INFLUENCE OF DOPING ELEMENT IN DISTRIBUTED HYDROGEN OPTICAL FIBER SENSORS WITH BRILLOUIN SCATTERING.

ABSTRACT

Distributed hydrogen optical fiber sensor with Brillouin scattering is an innovative solution to measure hydrogen in harsh environment as nuclear industry. Glass composition is the key point to enhance the sensing parameter of the fiber in the target application. Several optical fiber with different doping element were used for measuring hydrogen saturation. Permeability of optical plays a major role to the kinetic of hydrogen diffusion. Fluorine doped fiber increase the sorption and the desorption of hydrogen.

1 INTRODUCTION

Hydrogen is also an important parameter to monitor in radioactive disposal facility such as the envisioned French deep geological repository for long-lived high level and intermediate level wastes. It originates from (i) nuclear waste release (ii) and anoxic corrosion of metallic materials. Its monitoring aims at preserving retrievability of wastes: detecting unexpected release rates would be an indication of potential deterioration of waste packages. It also ensures exploitation security since hydrogen monitoring is a key factor in explosive risk management.

In 2011 in Fukushima nuclear site, deficient fuel cooling resulted in overheating of the fuel, enabling rapid oxidation and generation of large amounts of hydrogen, which ultimately led to the explosions and destructions of the reactor buildings at Units 1 and 3, and possibly fires at Unit 4.

The evaluation of the hydrogen concentration could have helped the exploitation security to manage the risk. Later, a strong need appeared for a hydrogen sensor than could handle very high radiation doses for short times, to characterize the damaged reactors, and the pools where the fuels are stored

Because of high gamma radiation doses, disposal cells are not accessible as soon as exploitation starts and the first nuclear waste package gets in to disposal cell. This implies the hydrogen monitoring system must be robust for decades without any maintenance. It also calls for remote sensing. There is a need for a fine mapping at the scale of the waste sizes, with many measurement points, such as truly distributed optical fiber sensors may provide. Since hydrogen releases are expected small (in the order of 430 mmol/hour releases for each intermediate level nuclear waste) daily evaluations and percent sensitivity would be satisfactory from the safety point of view. The hydrogen monitoring system is planned to work under n

ormal operating condition and, to withstand radiation exposure, in case of an accidental event (as sadly required in Fukushima nuclear disaster).

There are different kinds of hydrogen sensors commercially available and under development. Basic sensor principle is known from decades [1], [2]. Usually, to realize selective hydrogen sensors, specific interactions are selected, among which the most popular are catalytic reactivity and solubility of hydrogen with some noble elements such as palladium and platinum. Either the reaction itself (reaction heat, exchanged charge carriers) or the resulting changes in properties of the sensing material (resistance, volume expansion etc.) can be used to detect and quantify the hydrogen gas concentration. T. Hünter and al [1] classified hydrogen sensors technology in eight categories where he shows pros and cons in detailed. Only thermal sensors offer accuracy as small as ±0.2%. The others are limited to few per cents. Lifetimes are 5 years for the better cases. All these electronic--- ‑ based technologies offer multiplexing possibilities, however limited by cable length, and electronic switch. Concerning the optical optode or optrode [3], they are discrete sensors, limited by their sensitive length. Acoustic sensors are attractive but they are still in development. As a result, selection of a technology must be driven by operating conditions of the specific target application.

The emerging nuclear market imposes new requirements for a hydrogen sensing system able to endure harsh environments: high temperature (up to 300°C) and radiation (gamma rays and

neutrons). No sensor technology listed in [3] can survive such conditions in state because the electronic noise and signal spikes produce inaccurate results and/or unintelligible signals. What is more, electronic hydrogen sensors also poorly fulfil the imposed compatibility norms with respect to explosive atmosphere (ATEX certification).

Optical Fiber Sensors (OFS) offers many advantages compared to traditional electronic sensors: they are quite light, small (expected to be non-invasive) and insensitive to electromagnetic fields, not subject to metallic corrosion (unless a metallic cladding is chosen), and resist to high temperatures. They also make it possible to take measurements over great distances (in the kilometer range) taking advantage of very low attenuation coefficient and multiple sensors can be multiplexed in one fiber. Optical fibres are the only technology providing both distributed sensing and compatibility with radioactive environment.

Several developments of fiber optic sensors to measure the H2 concentration have been reported. Among optical fibre sensors, the previously studied solutions were mainly based on external coatings placed on the surface of the optical fibre, which only serves to convey information (to guide light). Palladium layers were thoroughly studied associated with Fabry‑ Perot cavities [4], on top of a Bragg grating [5]. Mg-Ti has also been tested [6]. These solutions lead to discrete sensors only. More recently, it has been proposed to make use of losses induced by hydrogen diffusion into optical fibres [7], [8]. Pairing absorption bands with a localization process such as OTDR provides distributed hydrogen sensing

2 DISTRIBUTED HYDROGEN OPTICAL FIBER SENSORS WITH BRILLOUIN SCATTERING

2.1 Brillouin scatterring

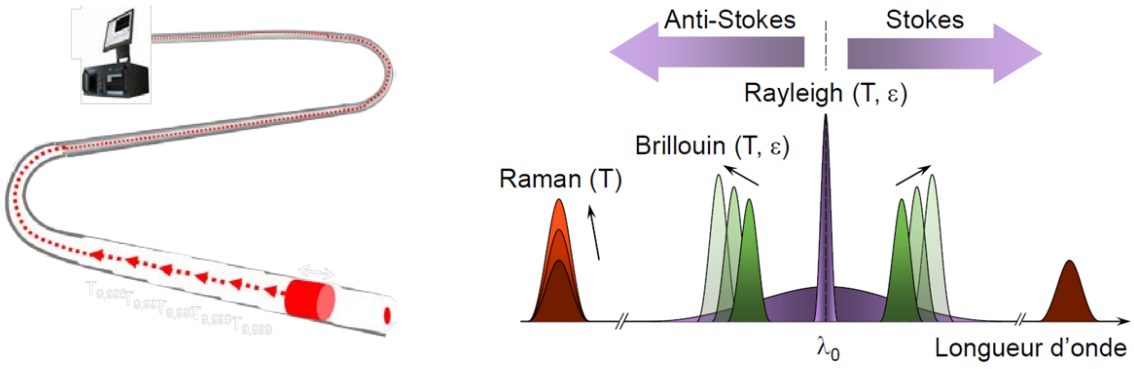

Figure 1: Backscattering spectrum of a monochromatic wave within an optical fiber.

As shown in Figure 1, the light backscattered by an optical fiber segment without any defects or abnormal characteristics is spectrally decomposed into three distinct peaks corresponding to three outstanding phenomena

The first relates to Rayleigh scattering, originated from interaction between the electromagnetic wave propagating in the fiber core and silica impurities. Intensity variations in the backscattered signal at the same wavelength as the injected wave are related with local optical fiber modifications: An abrupt return peak is interpreted as a mirror reflection (connector or damage on the fiber), and a sudden drop in intensity corresponds for example to shear loss. Beyond detection, to conduct temperature or strain measurements, the value of the Rayleigh backscattering signal in optical fibers must be associated with another technique, the simplest being an association with punctual sensors, such as microbend sensors or another configuration that incorporates pre-calibrated losses [9]. In this case the continuously-distributed aspect of the measurement would be lost. In single-mode fibers, polarization measurements may be added [10], parameter quite interesting when application requires pressure or magnetic field sensing.

Raman scattering originates from laser light photon interaction with thermal vibration of silica molecules (thermal phonons). The anti-Stokes absorption mainly depends on temperature. A number of commercially available distributed temperature sensing devices automatically compensate for this loss by analysing the ratio between the Anti-Stokes and Stokes absorption line intensities.

As sketched in Figure 1, another inelastic phenomenon occurs when an optical pulse is launched into an optical fiber, called Brillouin scattering. This Brillouin frequency shift ν_B is linked to the acoustic mode phase velocity [11]. As a consequence, the Brillouin shift variations are known to be proportional to temperature (ΔT) and strain (ε) variations [12] as in equation 1:

$$\Delta \nu_B = C_T \Delta T + C_\varepsilon \varepsilon \quad (1)$$

C_T and C_ε are characteristics of the optical fiber type. At the operating wavelength (1550 nm), for standard G652 single-mode fiber, C_T and C_ε are in the order of 1MHz/°C and 0.05 MHz/με [13]

2.2 Sensor principle

In [14], it was shown that Brillouin spectra shift toward high frequencies, as expected with the increase of refractive index before and after hydrogen exposure like illustrated in Figure 6 for a virgin then saturated sample. At 25°C, with acrylate fiber coating, the Brillouin frequency shift is roughly linear with hydrogen saturation in silica core, with a factor of 0.21 MHz per percentage of H_2. Sensitivity is a parameter that expresses the variation in the sensor response in function of the change of the measurand (in our case gas concentration in the silica matrix).In primary studied, the maximum sensitivity observed was 1MHz for 5% H_2 concentration level.

2.3 Sensing performance and Doping

Stability, response time, Linearity, responsiveness, dynamic range and resistance to harsh environment are function of fibre dopants. The detection-properties of optical fibres depend greatly on their core and cladding composition. Different optical fibers types were made with different doping elements, the table 1 summarize the sample use in the experiment. The samples consist in two coils of 20m of the same fiber coil, one let pristine and the other hydrogenated. Here are plotted the names, codes and types of the fiber samples used:

Table 1 Characteristics of the different samples

Fibre type	***Doping concentration (mol%)***
GeO_2-doped	*3,4*
fluorine	*1,25*
highly GeO_2-doped	*28*

3 EXPERIMENT

3.1 Hydrogenation

Hydrogen diffusion into silica has been thoroughly studied to enhance photosensitivity of optical fibers before fiber Bragg gratings writing [13]. For a standard single mode fiber made of silica, hydrogen diffusion coefficient D (in cm^2/s) is expected to follow Arrhenius equation:

$$D = A \exp(-Ea/RT) \qquad (1)$$

Where the pre-exponential factor A is considered independent of temperature and –Ea (activation energy)= -40190 is case of silica fiber, R = 8.314472 $J.mol^{-1}.K^{-1}$ is the gas constant and T the absolute temperature [5].

Following this equation, hydrogen concentration in air induces hydrogen migration into optical fiber silica core, reversible phenomenon with a saturation level. In the following, using (1) and assuming ambient temperature at 25°C, optical fiber exposure time will be converted into hydrogen concentration ratio to the saturation level into the optical fiber silica core.

Figure 2: Picture of the pressurized chambers and coil sample

In the first run, samples were placed into hydrogen pressurized chambers (15 MPa and 25°C), and measured at different duration of exposure. Total duration reached around 333 hours in 6 steps. It means that the hydrogenation wasn't continuous but made step by step. In the second run, samples were placed continuously under hydrogen during 648 hours in same condition as the run 1.

After the exposure the samples were stored at -25°C to make sure the hydrogen doesn't desorb. The measurements were made at normal pressure and temperature conditions. The room temperature was measured during the continuous measurements.

3.2 Measurement set up

Reference samples (dummy fiber coils) were also used to assess clearly the basics of the proposed system. They were prepared the same way as the samples, from same fiber coils. They underwent the same measurements and manipulations, but never been into hydrogen chambers. Samples were paired (exposed and dummy) with OZ optics B-OTDA (Brillouin Optical Time-Domain Analysis) device [6], working at 1550nm. It provides 1MHz spectral resolution, 10cm spatial resolution over a range of several kilometers. Brillouin scattering originates from optical mode and acoustic waves coupling in silica. When an incident wave propagates in the fiber, a frequency-shifted optical wave (Stokes or anti-Stokes) is created, and propagates backward. The frequency-shift, pointed as the Brillouin frequency υB, is proportional to optical and acoustic parameters with the following relationship:

$$\nu_B = \frac{2 n_{eff} V_A}{\lambda_0} \qquad (2)$$

Where n_{eff} is the effective index of the optical mode, λ_0 the operating wavelength and V_A the sound velocity in silica. Since refractive index is modified by hydrogen diffusion in silica through the formation of OH species in the glass. We demonstrate in previous paper [14] that induces a shift of the Brillouin frequency.

OTDR and spectral measurement enabled full Rayleigh scattering measurement

4 RESULTS

4.1 Rayleigh scattering

As illustrated in Figure 3, measured spectral attenuations confirmed three absorption bands appear in the attenuation spectra of exposed optical fibers, the most important at 1245nm and two smaller at 1165nm and 1130nm, consistently with [9][9]. At 1245nm, losses expressed in decibels increase linearly with hydrogen concentrations, as expected. It is worth noting that for our experimental conditions, we did not observe the OH-absorption-peak at 1380nm, in any of the three fibers. Spectral measurements were very similar for the three doped optical fibers. More precisely, influence of dopants resulted negligible at the complete saturation. However, fluorine-doped fiber seemed more sensitive at low hydrogen contents. As illustrated in Figure 2 on the right side, for 41h duration of exposure (calculated 15% hydrogen content in silica to the saturation level), fluor-doped fiber with the pure silica presents attenuation 5dB larger than the others .

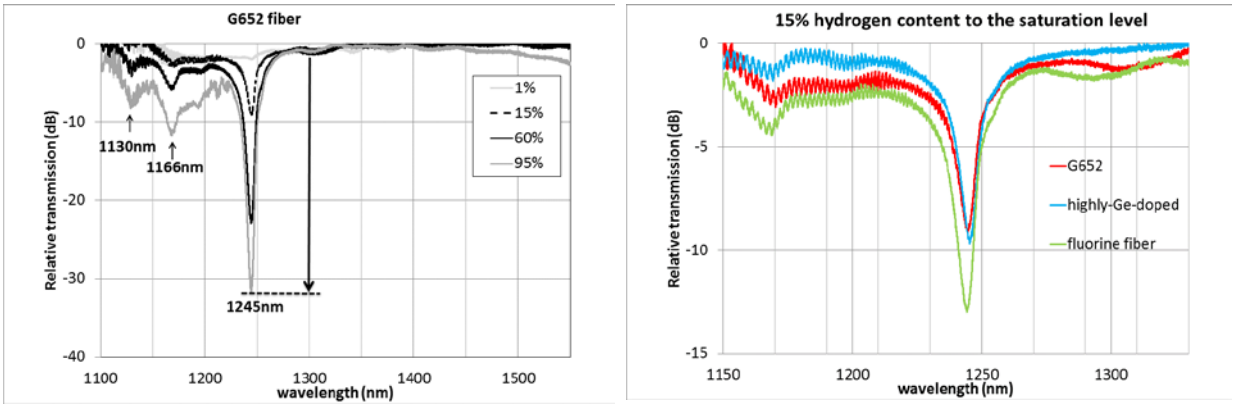

Figure 3: (left) Measured spectral transmission for three hydrogen contents, in the G652 fiber and (right) Focus on the 1245nm absorption peak, after 41h exposure to hydrogen, for the three fibers

We recall that the absorption signal at 1245 nm is directly proportional to the concentration of hydrogen the molecular core of the fiber. An approximate calculation method [17] allows to relate the concentration of molecular hydrogen in the measurement of the induced absorption at 1 .24 pm according to the equation:

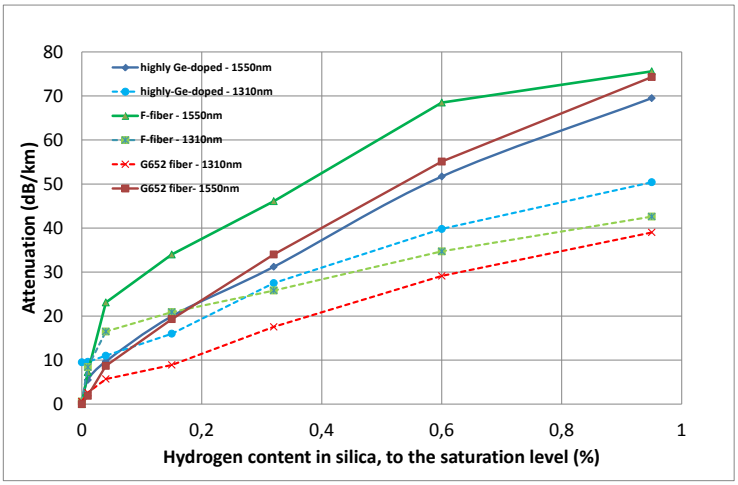

Figure 4: Measured attenuations at 1310nm and 1550nm for the three fibres, as a function of hydrogen content in silica

Distributed Rayleigh measurements were performed with an OTDR device. They confirmed (i) induced losses were perfectly homogeneous along the samples (ii) fluorine fiber is more sensitive than other fibers to small hydrogen exposure durations (Figure 4) results similar at saturation. Although attenuation in the C-band could appear limited in Figure 3 (in front of 1245nm band), it reached 70dB/km at saturation at 1550nm. Consistently with measured spectral attenuations, losses were smaller at 1310nm, limited to approximately 50dB/m at saturation.

4.2 Brillouin Measurement

Fig. 3 illustrates the capability to perform truly distributed hydrogen measurements, connecting dummy optical fiber coils with exposed fibers. In this example, obtained spatial resolution is approximately 2.5m.

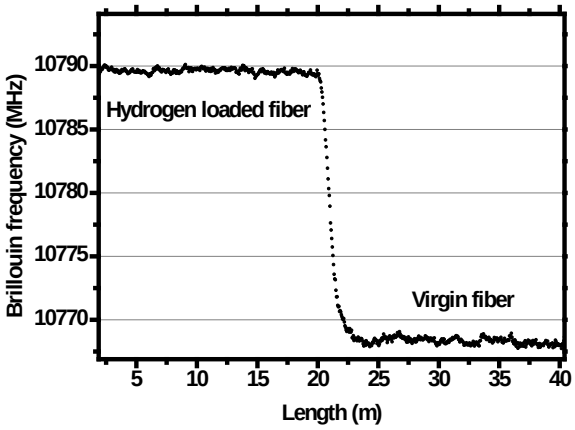

Figure 5: Measured maximal Brillouin frequency as a function of the distance along an optical fiber line made of hydrogenated and saturated sample and virgin (dummy) coils.

In Figure 6, we observed Brillouin scattering is modified by hydrogen content in optical fibers. Brillouin scattering shifts towards high frequencies. Brillouin frequency is reported in Figure 6 as function of calculated hydrogen content ratio to the saturation level in the silica core, for the three optical fibers. Brillouin frequency shift with hydrogen concentrations in the silica core is somewhat linear. Up to 21MHz shift is observed at saturation. Assuming standard coefficients (CT=1MHz/°C, Cε=0.05MHz/με), such a shift would induce an error in temperature (respectively strain) measurement in the order of 21°C (resp. 420µm/m). Similarly with Rayleigh scatterings results, the Brillouin frequency shift (BFS) of F-doped fiber revealed more sensitive to small amount of hydrogen than other fibers. At 1%, BFS is 3.6 where the others are 2.7 and 1 for Ge and high-Ge doped respectively; there is two loading rate for all the fiber. First one is related to Arrhenius law showed in the equation (1). The factor pre-exponential is affected by the doping element like we can see in the table 2. In fact, the diffusion coefficients of hydrogen molecules at 25°C is somewhat affected by the presence of doping. By the presence of Fluorine doping the factor is increasing, these results correlate the one shown in [18]. The crystal lattice is affected by the presence of fluorine.

Table 2: factor pre-exponential for different doping element

Doping element	A (pre-expotential factor)
Fluor	4.1

Ge	2.83
High- Ge	3.3

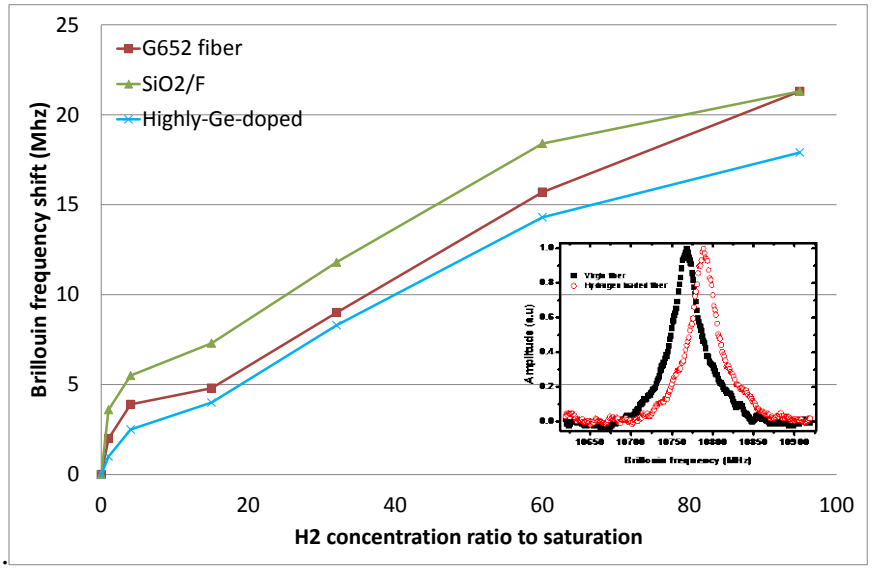

Figure 6: Measured Brillouin frequency shifts in 3 optical fibers as a function of calculated hydrogen content ratio to the saturation level in the silica core.

Hydrogen influence revealed reversible. Samples were left in the hydrogen room for thirteen days after the loading run. Then, Brillouin frequency was measured on loaded samples left at ambient temperature; It down-shifted towards its initial value within approximately 16 days. The same behaviour is observed for the fluorine sample for the desorption process. It is easiest to go in and out for hydrogen if the fluorine is in the glass composition.

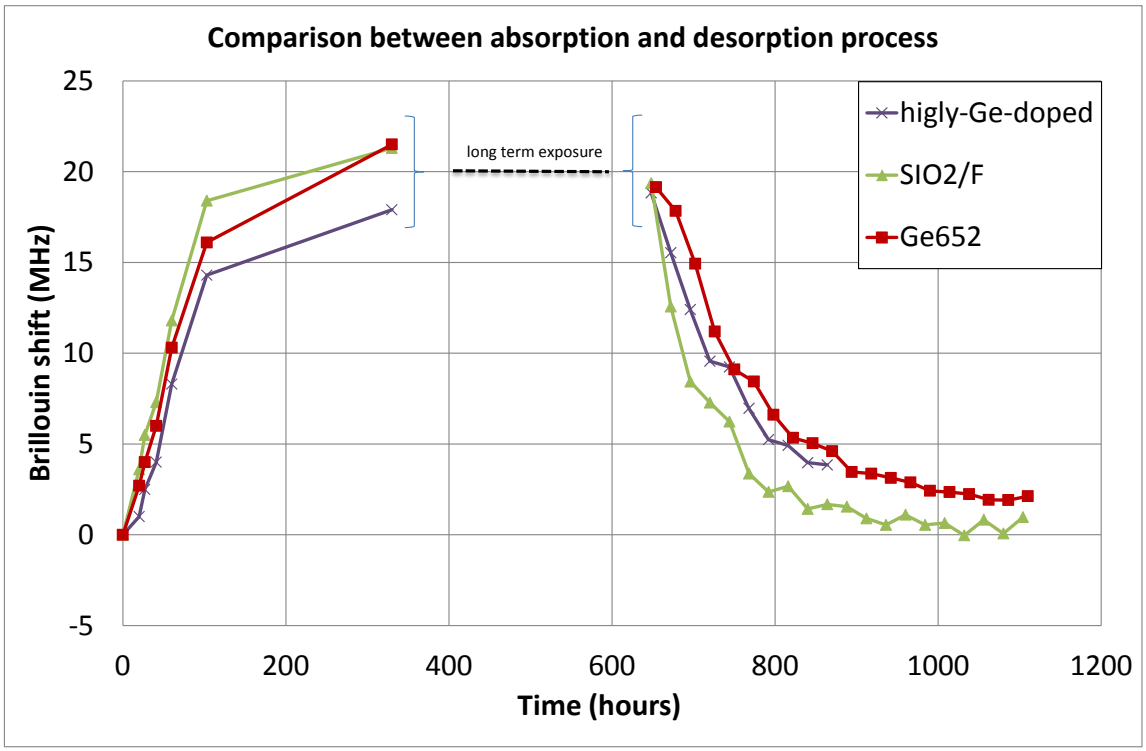

Figure 7: Brillouin frequency Shift during the sorption and desorption period

5. CONCLUSION

Hydrogen induces strong modification in propagation losses, especially near 1245nm. Brillouin scattering proved to be dependent on hydrogen content inside optical fibers, at least beyond 2% content. Observed shift reached 21MHz, whatever the tested optical fiber type. This demonstrates that optical fiber sensor using the Brillouin scattering is appropriate for hydrogen sensing. Performance of sensor is shown to be dependant of the doping compositing of the glass. Compared with Ge-doped fibers, Fluor-doped fibers appeared more sensitive to low hydrogen exposure and identical at saturation. the result show here is the one of the step to understand the main mechanism of the sensing process in order to design a suitable tool for hydrogen detection.

6. REFERENCES

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