Fiber optic based chemical sensor system for in-situ process measurements using the photothermal effect

Karl-Heinz Walker, Heinz Sontag

Dornier GmbH, Postfach 14 20, 7990 Friedrichshafen, FRG

ABSTRACT

A fiber optic sensor system based on the photothermal effect has been developed and applied to very low concentration measurements in solutions.

The sensor head comprises three closely spaced optical fibers for excitation, probe and reflected probe light. A combination of reflective and refractive miniature optics is used to focus the respective beams into the probe volume. If an absorbing substance is present the absorbed light power from the modulated excitation beam generates a refractive index gradient in the probe volume, which can be observed via deflection measurements of the non-absorbing cw probe beam. The reflective probe beam signal detected after phase synchronous demodulation is proportional to the substance concentration. Using a monochromatic lightsource with variable wavelength it is possible to discriminate different substances.

With this system we have analysed Cu-II concentrations in galvanic solutions from 1000 ppm down to concentrations below 1 ppm, thus reaching the sensitivity for waste-water control.

Applications for this chemical sensor system are in-line environmental and pollution control of water due to its very high sensitivity. The large dynamic range also makes it suitable for various in-line process control tasks.

1. INTRODUCTION

Photothermal spectroscopy is one of the most sensitive optical methods for trace detection in gases[1], liquids[2] and solids[3]. Being only sensitive to actual absorption in a sample, this technique is far superiour to standard photometric techniques, where small intensity changes have to be detected on a large background. Typically, the sensitivity of photothermal detection schemes is several orders of magnitude higher as compared to photometric measurements.[4,5]

Photothermal detection schemes[3,6] are based on thermally induced refractive index gradients associated with the absorption in the focal region of a modulated or pulsed excitation beam. The refractive index gradients can be detected by a probe beam through defocussing or deflection with extremely high sensitivity using simple optical schemes. The method is sensitive to non radiative relaxation processes where the optical excitation is converted to heat and is thus complimentary to fluorescence spectroscopy. By its nature, photothermal detection is not sensitive to elastic light scattering or window impurities and signal strength is highly linear over several orders of magnitude.

0-8194-0619-8/91/$4.00

The method thus extends the useful range of photometric detection significantly to lower concentrations. Typical applications are therefore in-line process, environmental or waste-water control.

So far, most applications have applied laboratory set-ups to demonstrate the sensitivity of the scheme and overcome stability and adjustment problems. The use of a small, rigid, preadjusted and flexibel sensor would make the method far more practical and extend its use significantly. We have therefore developed a sensor system based on a central optical unit and remote fiber-coupled sensorheads, which can easily be multiplexed. The sensor system can therefore by directly employed in nuclear, radiation or explosive environments. The system employs laser diodes, LED's and standard fiber optic components and thus yields a simple very cost-effective design with high efficiency. We have applied this system to galvanic waste-water control to monitor metalion concentrations down to the sub-ppm range.

2. EXPERIMENTAL

2.1 Apparatus

Figure 1 shows a block diagram of a photothermal deflection measuring system using optical fibers.

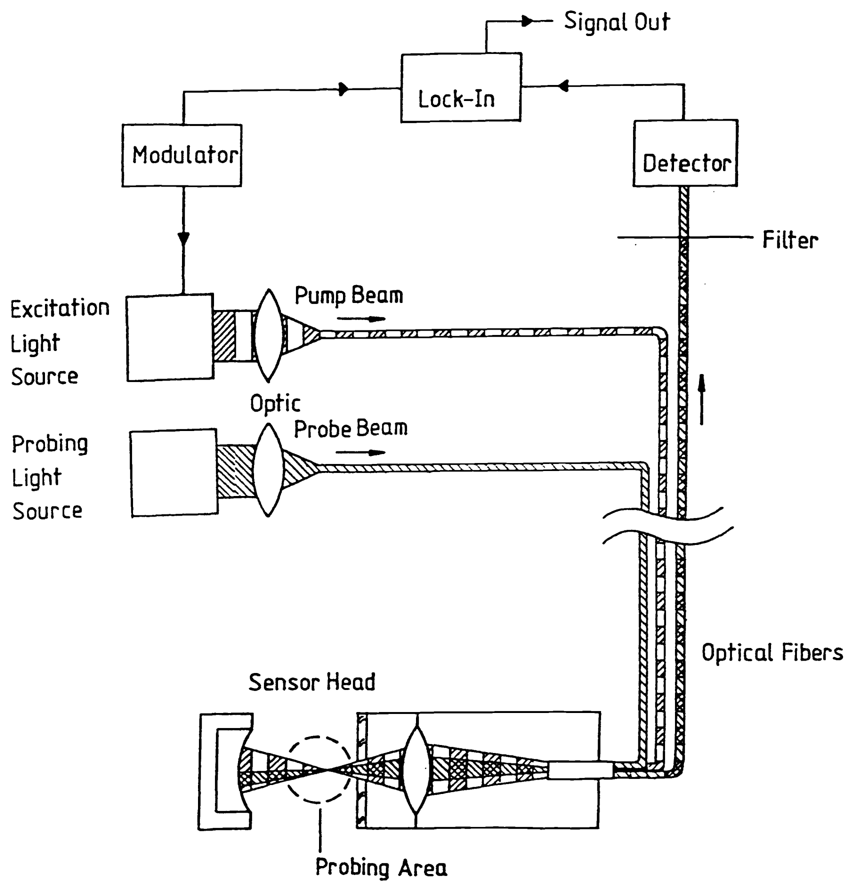

Fig. 1: Block diagram of the fiber optical system

The excitation light source is a directly modulated laser diode Sharp (LT 027, λ = 780 um) with a maximum output power of 10 mW. The light is coupled into a 100 μm quartz fiber and guided to the sensor head. An optical lens is used to image the fiberend and thus form a thermal lens within the sample area.

The probing light source is a cw argon-ion laser with an output power of 5 - 10 mW. The light is coupled into a fiber leading to the sensor. The excitation and the probing fiberend faces are mounted in a special fixture. By the imaging process, probe and excitation beam focus are closely spaced in a well-defined geometry. The deflection of the probing-beam is detected by reflecting the probe beam by a spherical mirror back to a third fiber acting as spatial filter to partially sample the probe-beam. This scheme is very sensitive to beam deflections.

The reflected probe is guided to a simple photodiode with an integrated preamplifier. In front of the diode an interference filter blocks the residual excitation light.

The photodiode output is amplified after phase-synchroneous detection by a standard lock-in amplifier. For data aquisition and analysis a HP 300 computer is employed.

The sensor is designed for in-situ measurements, so the head is built as a rigid metal device with a Kevlar protected fiber-pig-tail.

The sensor is shown in Figure 2.

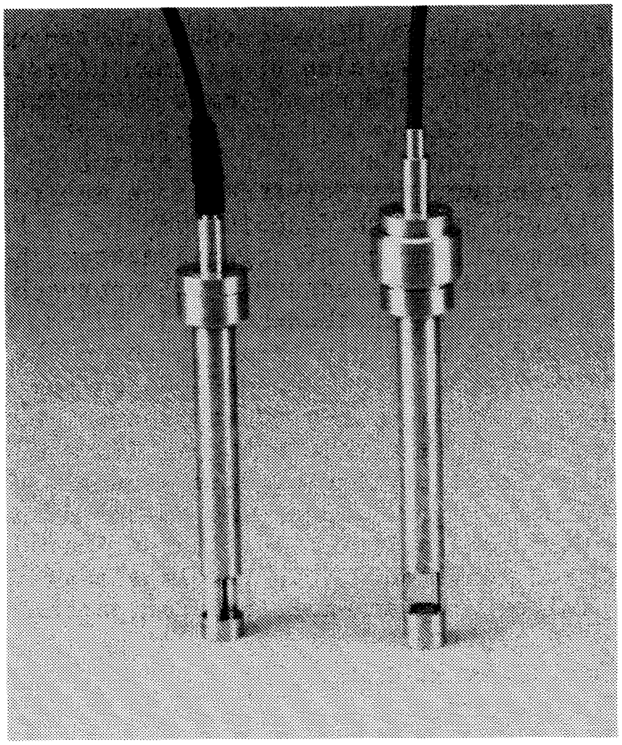

Fig. 2: Fiber optical sensor for in-situ measurements

The length is 15 cm with a diameter of 1 cm. A quartz window separates the optical components from the probing liquid.

2.2 Reagents

The measurements were performed with Cu-II (EDTA) in water, which has a strong absorption band in the red wavelength range (max. ~750 nm). Different concentrations between 1 ppm and 1000 ppm were prepared and calibrated using atomic absorption spectroscopy.

2.3 Results and discussion

The shape of the signals is shown qualitatively in figure 3. The upper curve corresponds to the modulated output of the excitation laser diode and the lower curve shows the resulting detector signal. These measurements were performed with a 1000 ppm Cu-II (EDTA) solution and a modulation frequency of 20 Hz.

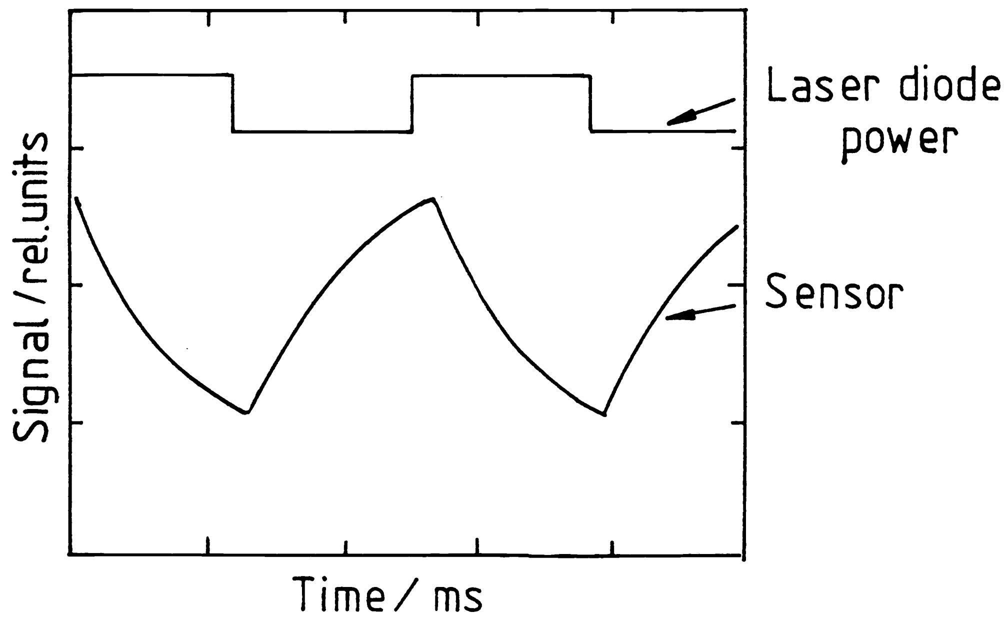

Fig. 3: Waveforms of the excitation ligth a) resulting deflection signal b)

If the excitation beam is present the probing beam is deflected, so the observed intensitiy changes gradually to a constant value. The signal amplitude is directly correlated to the substance concentration.

The performance of the sensor is demonstrated by the calibration curve shown in figure 4.

The experiments were also performed with Cu-II (EDTA) solutions in water. The lock-in signals using an excitation power of P [λ = 780 nm] = 10 mW were recorded over a concentration range of three decades.

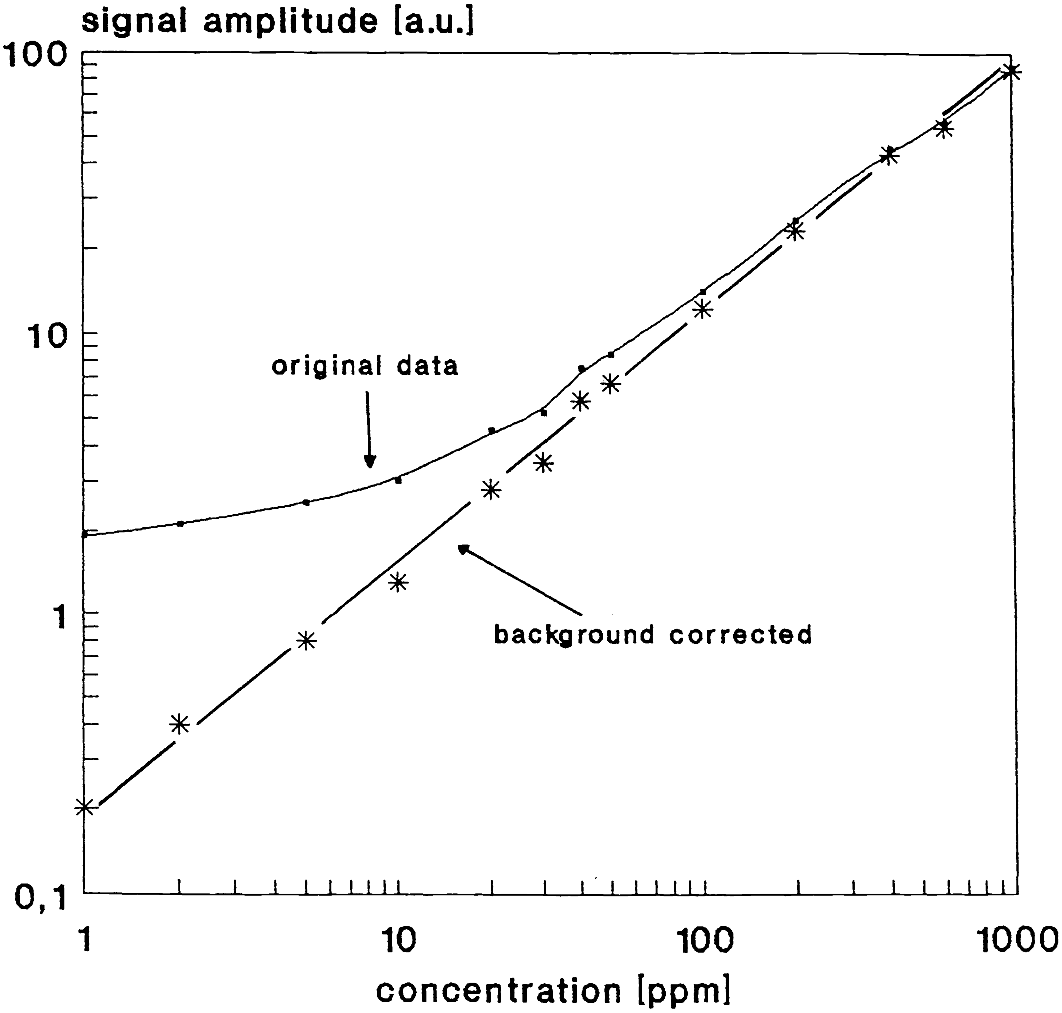

Fig. 4: Photothermal deflection signal versus Cu-II concentrations in water

After subtracting the background signal obtained from pure water, the signal is linear over the full concentration range of 3 decades corresponding to Cu-II concentrations ranging from 1 ppm to 1000 ppm.

A detection limit of 1 ppm Cu-II was achieved by using an excitation laser diode power of 10 mW where S/N = 4.

The main noise in this set-up was produced by the intensity fluctuation of the argon-ion laser and the mechanical instability of the fiber optic coupling system, which can easily be improved.

The use of commercially available fiber-coupled high-power laser diodes will thus extend the detection limit down to the ppb range. In order to eliminate the background, which is mainly caused the excitation beam modulating the return probe fiber optical properties, it would be advantageous to minimize the excitation beam reflection e.g. by employing a suitably coated dielectric mirror.

3. CONCLUSION

In order to identify low substance concentrations in water it has been demonstrated that a pure fiber optic sensor system based on photothermal effects can be realised. The system has demonstrated its ability for highly sensitive detection of absorbing substances in galvanic solutions.

A linear sensor response was obtained for Cu-II concentrations over a concentration range of 3 decades between 1 ppm and 1000 ppm. The limit of detection for Cu-II with this set-up was found to be 1 ppm, thus reaching the sensitivity of waste-water control. Significant improvements can be achieved by integration of the optomechanical devices as well as the use of high-power laser diodes. By using a multi wavelength excitation source, e.g. by multiplexed laser-diodes or a conventional monchromatic light source, multicomponent analysis of solutions can easily be performed.

4. REFERENCES

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