SUPPLEMENTARY MATERIAL

General Procedure and Recommendation to Implement the Method

1. Sampling - Samples should be analyzed directly without any delay if the method can be applied on site (i.e., with a mobile spectrophotometer). Spectra acquisition for one sample in three different media may usually take 10 min. If it is not possible, the sampled waters have to be retrieved by limiting contact with the atmosphere and stored without any headspace in glass bottles. This can be achieved by making the waters flow through the sampling bottle via an entrance and an exist needle in the stopper. Butyl stoppers are mandatory. The tubes that are used to fill the sampling bottle should be made of material with low permeability to dioxygen and water (i.e., polypropylene, polycarbonate, polyether ether ketone or polytetrafluoroethylene). A large syringe or a pump can be used at the bottle outlet to ensure outflow. Once the bottle is full and the liquid has circulated enough to replace three time the volume of the bottle, the system can be dismantled and the bottle stored at low temperature (4 °C) and away from light. It is recommended to use sterile material and to add a 0.2 µm filter at the bottle inlet to discard any microbes that may latter change the chemistry of the sulfur species. This type of samples should be analyzed as soon as possible even if a storage of 1 or 2 weeks is usually accepted.

2. Choice of Dilution Level - For samples of unknown chemistry, we generally recommend employing a 10 ×dilution in 10 mL tubes (1mL of sample in 9 mL of buffer). This dilution is important enough to limit major interferences and still low to be sensitive. However, if possible, it is better to test additional levels of dilution (for instance, 5 × and 40 ×) to assess if interferences occur but also to optimize the sensitivity of the measurement. In any case, the dilution tubes should be already filled with buffer before adding the sample to limit oxidation and the measurement should be performed by retrieving with a syringe the desired sample volume, filtering it at 0.2 µm and adding it into the three pH-buffered media. The spectrum acquisition should start no later than 3 min after dilution.

Note that each pH-buffer media must be freshly prepared (< 1 month) and designed solely for one level of dilution (see Materials and Methods section). This is mandatory for low dilution levels (<10 ×), while the same pH-buffered media as the one used for the 10 × dilution may be employed for higher dilution levels, the adjustment of the pH-buffered medium becoming then insignificant.

3. Spectral Acquisition - The parameters recommended for acquisition are the following:

- cuvette of 10 mm in length
- absorbance spectrum range between 220 and 300 nm
- scanning speed close to 32 nm/min
- data bunching interval of 0.1 nm

4. Second Derivative Spectra - Spectrum processing can be done latter and is achieved with an interval $\Delta\lambda$ of 8 to 15 nm. The key values at specific wavelengths are then noted for each corresponding pH-buffered media (i.e., $\mathbf{N''_{250}}$, $\mathbf{AC''_{250}}$ and $\mathbf{H''_{278}}$).

5. Comparative Measurements with Standardized Methods Performed on Groundwater Naturally Containing Reduced Sulfur Species

Groundwater from the Dogger formation (Loiret, France)	Values measured with the present method	Values measured with standardized methods*
Total sulfide (ppm)	0.012	0.010
Total sulfite (ppm)	9.051	12.800
Total thiosulfate (ppm)	22.879	NA

* details on the standardized methods are given in the Material and Methods section. Thiosulfate measurements with ion-exchange chromatography did not give any stable results regarding the different levels of dilution and were thus considered as invalid (NA: not available).

6. Comparative Measurements Obtained on Fresh Water Spiked with Sulfides (present method vs. SPECTROQUANT® test kit N° 1.147779.0001)

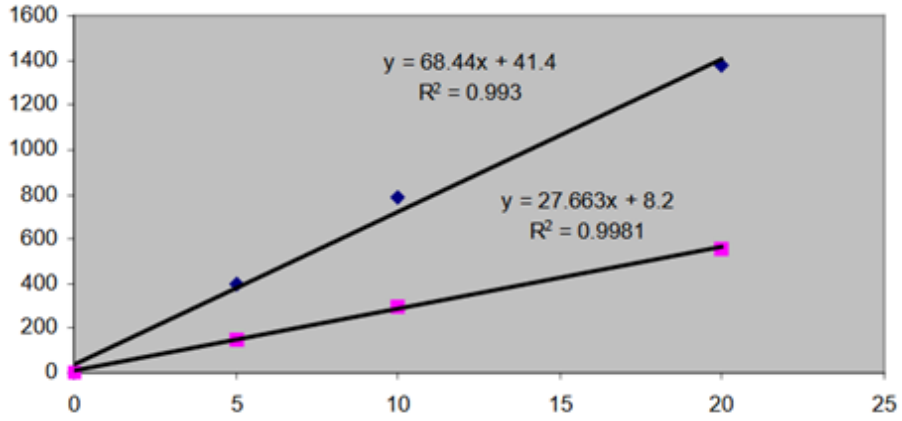

FIGURE S1: Results of the linearity comparison test between the present method (square, normalized values on the *y*-axis) and the SPECTROQUANT® test kit N° 1.147779.0001 (diamond, absorbance values on the *y*-axis) to corresponding additions of sulfide content (in mM on the *x*-axis) .