

# **Fiber optic interrogator based on colorimetry technique for in-situ nitrate detection in groundwater**

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Nitrate poisoning occurs when nitrite is absorbed into the blood, where it changes the red-colored blood pigment, called hemoglobin, to methemoglobin. Hemoglobin carries oxygen from the lungs to the other tissues, but methemoglobin cannot carry oxygen. Poisoning occurs when the methemoglobin concentration in the blood stream is so high that the oxygen carrying capacity of the blood is reduced to a critical level. Over the years nitrate contamination has acquired alarming proportions due to seepage of nitrates of fertilizers into the soil. Though several methods of monitoring nitrate concentration have been devised with some success, there is still a persistent need for devising easily deployable and insitu techniques for monitoring nitrates in groundwater. Fiber optic techniques are capable of meeting these requirements, besides offering several other important advantages. Fiber optic nitrate detection sensors have thus become quite attractive and are currently being investigated to address the high costs associated with the existing nitrate concentration monitoring procedures. This paper describes fiber optic interrogator for in-situ nitrate detection in groundwater based on colorimetry technique.

Keywords: fiber optic sensors, nitrate concentration, groundwater, colorimetry.

## **1. Introduction**

Nitrate concentration in excessive levels can have harmful biological consequences. The current drinking water standard and health advisory level is of 45 ppm nitrate based on the human health risks due to nitrate consumption [1]. Although there have been studies performed attempting to link nitrate consumption to various diseases, only methemoglobinemia (also infant cyanosis or blue-baby syndrome) has been proven to result from ingestion of water containing high nitrate concentrations, above 10 ppm [1].

Cases of blue-baby syndrome usually occur in rural areas, which rely on wells as their primary source of drinking water. Often these wells become contaminated when they are dug or bored and are located close to cultivated fields, feedlots, manure lagoons or septic tanks [2]. The most contaminated wells are usually those that were dug rather than drilled and have poor or damaged casings [3]. Until re-

cent awareness of the dangers of nitrate contaminated groundwater prompted testing for nitrate concentrations, along with other contaminants, wells with dangerously high nitrate concentrations usually went unnoticed till health problems were brought to attention. A few isolated cases of methemoglobinemia have served as the catalyst for what has grown into a broad awareness and concern for nitrate contamination.

Methemoglobinemia is the condition in the blood, which causes infant cyanosis or blue-baby syndrome. Methemoglobin is probably formed in the intestinal tract of an infant when bacteria converts the nitrate ion to nitrite ion [2]. One nitrite molecule then reacts with two molecules of hemoglobin to form methemoglobin. In acid mediums, such as the stomach, the reaction occurs quite rapidly [2]. This altered form of blood protein prevents the blood cells from absorbing oxygen, which leads to slow suffocation of the infant and finally may lead to death [2]. Because of the oxygen deprivation, the infant will often take on a blue or purple tinge in the lips and extremities, hence the name, blue baby syndrome [3]. Other signs of infant methemoglobinemia are gastrointestinal disturbances, such as vomiting and diarrhea.

Treatment of infant cyanosis is simple once the condition has been recognized. If the patient is mildly affected, then he/she must simply refrain from drinking from the contaminated well and the body will replenish the hemoglobin by itself in a few days [3]. However, if the patient is severely cyanotic, methylene blue must be administered intravenously in a dosage of 1–2 mg/kg of body weight for a ten-minute period and improvement should be prompt [3].

Methemoglobinemia most often affects infants of less than six months in age. Several factors make infants more susceptible to nitrate compounds than adults. The primary reason is that infants possess much less oxidizable hemoglobin than adults, so a greater percentage of their hemoglobin is converted to methemoglobin, which greatly decreases the blood's ability to carry oxygen. Other possible reasons are that nitrite ions may be more strongly bound by infantile hemoglobin due to immaturity of certain enzymes, and that the kidneys of infants have inferior excretory power, which may favor retention of nitrite for longer periods of time [2].

Steps can be taken to prevent the child from becoming a victim of methemoglobinemia. Residents of rural areas should have their wells tested, especially if pregnant women or infants are consumers of the well water. If the well is contaminated, other water source alternatives like safe wells, bottled water, a new, deeper well, or a water purification system, which is capable of removing the nitrates [3] should be used. Cyanotic babies usually contract methemoglobinemia from the water used to prepare their formulas. Formulas, which use diluted whole milk, are less risky than those prepared from powdered or evaporated milk requiring large amounts of water in preparation [4]. Breast feeding or the use of bottled water in formula preparation offer the safest solution, especially if the groundwater quality is unknown [3].

Since 1945, there have been over 2000 cases of infant methemoglobinemia reported in Europe and North America with 7 to 8 percent of the afflicted infants dying (Rail, 1989). However, problems can be severe as shown in a specific 1950 report, there were 144 cases of infant methemoglobinemia with 14 deaths in a 30 day period in Minnesota [3]. This of course was an isolated case. However, it shows that nitrate concentrations in well water can increase to deadly levels rapidly and the issue of nitrate contamination should not be ignored.

Nitrate represents a potential risk because of nitrosation reactions which, with appropriate substrates present, form N-nitroso compounds, which are strongly carcinogenic in animals [5]. In other areas of the world such as Columbia, Chile, Japan, Denmark, Hungary, and Italy, similar studies have suggested a correlation, although there still exists no concrete evidence to support this theory [5].

Over the years, several methods of monitoring nitrates have been devised with some success. At present, there are only a few methods of determining in-situ nitrate concentration using optical fibers. Therefore, a persistent need exists for developing in-situ and cost-effective techniques for this purpose. Optical fiber based techniques are capable of in-situ measurements besides offering several other attractive features such as small size, flexibility and geometric versatility, light weight, inherent immunity to EMI/ RFI, low-loss, large bandwidth, increased sensitivity, resistance to corrosive and hazardous environments, non-intrusive, distributed sensing and compatibility to optical fiber data telemetry systems. A distributed and on-line optical fiber sensing system for nitrate detection will help reduce the costs associated with conventional systems.

Fiber optics systems based on direct absorption spectroscopic techniques investigated by some research groups have relied on using single fiber elements for recording the light signal reflected off the specimen at different wavelengths [6]. The present paper reports on a simple and alternate technique based on the color matching principle of colorimetry for detection of nitrates induced color changes in reagent. In contrast to single fiber elements, the present technique employs a thin Y-shaped optical fiber lightguide/bundle, which increases the quantity of light energy coupled from a white light source resulting in the ease of optical signal processing. The technique actually involves detection of the blue color formed when reagent comes in contact with nitrates. For applications, where accuracy requirement is not very critical, fiber optic sensing techniques based on multimode optical fibers/bundles and components offer the advantages of simple construction, enhanced coupled optical power, ease of alignment and implementation and cost-effectiveness.

## 2. Principle

The principle of colorimetry is well-established but owing to the use of fiber optics, this technique has now become quite versatile and useful. In fact, the utilization of optical fiber technology for color sensing represents a major advance in visible and

near IR photometry. It is now possible to perform in-situ on-line non-contact color measurements of samples [7].

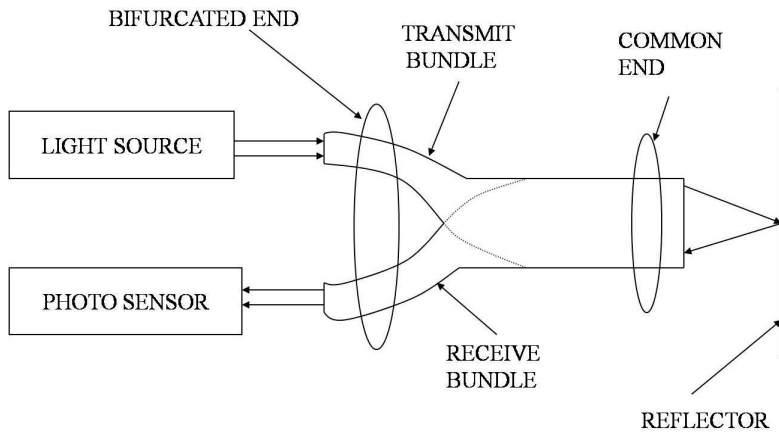


Fig. 1. Arrangement of an optical fiber Y-guide (bifurcated bundle) for reflection of light from sample.

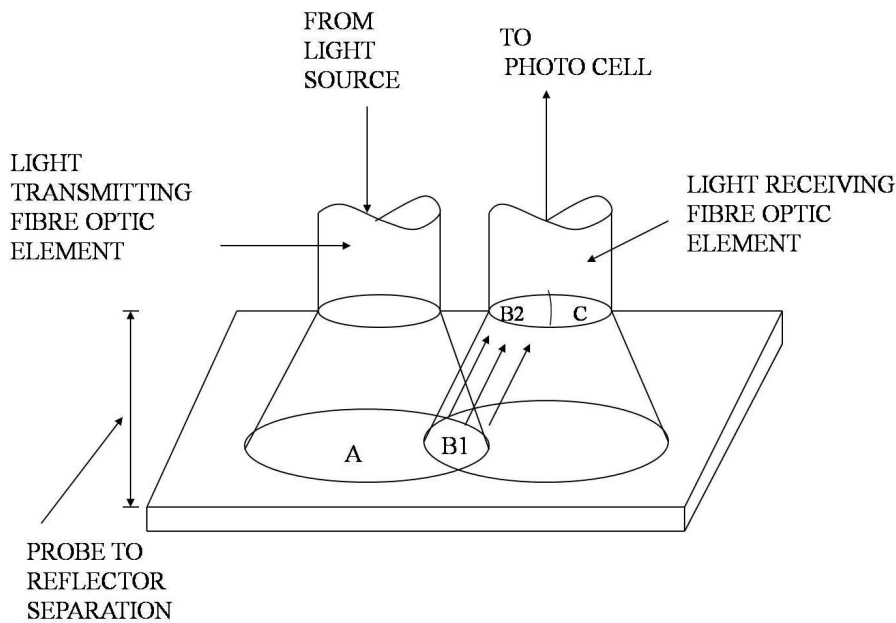


Fig. 2. Reflected light monitoring mechanism of adjacent optical fibers.

Through one arm of the optical fiber Y-guide, white light coupled from the source is made incident on the sample to be monitored for color changes and the reflected signal is carried by another arm of the Y-guide to a photo-detector. A complementary color filter is used before the photo-detector because color of the

light absorbed is complimentary to the color of the corroded specimen and it is the intensity of the complimentary color that varies with color concentration of the sample. The accuracy of color measurement using this technique depends on the proper selection of the complimentary filter. The reflected light signal consequently varies in proportion to the color of the sample and, thus it is possible to assess the nitrate contamination.

The technique is based on the principle of light being reflected off the specimen and then received back through a receive branch of a bifurcated fiber optic bundle (Y-guide) on to a photodiode. Keeping the displacement between the common end of the bundle and the target specimen as fixed and equal to that for the peak sensitivity value, the quantity of light reflected by the specimen gives a direct measure of nitrate contamination and it is displayed in the form of an electrical signal.

In the bifurcated fiber bundle developed and employed, one group of fibers transmits light from a stable source to a target reflector surface. The other group receives the light reflected from the target and transports it back to a photo-detector, which converts it to an electrical signal proportional to the intensity of the reflected light as depicted in Fig. 1, while Fig. 2 depicts the action of an adjacent pair of fiber optic light transmitters and receivers as used to detect the position and/or quality condition of a reflective surface relative to the ends of the optical fibers.

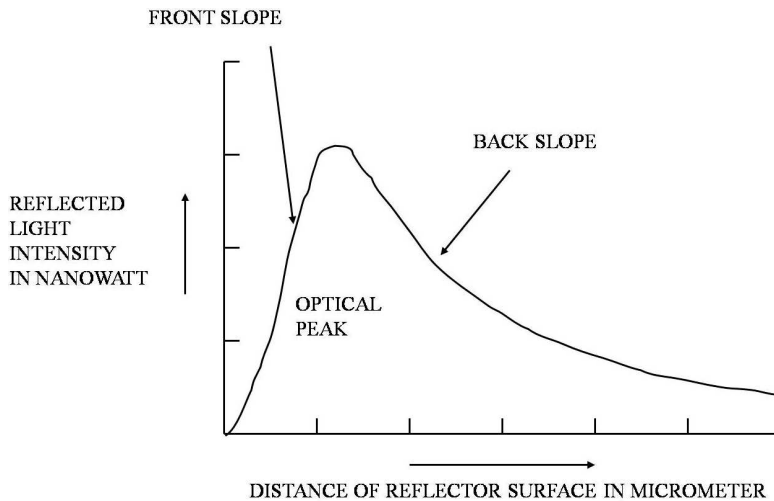


Fig. 3. Optical fiber Y-guide transducer response curve.

Evidently, as the reflecting surface moves away from the set of optical fibers, the area A illuminated by the transmitting fiber optic element becomes larger and larger. The illuminated area of interface B1, which is providing light to the surface of the receiving element B2 also grows increasingly larger. There is rapid and linear growth in the signal output as more of surface C is illuminated, e.g. as the probe to target displacement increases, and increasing amounts of light are captured by the receiving

fibers. This portion of the response curve is referred to as the “front slope” region. The point at which the entire surface C becomes covered with light is referred to as the “optical peak” point of the response curve as shown in Fig. 3.

This is a well-known experimental response curve of Y-guide type of reflective sensors which are quite popular amongst the intensity modulated fiber optic sensors. As the surface moves further away, the size of area B2 becomes larger than area C, reducing the detected light intensity. The light intensity-monitoring photosensitive detector output then begins to decrease, resulting in the back slope characteristic, where the signal decreases proportionally to the square of the displacement between the probe and the target surface, because a continued increase in displacement will cause the diverging field of reflected light to exceed the field of view of the receiving/detector fibers producing a reversal in the output vs. displacement signal relationship. This also becomes clear from the geometry of the arrangement used that as the target is moved away from the probe, the area of the illuminated spot on the target increases in direct proportion to the square of the displacement, while the interception of the reflected light by the fiber probe will correspondingly decrease in proportion to the square of displacement. Actually, these displacement dependent measurements of light coupling are based on the interaction between the field of illumination of the transmitting/source fibers and the field of view of the receiving fibers [8–10].

The extremely rapid signal rise in the front slope region of the response curve permits high sensitivity measurements, while the back slope region is used for measurements at greater displacements, where sensitivity, linearity, and accuracy requirements are less demanding. The “optical peak” region is used for optical inspection and comparison of surface conditions since at this position, the output signal is more sensitive to light intensity variations than changes in displacement. The distribution of fibers at the common (distal) end of the bundle is a major factor determining displacement range and slope sensitivity of the probe. For example, the greater displacement sensitivity is obtained with a staggered/random fiber array [8–10]. Fiber optic colorimetry technique has been earlier also used for various applications like detection of corrosion of civil structures, etc. [11–13].

### 3. Experimental details

The experimental arrangement realized in the laboratory for detection of nitrates in water is schematically depicted in Fig. 4.

The set up employs an indigenously built thin Y-shaped fiber optic bundle with half portion (a semi-circle) of its common end made from the source fibers and the other half from the detector fibers. The length of the fiber lightguide used is about 0.5 meter with both the source and detector arms being 15 cm long. The diameter of the common end of the lightguide is 5 mm, while the source arm and detector arm end faces have a diameter of about 1.8 mm. This lightguide was developed indigenously using optical glass fibers of 60/120  $\mu\text{m}$  size. Light from a 50 watt quartz halogen lamp driven by

a 12V (DC) stabilized power supply, was coupled to the source arm of the bundle using suitable optics. The water specimens were prepared in the laboratory by adding varying concentration of nitrate salts in water. The specimen is located very close to the common end of the Y-guide at a displacement of 5 mm, which corresponds to the peak sensitivity of the response of the lightguide and the reflected light picked up by the other arm of the bundle is made to pass through a complementary filter (yellow) before it is incident on a photo-detector. The complimentary filter used in the present investigations is a commercially available interference filter with a typical bandwidth of 15 nm. The light reflected off the sample is made incident on a silicon positive-intrinsic-negative (PIN) photo-detector of the fiber optic interrogator through a complementary filter. The block diagram of fiber optic interrogator is shown in Fig. 5.

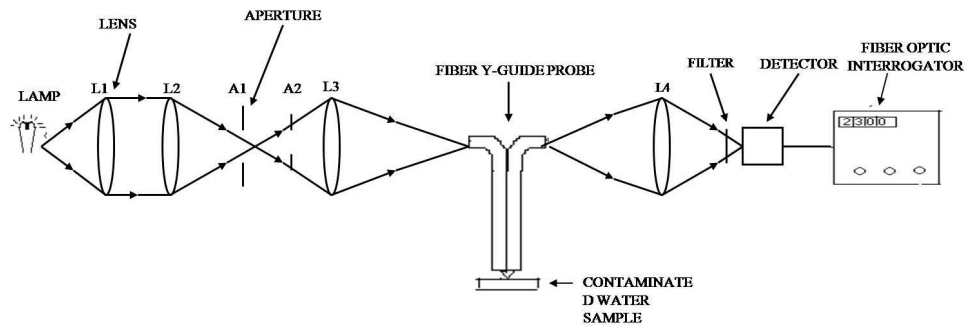


Fig. 4. Experimental schematic of in-situ fiber optic colorimetry technique for detection of corrosion.

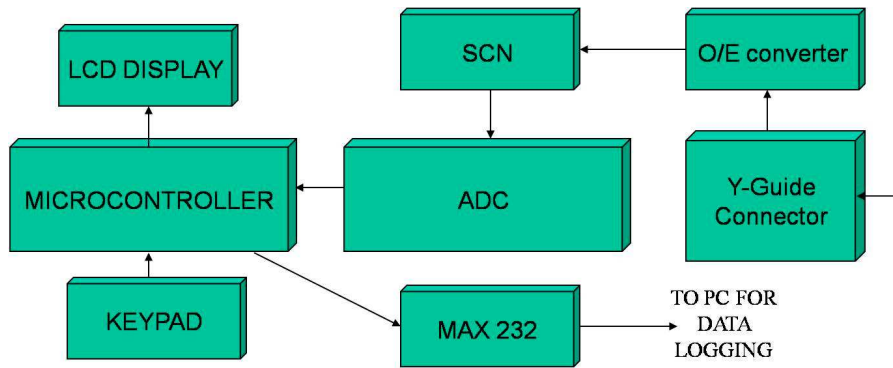


Fig. 5. Block diagram of fiber optic interrogator.

The output of the PIN photodetector is amplified and converted to digital using ADC and then a microcontroller displays it on the LCD panel. An RS232 interface has been implemented for PC connectivity. The programming of the microcontroller has been implemented in native MCS51 keeping the code compact and modular. Nitrate concentration measurement of water samples was thus carried out by adding the reagent in different samples and taking the readings.

## 4. Results

Data were recorded for a fixed displacement between the fiber end and water sample mixed with nitrate detection reagent (dimethylamine) both for pure water and contaminated water and the results have been found to be reproducible. A typical variation between concentration of nitrates in water solution and the reflected optical power is shown in Fig. 6.

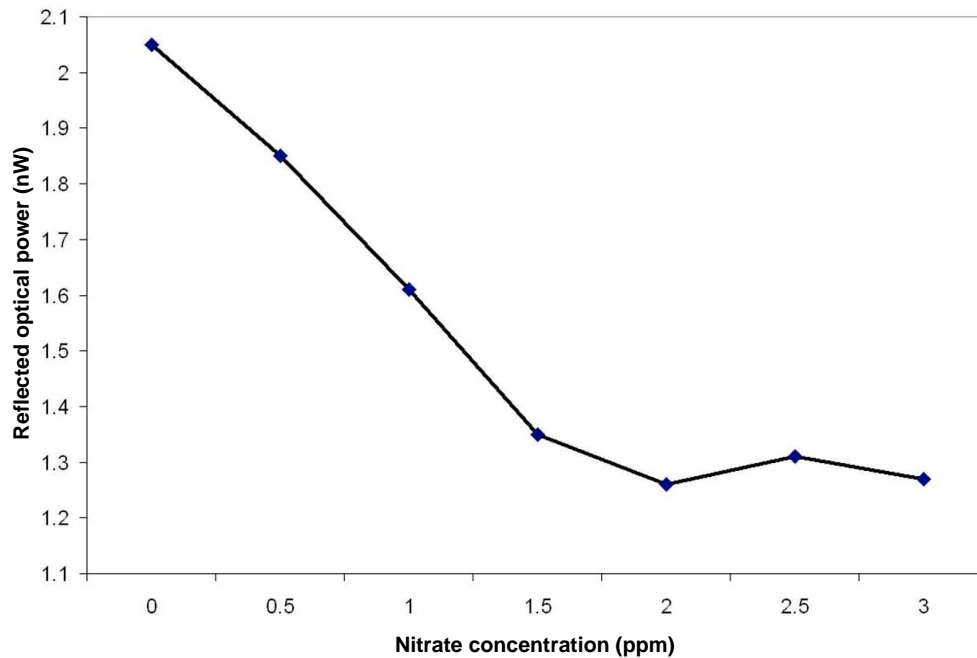


Fig. 6. Variation of reflected optical power with change in nitrate concentration in water sample.

It clearly indicates that at low concentrations, there is a linear increase in absorption (e.g. a decrease in reflected optical power) of the complementary color with the increase of concentration of nitrates which, however, tries to saturate at relatively higher concentration.

Different concentrations of nitrate ions in water samples were realized using titrations and then by mixing same quantity of reagent and concentrated sulphuric acid different reading were taken keeping the distance of the fiber end from the water sample constant.

## 5. Discussion

This simple technique based on the principle of the colorimetry employing fiber optic bundle enables in-situ monitoring of the nitrate contamination in water. Such colori-



metric fiber optic probes can be embedded into the boreholes dug in the ground at pre-determined sites for convenient monitoring of the contamination level. The technique can be easily calibrated using standard nitrate concentration water specimens. However, due to non-availability of standard specimens, such a calibration could not be undertaken. This technique is very useful to study the underground nitrate water contamination and further investigations are planned to be pursued in this direction in future. The technique can also be used for remote/in-situ monitoring of boilers and other critical structures located in harsh environments such as in chemical industry, nuclear reactor buildings, mines etc.

## References

- [1] KROSS B.C., HALLBERG G.R., BRUNER D.R., CHERRYHOLMES K., JOHNSON J.K., *The Nitrate Contamination of Private Well Water in Iowa*, American Journal of Public Health, **83**, 1993, pp. 270–2.
- [2] COMLY H., *Cyanosis in infants caused by nitrates in well water*, JAMA, **129**, 1945, pp. 112–6.
- [3] JOHNSON C.J., BONRUD P., *Methemoglobinemia: is it coming back to haunt us?* Health Environment Digest, **1**(12), 1988, pp. 3–4.
- [4] LUKENS J.N., *The legacy of well-water methemoglobinemia*, JAMA, **257**, 1987, pp. 2793–95.
- [5] FORMAN D., AL-DABBAGH S., DOLL R., *Nitrates, nitrites and gastric cancer in Great Britain*, Nature, **313**, 1985, pp. 620–5.
- [6] FUHR P.L. *et al.*, *Fiber optic corrosion sensing for bridges and roadway surfaces*, Proceedings SPIE, **2446**, 1995, pp. 2–8.
- [7] NAHAR SINGH *et al.*, *Development and experimental investigations of a fiber optic color sensing probe*, Journal of Scientific Industrial Research **58**, 1999, pp. 359–63.
- [8] *Intensity Modulated Fibre Optic Sensors* (Chapter 23), Fundamentals of Fibre Optics in Telecommunication and Sensor Systems (Ed. Bishnu P. Pal), Wiley Eastern Limited, New Delhi, 1992.
- [9] HOOGENBOOM L. *et al.*, *Theoretical and experimental analysis of a fibre optic proximity probe*, Proceedings SPIE, **478**, 1984, pp. 46–57.
- [10] DAVIS Ch.M., *Fiber Optic Sensor : an overview*, Optical Engineering **24**(2), 1985, pp. 347–51.
- [11] MIGNANI A.G., MENCAGLIA A.A., *Direct and chemically-mediated absorption spectroscopy using optical fiber instrumentation*, IEEE Sensors Journal **2**(1), 2002, pp. 52–7.
- [12] KUMAR DATTAMAJUMDAR A., BLOUNT P.L., MYERS J.A., PROCTOR A.H., GOLDMAN B.H., REID B.J., MARTIN R.W., *A low-cost fiber-optic instrument to colorimetrically detect patients with Barrett's esophagus for early detection of esophageal adenocarcinoma*, IEEE Transactions on Biomedical Engineering **48**(6), 2001, pp. 695–705.
- [13] SINGH N., JAIN S.C., AULAKH N.S., CHHABRA J.K., SINGH M.L., AGGARWAL A.K., BAJPAI R.P., *Fiber Optic Colorimetry Technique for in-situ Measurement of Corrosion in Civil Structures*, Experimental Techniques, **28**(1), 2004, 23–26.

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