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ABSTRACT

Optical fibers, analytical chemistry, and fluorescence spectroscopy have been integrated to form the new technology of remote fiber fluorimetry. Among the many potential applications of this technology is the measurement of volatile organochlorides in ground water and in the vadose zone. The key to this application was the development of a fiber optic chemical sensor (FOCS) with sub-ppm sensitivity for, at least, chloroform and trichlorethylene (TCE). We present here the concept and instrumentation of remote fiber fluorimetry, the design and

laboratory evaluation of an organochloride FOCS, and preliminary field results of the application of the FOCS to contaminated well water.

I. INTRODUCTION

In order to provide adequate protection of water sources, methods of detecting low concentrations of toxic contaminants are urgently needed. The public health, as well as the public's confidence in domestic water supplies, requires an early warning system so that prompt action may be taken to track down the sources of the contamination and to take appropriate steps to protect the public.

The ideal monitoring system for ground water would provide in-situ determination of the levels of potential contaminants at very low concentrations. The techniques and instrumentation would be inexpensive to install and maintain, capable of automatic operation, and would give reliable results when used by technicians with only modest levels of technical training.

Remote fiber fluorimetry (RFF) is an emerging technology that has the promise of meeting the above criteria. The ability to do RFF depends on the use of low-loss optical fibers for transmitting visible light. These are the outgrowth of the needs of the communication industry for larger bandwidth communication cables than were feasible with electrical technology. This led to optical cables capable of transmitting infrared radiation over many kilometers with very little attenuation.[1] The availability of these fibers also gave rise to the new technology of remote fiber sensors.[2] The first sensors, designed to collect information from remote locations over optical fibers, relied on the fact that alterations in a specific physical property of the medium being probed would cause a predictable change in the transmission characteristics of the optical fiber. Acoustic

waves, acceleration, strain, position and magnetic field are some of the physical properties measured with these initial sensors.

The applications and versatility of remote fiber sensors were greatly increased when chemical sensors and optical spectroscopy were added to the remote detection scheme.[3-5] Now the technique is no longer restricted to measuring physical properties that change fiber transmission, but can be extended to both organic and inorganic chemical analyses.

A description of RFF and its application to groundwater analysis of chloroform follows.

II. INSTRUMENTATION

A. Remote Fiber Fluorimetry

The RFF concept is shown schematically in Figure 1. The key components of the system are the spectrometer, an optical coupler, and the fiber optic chemical sensor (FOCS). Here, excitation light of the appropriate wavelength is focused into single-strand optical fibers. The optical fiber transmits this excitation to the sampling region and, hence, the FOCS. In this application the interaction of the FOCS with the target molecule generates a fluorescent product. The excitation light subsequently produces fluorescence in the FOCS. A small amount of this fluorescent light is collected by the optical fiber and returned to an optical coupler that has been specifically designed to separate the excitation light from the returning fluorescent light. The fluorescence is finally directed into a spectrometer for spectral analysis. The intensity of signal in a specific wavelength band (or bands) is related to the chemical information being sought.

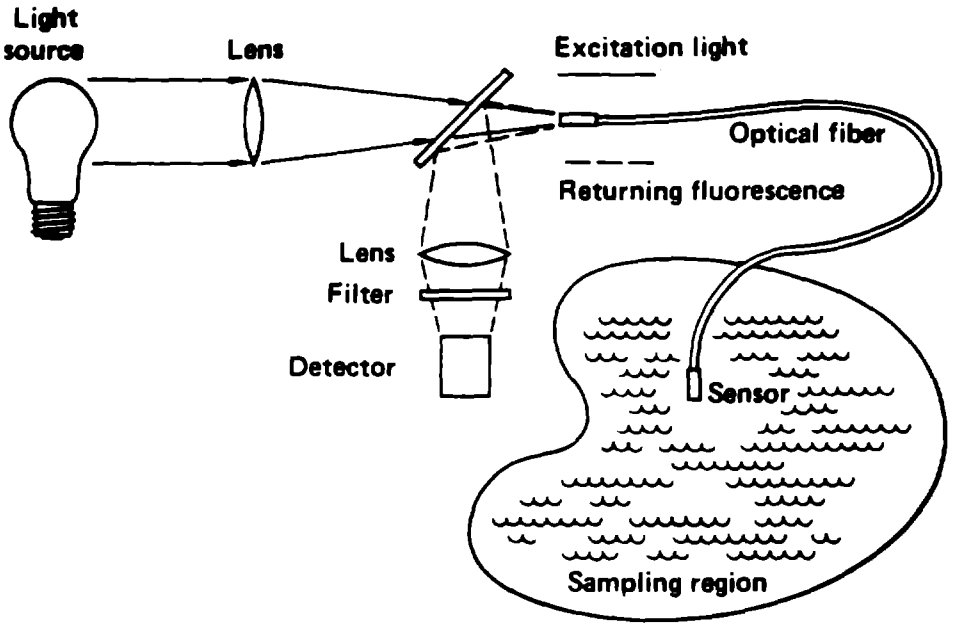

FIGURE 1.
Schematic of the remote fiber fluorimetry concept.

B. Remote Fiber Spectrometer

Figure 2 is a schematic representation of a portable spectrometer that was used for the work described here. The excitation is a Spectra-Physics model 162-A04, air-cooled, argon-ion laser. The laser beam (514.5 nm) is expanded and then reduced in intensity (typically to 1-10 μW) by a series of neutral density filters. It is then directed through a dichroic mirror (DM) and focussed into an optical fiber. The returning fluorescence is reflected at high efficiency (> 85%) by the DM and directed into one of three photomultiplier tubes (PMTs) for analysis. Spectral sorting is performed by bandpass filters that are placed in front of the PMTs. The output of the PMTs is electronically conditioned and subsequently recorded on strip chart. An automatic shutter exposes the FOCS to the laser

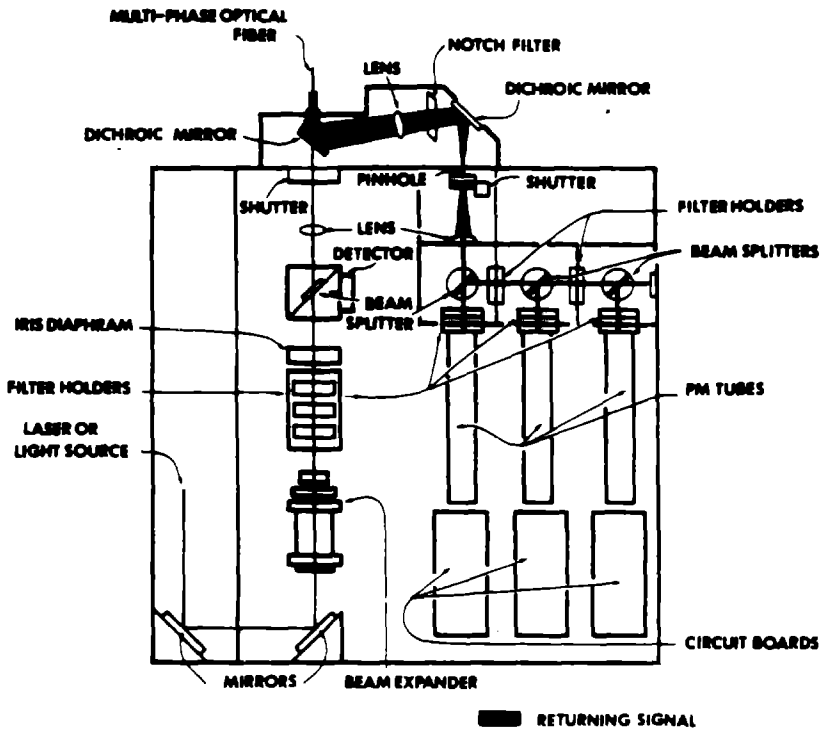

FIGURE 2.
Schematic of a portable fiber fluorimeter.

excitation for a preset duration and frequency. The work described here employed a single PMT.

C. Organochloride FOCS

The organic chloride FOCS is based on the work of Fujiwara[6] who demonstrated that the absorbance of basic pyridine changed when it was exposed to various organochorides. This change in absorbance was shown to be a quantitative measure of the presence of these compounds. The absorbance has been shown to be caused by the formation of a chromophore (Figure 3). In the organic chloride optrode, fluorescence of the chromophore is used to

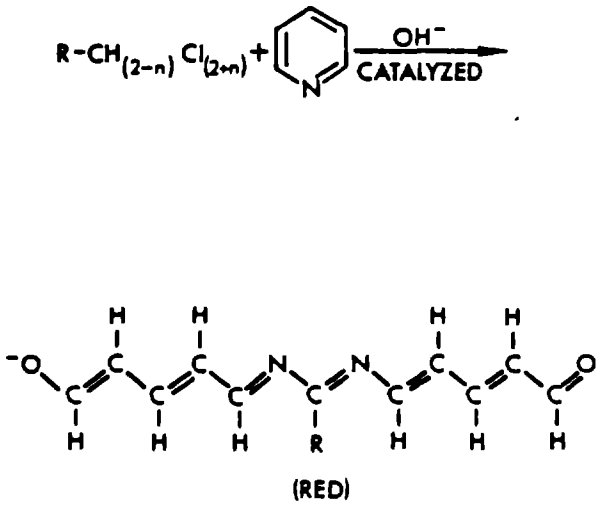

FIGURE 3.
Chemical basis of the Fujiwara reaction.

determine how much absorbing product is formed. In fact, fluorescence intensities can be directly related to organic chloride concentrations.

The Fujiwara reaction has been evaluated as both one- and two-phase chemical systems.[7-9] The FOCS described here is designed with a two-phase chemistry (neat pyridine and 10 to 11 M KOH). It was developed after evaluating all of the shortcomings reported in the literature for the Fujiwara reaction. These are loss of pyridine, inability to maintain pyridine pH, variations in water content, lack of sensitivity and loss of dye color. These drawbacks are overcome by optrode and fluorimeter design.

The FOCS configuration used in this work is shown in Figure 4. Here a polymer-clad fiber of 200 µm diameter is stripped of cladding for a distance of approximately 1 cm from its terminus and then epoxied into a volumetric glass capillary of 500 µm internal diameter. A two-phase chemical system is then formed by first placing, with microsyringe, the KOH solution

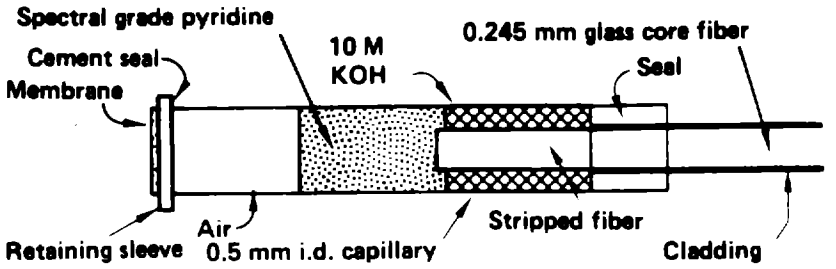

FIGURE 4.
Configuration of the organochloride FOCS.

around the exposed fiber and then placing the pyridine to form a sharp interface. An air space is left between the end of the capillary and the pyridine. Consequently, this FOCS is designed to measure volatile compounds. The capillary is then capped with a membrane. This membrane must keep the pyridine in, keep water out, pass organochlorides with reasonable diffusion rates, and be stable in the presence organochloride and pyridine vapors. Mylar is currently the membrane of choice, however, research is continuing in an effort to find an optimal membrane.

III. RESULTS

A. Laboratory Calibration

Chloroform was chosen as the organochloride for initial testing and validation of the FOCS. Laboratory tests were carried out using dilute solutions of chloroform in water. All chemicals were of reagent grade. The chloroform solutions were prepared by first dissolving the chloroform in a minimum amount of alcohol (< 2% of the final volume) and then diluting with water to make a 1000-ppm stock solution. This was then diluted with water as required to make 100-ppm and 10-ppm working solutions. These solutions were kept in bottles that had been

previously conditioned with chloroform solution. The bottles were sealed with Teflon gaskets until ready for use.

Figure 5 shows the results obtained form a 100-ppm chloroform solution (10 μW of laser power were used). The fluorescent intensity begins to increase almost immediately and is increasing at a rate of about 2700 counts per second per minute after about 2 hours. Because the rate of creation of chromophore is diffusion controlled, the increase in emission intensity might be expected to follow a Fick's law type of behavior. However, the influence of the membrane on the chloroform diffusion is not yet clear and present attempts to fit laboratory data to a diffusion-controlled model have not been completed.

The response curve for a 10-ppm chloroform solution looks similar to that for the 100-ppm solution; i.e., there is an immediate response with the curve being linear after about 2 hours. The rate after this initial start-up time is about

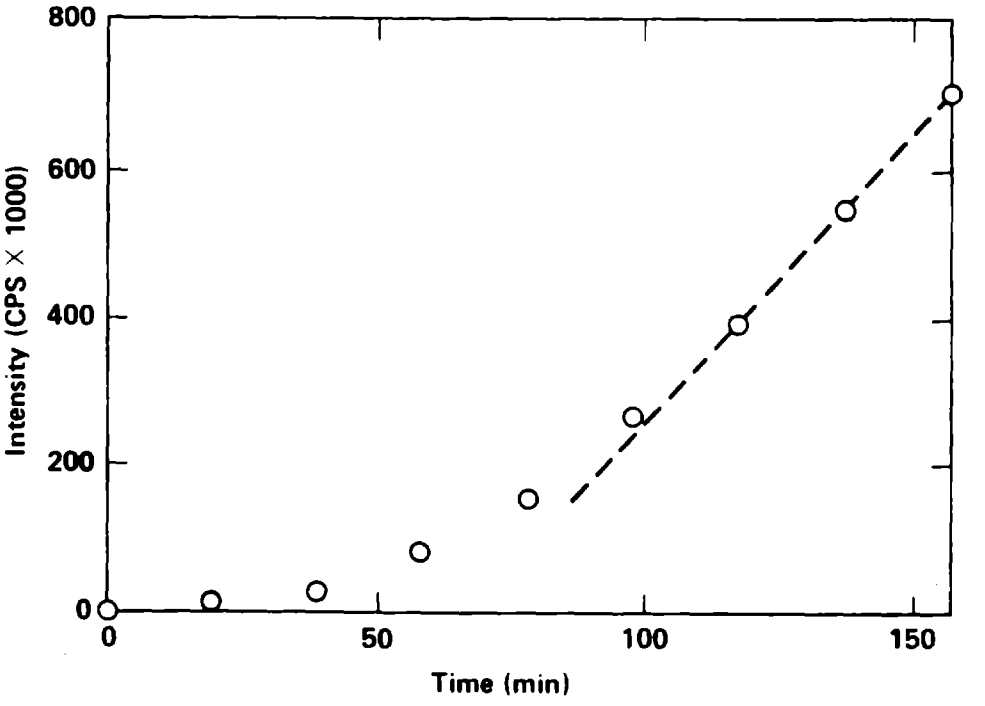

FIGURE 5.

Results of exposure of organochloride FOCS to 100-ppm chloroform laboratory-test solution.

300 counts per second per minute or approximately 10% of that for the 100-ppm solution. This is as expected for a diffusion-controlled process that is linearly dependent on concentration.

Working curves generated from these laboratory calibrations intersect the origin and are considered valid for determining chloroform concentrations of unknown samples that have been probed with identical FOCS.

B. Preliminary Field Tests

Preliminary field testing was conducted at the Pittman lateral transect in Henderson, Nevada. This site was chosen because (1) it possessed a chloroform groundwater plume in a near-surface unconfined aquifer, (2) it had an existing monitoring-well network, (3) periodic grab-sample chemical analyses were being performed, and (4) it had easy access.

The FOCS used for the field test were all freshly prepared at the field site and attached to the end of either 15- or 20-m optical fibers (Valtec 200/240). Laser power levels were measured before and after each sensor test.

Figure 6 shows typical results obtained in the field. All intensities measured are corrected for background. After insertion in the well, the FOCS initially exhibits a slow increase in signal. This can be attributed to the mass of the sensor and its protective housing coming into equilibrium with the chloroform concentration. After equilibration, usually 1 to 2 hours, the rate of increase in signal assumes a nearly linear shape. This linear portion of signal increase has a value of 4.1 k-counts/s (kCPS)/h/10 μW. The laboratory calibration of this sensor indicates that 1 ppm chloroform should give a slope of 3.0 kCPS/h/10 μW. This yields a result of 1.4 ppm of chloroform for this measurement. Repeated measurements in this well (#625 Pittman Lateral) gave values ranging from 0.8 to 1.4 ppm. A grab sample taken from this well within two weeks of

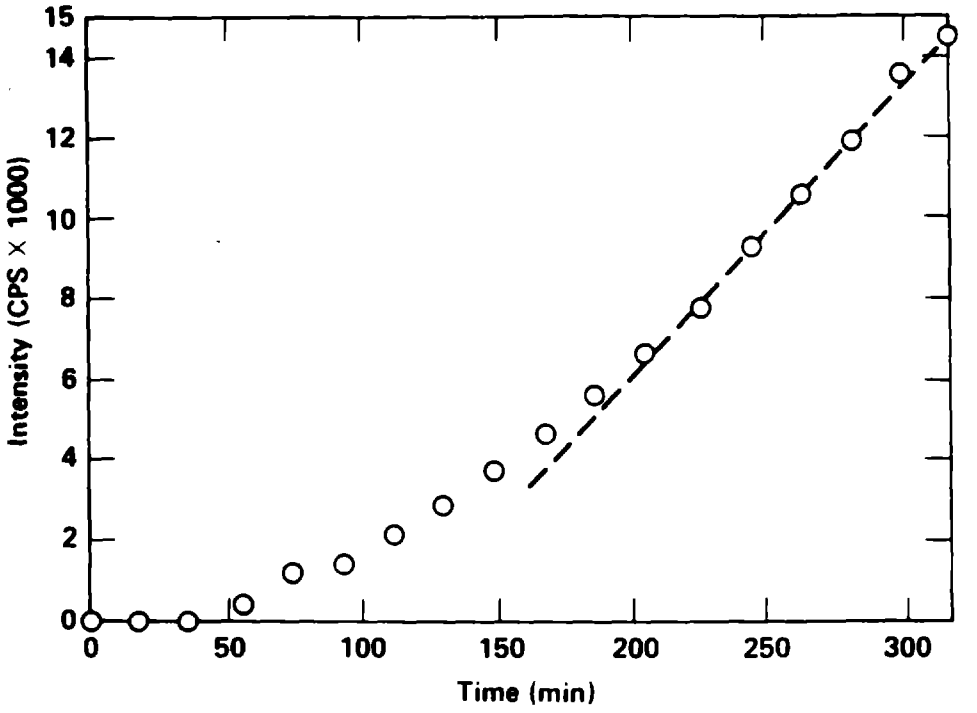

FIGURE 6.
Fluorescent signal obtained after insertion of organochloride FOCS into a chloroform-contaminated test well. Rate of increase of signal indicates approximately 1.4 ppm of chloroform.

our study showed 0.85 ppm by gas chromatography. These results are in very good agreement considering the preliminary state of this RFF application and the difficulty in quantitatively sampling trace quantities of chloroform.

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