A minor increase of the hydrogen values up to 31 ppm is also noticeable at the transition zone, between the centre of the feature without vegetation and the sparse vegetation located in the internal ring.

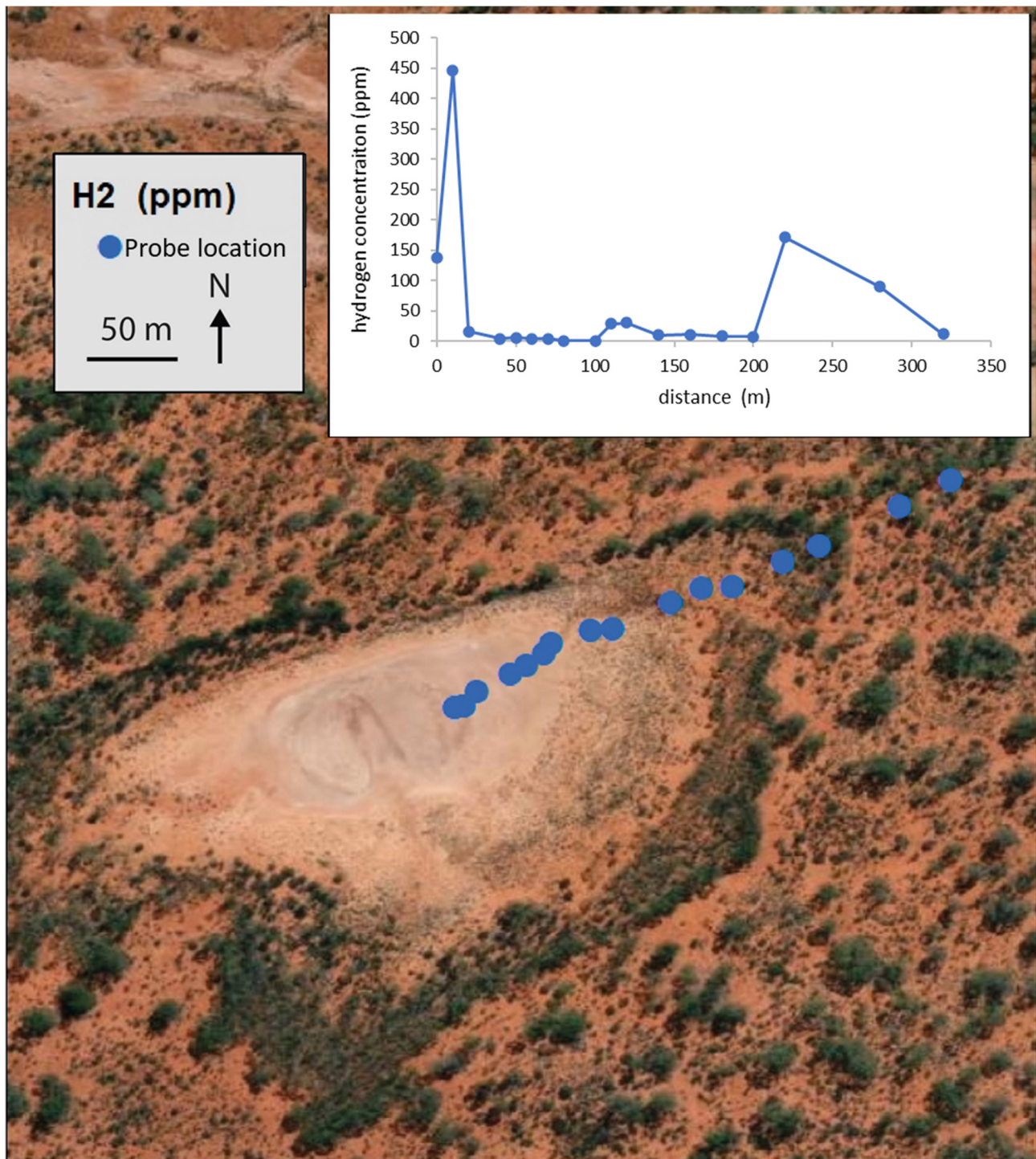


Figure 6. Soil-gas hydrogen measurement with GA5000 along a natural seep profile located north of Coolgardie, WA.

As stated in the introduction, elevated levels of hydrogen in the soil have been associated with “fairy circles”, or circular surface features, particularly in several countries including Australia, Russia, USA, and Brazil. Various theories have been proposed for the origin of hydrogen in these observations. One of these is through the generation of hydrogen from water via water/rock interactions. Several possibilities for this exist, including the process of serpentinization, which occurs when sea water comes into contact with ultramafic rocks along mid ocean ridges and which has been well studied [24,25]. In

essence, this is a redox process where Fe^{2+} from certain rocks is oxidized to Fe^{3+} and H_2O is reduced to form hydrogen. This has also been suggested as a source for hydrogen observed in continental settings if Fe^{2+} rocks are present, such as the hydrogen seep in Brazil [10]. Another possible source for the hydrogen is by degassing of the Earth's mantle or core, which is left over from planetary formation as the early solar system contained abundant hydrogen [26,27]. Another possible source is by mechano-radical processes. Here, constant shearing along tectonic faults causes dissociation of Si-O bonds in silicates, producing surface radicals that can react with water to form hydrogen [28]. Other theories include the decomposition of organic matter and biological activity [26].

The present study revealed hydrogen concentration values of up to 447 ppm in the field. While one of the motivations for studies of fairy circles is for potential commercial development, there are still insufficient data on what level of hydrogen in the soil would indicate a potentially economic hydrogen resource. Studies on fairy circles in the Carolina Bays, USA, found soil hydrogen concentrations above 1200 ppm, although no deeper wells were drilled to evaluate the concentration at a greater depth [11]. Studies on fairy circles in the São Francisco Basin, Brazil, however, which gave soil hydrogen levels of up to 547 ppm, were associated with hydrogen concentrations of up to 40 mol% from nearby wells that were 1500 m deep. This indicates that surface anomalies can be used as an indicator for significant hydrogen deposits. The most significant discovery to date has been in Mali, where gas comprising 98% hydrogen was produced from the Bougou-1 well as a pilot program and was used to supply energy to the local village for about 5 years. Soil hydrogen concentrations across a circular feature near the well reached up to 600 ppm, indicating this as a possible level where useful quantities of hydrogen are present [5].

The Coolgardie area field study returned extremely variable concentration of hydrogen in soil gas along a seep profile, from 0 to more than 400 ppm. These variations can indicate different domains in the seep and location of the free gas escaping; however, numerous external parameters, such as the soil composition and humidity, could influence these variations. For instance, some authors recommend the use of a portable drill operating in percussion mode only (no rotation of the drill bit) [29,30] so as to prevent any production of hydrogen gas through heating/cracking of the organic matter [31–33] and through “mechano-radical” processes linked to the dissociation of silicates in water-saturated rocks [34,35]. This process is supposed to be the origin of high concentrations of H_2 in soil gas associated with active tectonic faults [36,37]. Note that in the case of the Gironde study [29], all drilling made with a rotary drill bit always produced hydrogen concentrations of at least 1000 ppm. This observation highlights the importance of the baseline and type of soil drilled. For instance, in the case of the CSIRO Moora study [12], with the rotary drilling method, the authors observed a fluctuation in the values from 0 ppm, outside of the fairy circles, to 96 ppm in the external ring of the fairy circles. The measurement location and range of values was repeated over three field campaigns and drilling of similar soils outside of the zone of interest returned a zero-hydrogen concentration. This shows the importance of baseline studies and tests, including the heating and water saturation of new soil types, or performing systematic soil XRD analysis.

4. Conclusions

We have shown that the GA5000 gas analyser is a practical and simple method for the detection of hydrogen seeps, which may be relevant for natural hydrogen exploration. Furthermore, the sensor provided readings within 20% of the expected theoretical values and the effect of methane interference on the sensor response was minimal. The methane interference must be interpreted with caution, considering that the presence of high methane concentrations (>10,000 ppm) was not investigated in this study. Although this technique is useful for understanding the presence or absence of hydrogen in near surface seep settings, it does not provide any insight on the hydrogen flux, evolution with time, and potential underlying reservoir. However, we recommend using this sensor as part of a multi-gas survey, with the complementary use of sensors for other gases such as methane/ethane and carbon

dioxide. This study is the start of a larger planned monitoring program that will involve a more detailed and long-term measurements of hydrogen concentration and fluxes.

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