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The H₂-CO₂ system for H₂ and CO₂
continuous monitoring in soil gases

196



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Rapporti tecnici INGV

THE H₂-CO₂ SYSTEM FOR H₂ AND CO₂ CONTINUOUS MONITORING IN SOIL GASES

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196

Indice

	Introduction	5
1.	The automated H ₂ -CO ₂ system	5
2.	H ₂ sensor unit: hydraulic and electronic plans	6
3.	H ₂ -sensor unit: tuning tests for the best electric impedance of the external circuit	10
4.	H ₂ concentration measurement method	11
	References	13

Introduction

The gases released from magmas upon their ascent toward the surface play a key role for determining both the style and dynamics of the volcanic eruptions. During paroxysmic activities, large amount of gases are emitted through the eruptive columns, uprising up to several kilometers above the volcanic vents. Furthermore, during interruptive phases, several volcanoes continuously discharge gases through the plume and the fracture of the volcanic pile.

On the other hand, several authors showed that gases dissolved in ground-water [Irwin and Barnes, 1980; Igarashi et al., 1995; De Gregorio et al., 2005; Chiodini et al., 2011] or emitted by diffuse degassing [Carapezza et al., 1980; Wakita et al., 1980; Satake et al., 1984; De Gregorio et al., 2002] underwent sharp changes before big earthquakes, suggesting that gas pressure play a fundamental role in modifying the strength to mechanical strain, lowering the resistance to movement through the crustal faults and advancing seismogenetic processes [Kristin et al., 2011].

Starting from this kind of considerations, the investigation of the gaseous emissions in natural systems provides several implications for hazard assessment in volcanic and seismic areas. Since several time, these investigations were performed by direct collection of gases and their transport in the laboratory for determining the gas composition. This procedure allows monitoring a large number of sampling sites, but discontinuous in time. A different approach involves the use of remote sensors directly installed in field for performing several analyses per day of single components. This approach requires several efforts for searching new materials and innovative technologies, providing huge amount of information on the short-term processes that shall be neglected by discontinuous surveys.

Since several time, the soil gas monitoring in seismic and volcanic areas is based on the measurements of CO₂ flux. Our automated system, designed for improving the tools for continuous geochemical monitoring of soil gases in volcanic and seismic areas, allows measuring the H₂ concentration and the CO₂ flux by using a hydrogen fuel cell and an IR spectrophotometer. The H₂-CO₂ system underwent the qualification procedure in laboratory and preliminary field-testing aimed to check the full efficiency of the components and for tuning the setup for its effective application for H₂ and CO₂ continuous monitoring.

In this report we describe the technical details of the H₂-CO₂ system and the results of the laboratory tests performed with the aim of measure in continuous the H₂ concentration and CO₂ flux in geothermal, seismic and volcanic areas. Furthermore, the results of the preliminary field experiment performed at Mt. Etna were illustrated

1. The automated H₂-CO₂ system

The H₂-CO₂ system consists of the main unit (MU) and the H₂-sensor unit. A solar panel and a lead battery provide the power supply required for operating all electric components throughout the daytime.

In a water-proof plastic box of 60 x 45 x 25 cm³, the MU hosts the Gascard II spectrophotometer, the fluxmeter (range 0 – 1.0 l min⁻¹), temperature (T) and pressure (P) sensors, the data logger, the radio/modem transmitter and all the additional electronic and hydraulic components needed for measuring the CO₂ flux.

Both temperature and pressure sensors provide the monitoring of atmospheric parameter for evaluating the environmental effects on flux measurements and chemical composition of the soil gases.

The Gascard II consists of an infrared spectrophotometer designed for accurate and reliable measurement of the CO₂ concentration. The sensor head is based on a technique that provides true, dual wavelength infra-red sensing with no moving parts, resulting in a low drift, high accuracy sensor with fast response time and low power consumption. The Gascard II onboard the H₂-CO₂ can measure CO₂ concentration in a range of 0-100 % vol.

Its sensitivity is 16mV %vol⁻¹, while the accuracy of the measurement of the CO₂ concentration is ± 2% of range. The repeatability at zero is ± 0.3%, while the repeatability at span is ± 1.5 %. Finally, the input voltage requirement is 24V dc and warm-up time is 1 minute.

The H₂-CO₂-system accomplishes the CO₂ flux measurements according to the dynamic concentration method proposed by Gurrieri and Valenza (1988) and accurately calibrated through laboratory experiments by Camarda et al. (2006a). In agreement with that method, the CO₂ flux measurements were performed by inserting a special probe into the soil up to a depth of 50 cm.

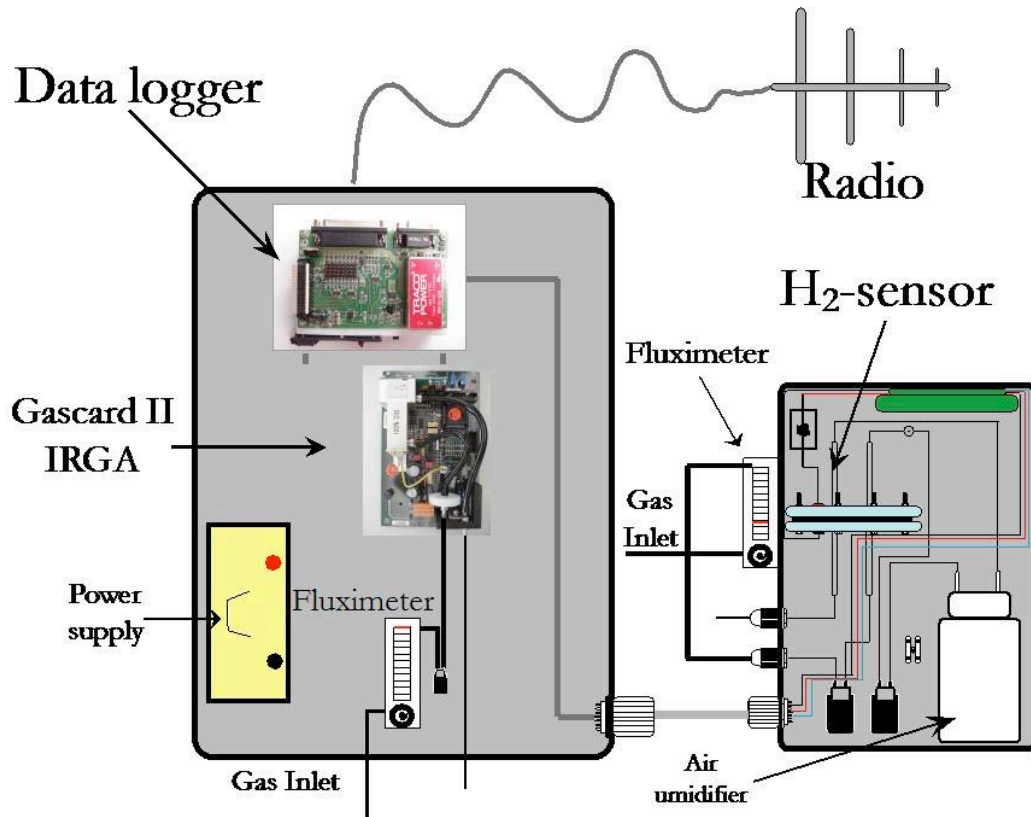


Figure 1. Schematic view of the components of the H₂-CO₂ system.

Throughout the measurement cycle, the soil gases mix with the air entering through a calibrated opening on the head plug of the probe. In a few seconds, the system attains a stationary state and the CO₂ concentration became constant. In steady state conditions, by pumping the gases at a constant flux rate, the CO₂ concentration (named *CO₂ dynamic concentration*) is directly dependent from the CO₂ flux from the soil. According to Camarda et al. (2006a), the empirical relationships between the CO₂ dynamic concentration and the CO₂ flux is

$$\varphi_{CO_2} = (32 - 5.8 \cdot k^{0.24})C_d + 6.3 \cdot k^{0.6}C_d^3$$

where C_d is the CO₂ dynamic concentration (vol%), φ_{CO_2} is the CO₂ soil flux (Kg m⁻² d⁻¹) and k is the soil permeability (Darcy) measured in field [Camarda et al., 2006b]. In order to obtain short response time and bound the error made by the soil permeability, the sampling flux rate of the soil gases is set to 0.8 l min⁻¹ [Camarda et al., 2006a].

Beside MU, the H₂-CO₂ system has been equipped with the H₂-sensor unit that allows the H₂ concentration measurement. The automated system has been designed for sampling and analysing soil gases using the working principle of hydrogen-air fuel cells. The electronic and hydraulic components required for using the fuel cell as H₂-dedicated sensor have been carefully tested in laboratory and will be described in detail in the following part of the report.

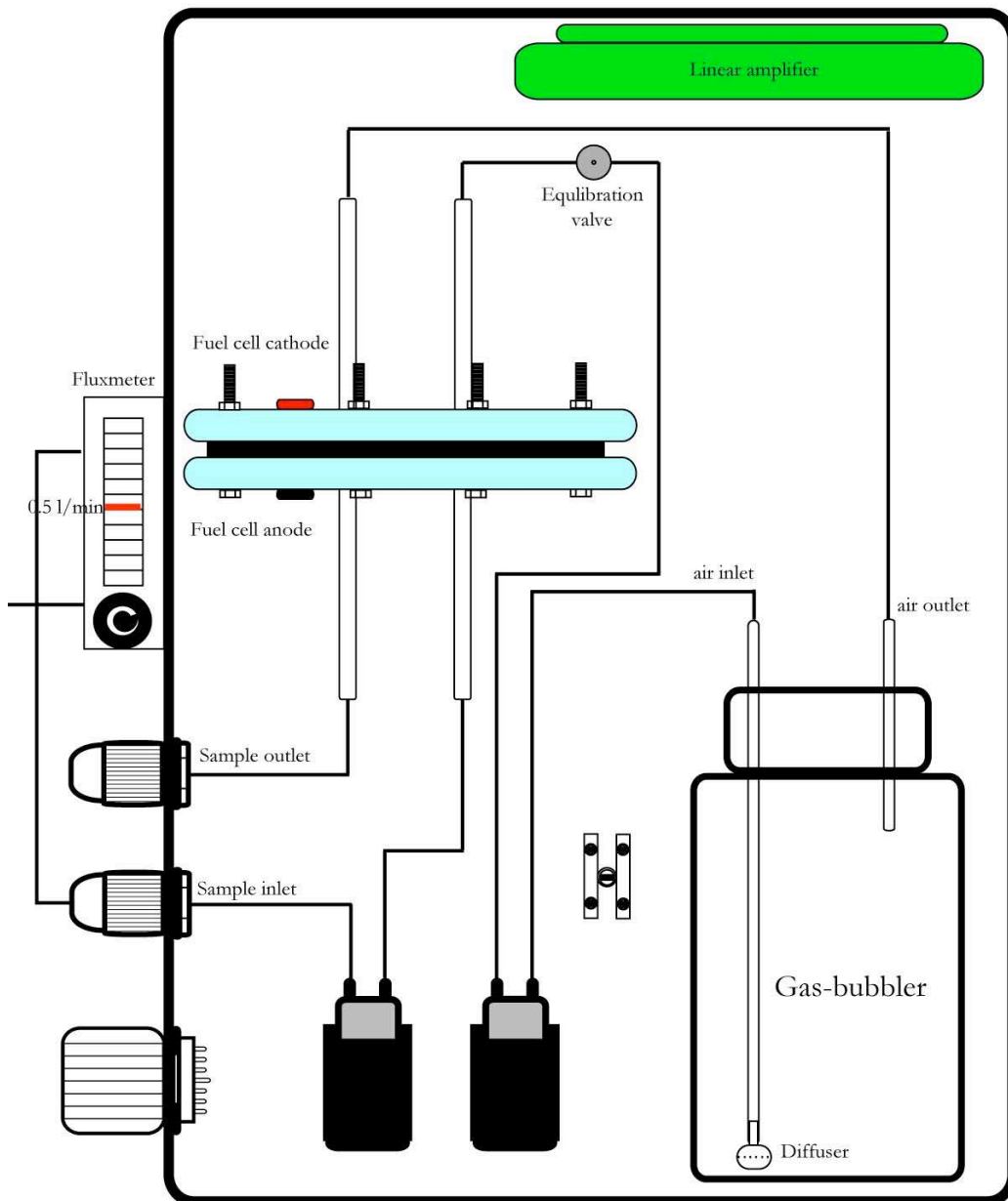
2. H₂ sensor unit: hydraulic and electronic plans

The fuel cells are electrochemical devices able to convert the energy of a fuel, the hydrogen, in electric energy through the inverse electrolysis reaction. A solid electrolyte membrane (also named Proton Exchange Membrane – PEM) divides the cell electrodes. By oxidation of H₂ at the anode of the cell, hydrogen ions move through the PEM toward the cathode, where electrons provided by the external circuit reduce oxygen molecules of the air, thus producing water. In order to measure the changes of reducing capacity of soil

gases, several authors [Carapezza et al., 1980; Sato et al., 1982; Sato and McGee, 1982; Sato et al., 1985; Wakita et al., 1980] proposed the use of fuel cell systems.

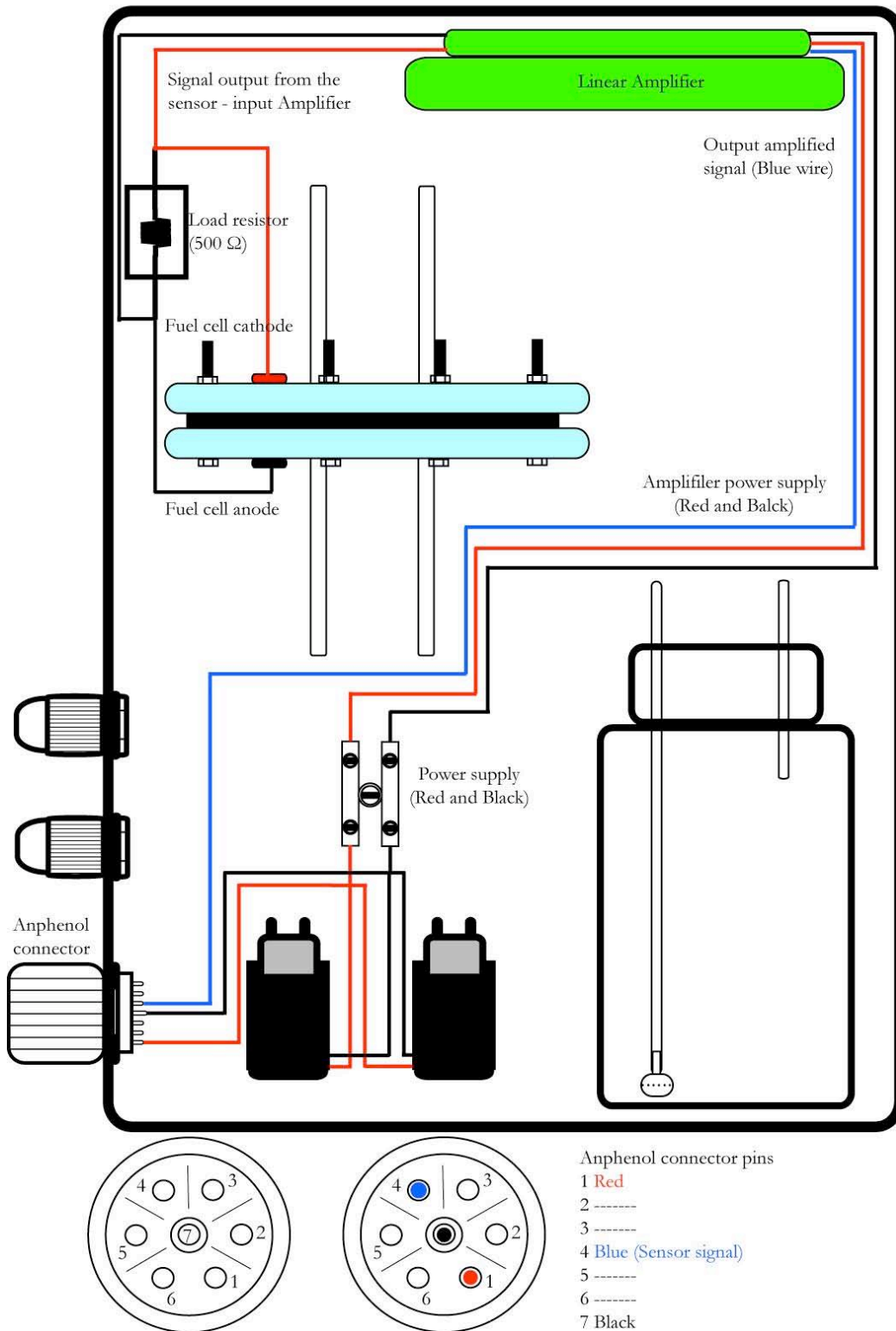
The main difference with our scheme is the housing of the sensing system improving its robustness and preventing detrimental effects of the potential contact with solid or liquid compounds of the soils.

Idraulic components



a)

Electric connections



b)

Figure 2. Hydraulic (a) and electronic (b) schemas of H₂ sensor unit.

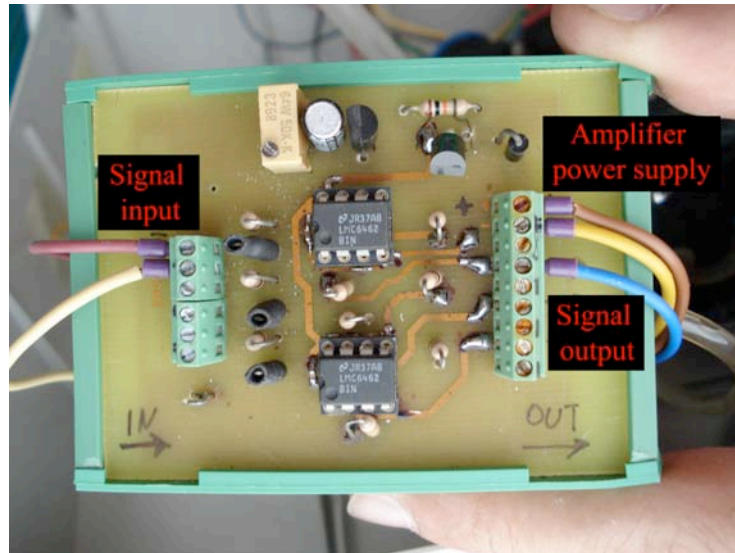


Figure 3. Linear amplifier of the signal output of the fuel cell.

The H₂ sensor has been housed within a plastic case 20 × 25 × 9 cm³ containing also all the additional hydraulic and electric components (Figure 2-a): two membrane pumps (max free flow rate 1.8 l min⁻¹), a fluxmeter (range 0 – 1.0 l min⁻¹), an equilibration valve, a gas-bubbler of volume 500 ml water-filled up to the half height, the external electric loop of the sensor with the measurement resistor and a linear amplifier (10x) of the signal output from the fuel cell (Figure 3).

Throughout the measurement cycle, the pump switches on for sampling the soil gases at a constant rate of 0.5 l min⁻¹. Silicon tubes, passing through two panel hose connectors, providing soil gases inlet and outlet, allow flowing the gases toward the anode (sensing electrode) of the fuel cell.

The gas-bubbler allows saturating with water vapor the air entering the cathode (reference electrode) of the cell, improving the water management of the sensor. The membrane pump pushes air into the gas-bubbler having an inner diffuser that allows the fast saturation in water vapor through the formation of small diameters air-bubbles (~ 1 mm). As can be seen in Figure 2-a, the fuel cell cathode, the membrane pump and the gas-bubbler form a loop made of silicon tubes that communicates with the atmosphere through the equilibration valve.

Amphenol connector provides the electrical connection between the H₂-sensor unit and the MU of the H₂-CO₂ system. The pin connection detail reported in Figure 2-b shows that red and black wires provide the power supply for membrane pumps and linear amplifier (Figure 2-b) able to convert the electric output produced by the cell into a powerful electronic signal.

The operating principle of the H₂-sensor requires the hydrogen oxidation reaction at the anode of the cell and the oxygen reduction reaction at the cathode, providing an electric current through the external connection of the electrodes. The electric current (*I*) is measured by the voltage drop across the load resistor, in agreement with the Ohm's law:

$$V = R \times I$$

Therefore, the load resistor results a kinetic-limiting component affecting the reduction reaction occurring at the cathode, the sensitivity of the H₂-system and the magnitude of the signal output from the cell. According to Sato and McGee (1980), the proportionality between the sensor signal and the impedance of the circuit is fairly linear as long as the load resistor is smaller enough. High load resistor in between the electrodes makes non-linear and slower the response of the H₂-sensor. A series of specific tests allowed calibrating the load resistor, by optimizing the performance of the sensor (see later).

In order to amplify the sensor signal, the input pins of the linear amplifier are connected in parallel to the load resistor in between the sensing and reference electrodes of the cell. Since the operating principle of the sensor is a reversible redox process, some negative voltages can temporarily establish between the fixed polarities of the electrodes. A voltage offset (VOS) of 1 V corresponding to the absence of hydrogen at the sensing electrode of the sensor allows changing the voltage of the linear amplifier to obtain the output signal

in the range of positive values. The blue wire provides the connection between the linear amplifier and the data logger (Figure 2-b).

3. H₂-sensor unit: tuning tests for the best electric impedance of the external circuit

Before operating within the H₂-CO₂ system, specific tests allowed tuning the H₂ sensor. In particular, since affecting sensitivity, resolution and response time of the sensor, a few tests have been performed to select the best load resistor of the sensor. Tests were performed at controlled temperature and pressure conditions with the aim to optimize either the performance of the sensor or the electronic equipments needed to transform the electric output of the cell into a sensitive and robust electronic signal.

The standard gases, having H₂ concentration up to 300 ppm vol., enter at constant flux rate through the sensing electrode for a time long enough to attain the stationary value of the sensor signal (flat segments of the signal-time curves in Figure 4-a and Figure 4-b). This maximum stationary voltage drop represents the signal of the sensor proportional to the H₂ concentration within the mixture. Between subsequent tests the sensor has been flushed with air in order to set the zero voltage across the load resistor corresponding to the absence of H₂ at the sensing electrode.

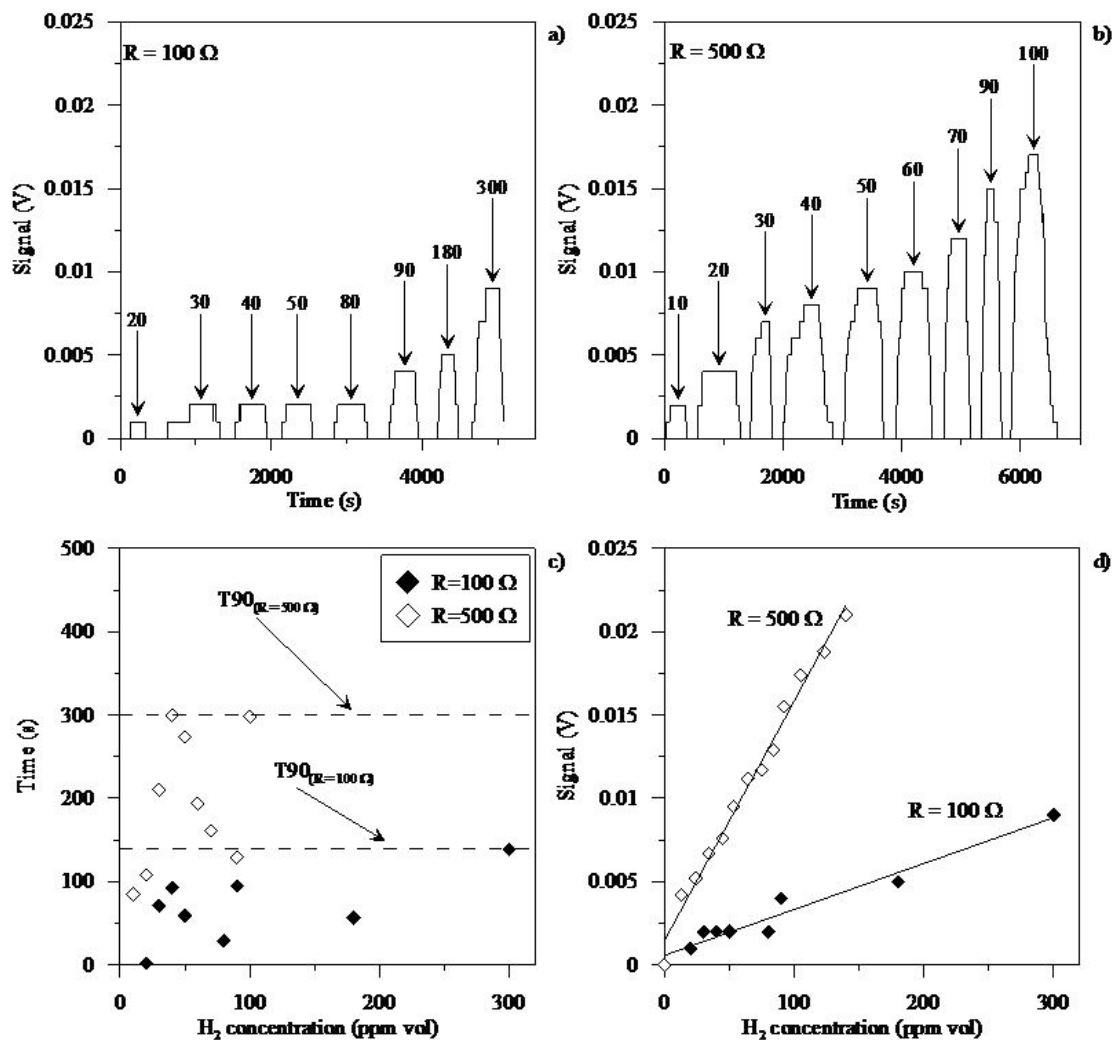


Figure 4. Calibration of the load resistor for the external circuit of the cell. a) 100 ohm load resistor; b) 500 ohm load resistor; c) comparison of the T₉₀ of the sensor with 100 ohm (black diamonds) and 500 ohm resistor (white diamonds); d) signal vs concentration curve with 100 ohm (black diamonds) and 500 ohm resistor (white diamonds).

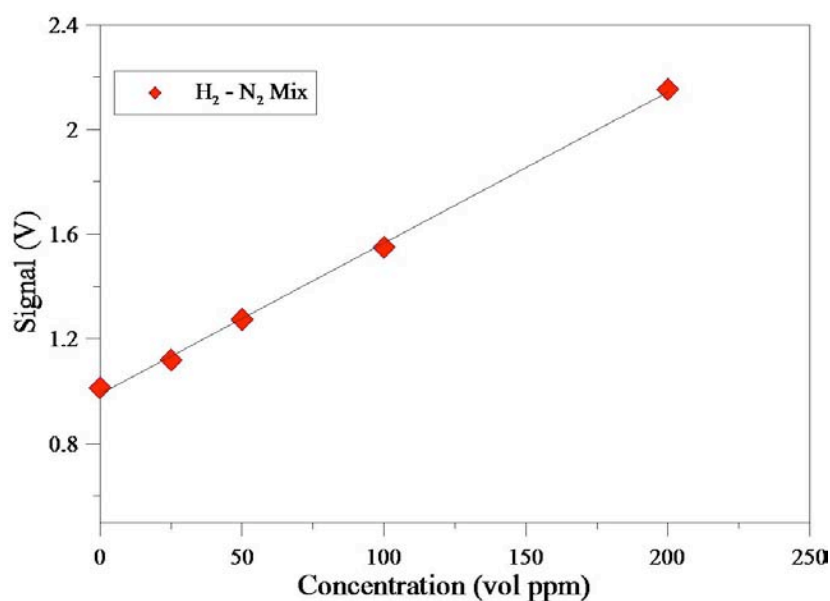


Figure 5. Calibration line of the H₂-sensor onboard the automatic H₂-CO₂ system used to perform the measurements in the field. The standard mixtures are made by dilution of a H₂-N₂ mixture (H₂ = 200 ppm vol.) with air.

The results obtained by using a 100 ohm resistor indicates that the minimum difference of H₂ concentration providing the sensitive change of the sensor signal was about 90 ppm vol. (Figure 4-a).

Figure 4-b shows the test results obtained by using the 500 ohm load resistor within the circuit, indicating the improvement of either the sensor signal per unit concentration of H₂ or the resolution of the sensor. Indeed, the change of about 10 ppm vol. in H₂ concentration within the mixture provides a sensitive increase of the sensor signal. Moreover, the improvement of the signal/concentration ratio is well defined in Figure 4-d, indicating that by using 100 ohm resistor the sensitivity of the H₂ sensor is near 0.03 mV ppm⁻¹, while the sensitivity obtained setting the system with 500 ohm load resistor results 0.2 mV ppm⁻¹.

The time (T₉₀) required for achieving the 90% of the signal proportional to the H₂ concentration depends on the load resistor value of the circuit and it is independent from H₂ concentration within the mixture (Figure 4-c). Finally, Figure 4-c shows that T₉₀ doubles by changing the load resistor from 100 to 500 ohm. Although the best setting of the H₂ sensor would requires the lowest response time, the 500 ohm load resistor included into the external circuit of the fuel cell provides better signal to concentration ratios and higher resolution toward H₂ concentration.

Before the field testing performed at Mt. Etna, the H₂-unit of the H₂-CO₂ system, equipped with a load resistor of 500 ohm (Figure 5) and a linear amplifier of the signal, underwent an accurate calibration procedure using the hydrogen standards having H₂ concentration up to 200 ppm vol. Moreover, the Gascard II was calibrated using standards having 100% vol. and 30% vol. CO₂ concentration.

4. H₂ concentration measurement method

H₂ concentration measurements were performed by inserting into the soil up to a depth of 50 cm a dedicated probe, atmosphere-proof at the head plug, close to the CO₂ flux measurement site. The gases entering from the bottom of the probe are sampled at a constant flux rate of 0.5 l min⁻¹ and analysed by the H₂-sensor unit.

The time required for full implementation of the measurement cycle with the H₂-CO₂ system is seven minutes. This time is longer enough than the response time of the sensors. In field applications, the measurements are performed once per hour and stored on the solid state memory onboard the system. Once a day, data are transmitted to the Istituto Nazionale di Geofisica e Vulcanologia (INGV-PA) through scheduled radio/modem transmission. Moreover, at any time of the day, it is possible the download of the measurements for data processing in near-real time.

Figure 6 shows the results of the first field tests carried out at Mt. Etna during 2008 with the aim to check the performance of all the components, by stressing and tuning the H₂-CO₂ system for continuous H₂-CO₂ monitoring in volcanic, seismic and geothermal areas.

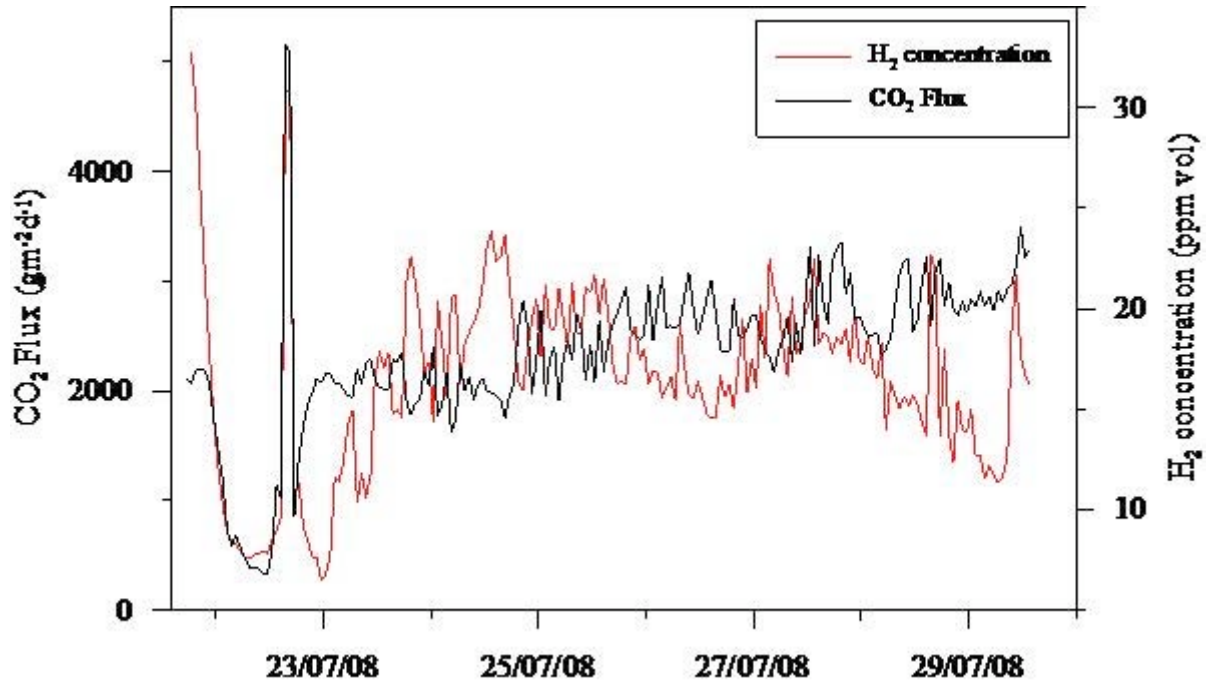


Figure 6. Time series of H₂ and CO₂ signals obtained at Mt. Etna during 2008.

During the experiment performed at Torre del Filosofo, at the summit area of the volcano during the 2008-2009 eruption, both signals exhibited several variations. The CO₂ flux showed an increasing trend from 500 up to 3500 g m⁻² d⁻¹, with several variations close to the average 2400 g m⁻² d⁻¹. At the same time, the H₂ concentration exhibited smaller variations, with an average value of 15 ppm vol. This behaviour well correlates with the typical activity of effusion from eruptive vent opened within the Valle del Bove and the persistent degassing from the summit crater characterizing the volcanic activity at the time of the experiment.

The results obtained through laboratory experiments as well as during tests performed at Mt. Etna, allowed optimizing the functionalities of the system for measuring the H₂ concentration and the CO₂ flux. Moreover, they strongly support the reliability of the H₂-CO₂ system for H₂ and CO₂ continuous monitoring at active volcanic and seismic areas.

References

- Camarda, M., Gurrieri, S., Valenza, M., (2006-a). CO₂ flux measurements in volcanic areas using the dynamic concentration method: the influence of the soil permeability. *Journal of Geophysical Research*, 111.
- Camarda, M., Gurrieri, S., Valenza, M., (2006-b) In situ permeability measurements based on radial gas advection model: Relationship between soil permeability and diffuse CO₂ degassing in volcanic areas. *Pure and Applied Geophysics*, 4, 897-914.
- Carapezza, M., Nuccio, P. M., Valenza, M., (1980). *Geochemical precursor of earthquakes: high pressure science and technology*. Edited by B. Vodar and Ph Marteau, Elsevier, New York.
- Chiodini, G., Caliro, S., Cardellini, C., Frondini, F., Inguaggiato, S., Matteucci, F., (2011). Geochemical evidence for and characterization of CO₂ rich gas sources in the epicentral area of the Abruzzo 2009 earthquakes. *Earth and Planetary Science Letters*, 304, 389-398.
- De Gregorio, S., Diliberto, I.S., Giammanco, S., Gurrieri, S., Valenza M., (2002). Tectonic control over large-scale diffuse degassing in eastern Sicily (Italy). *Geofluids*, pp. 273-284.
- De Gregorio, S., Gurrieri, S., Valenza, M., (2005). A PTFE membrane for the in situ extraction of dissolved gases in natural waters: Theory and applications. *Geochem. Geophys. Geosyst.*, 6 (9).
- Gurrieri, S. and Valenza, M., (1988). Gas transport in natural porous mediums: a method for measuring CO₂ flows from the ground in volcanic and geothermal areas. *Rendiconti SIMP Carapezza M. Memorial Volume*, 43- 4, 1151-1158.
- Hughes, K.L.H., Masterlark, T., Dooney, W.D., (2011). Pure-fluid migration and the timing of the 2005 M 8.7 Nias earthquake. *Lithosphere*, 3, 170-172.
- Igarashi, G., Saeki, S., Takahata, N., Sumikawa, K., Tasaka, S., Sasaki, Y., Takahashi, M., Sano, Y., (1995). Ground-water radon anomaly before the Kobe earthquake in Japan. *Science*, 269, 60-61.
- Irwin, W.P. and Barnes, I., (1980). Tectonic relations of carbon dioxide discharges and earthquakes. *Journal of Geophysical Research*, 85, 3115-3121.
- Satake, H., Ohashi, M., Hayashi, Y., (1984). Discharge of H₂ from atotsugawa and Ushikubi faults, Japan, and its relation to earthquakes. *Pure and Applied Geophysics*, 122, 185-193.
- Sato, M. and McGee K.A., (1980) Continuous monitoring of hydrogen on South flank of Mount St. Helens. *Geological Survey Professional Paper 1250 - The 1980 eruption of Mount St. Helens, Washington*. In *The 1980 Eruption of Mount St. Helens, Washington* Ed. P. W. Lipman and D. R. Mullineaux.
- Wakita, H., Nakamura, Y., Kita, I., Fujii, N., Notsu, K., (1980). Hydrogen Release: New Indicator of Fault Activity. *Science*, 210, 188-190.

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